Proton Beam Writing in Gallium Arsenide

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Summary

Proton Beam Writing (PBW) is a direct write technique that employs a focused MeV proton beam which is scanned in a pre-determined pattern over a target material which is subsequently electrochemically or chemically etched and developed. The ultimate depth of the structure is determined by the range of the protons in the material and this allows structures to be formed to different depths.

PBW has been successfully employed on etchable glasses, polymers, and semiconductor materials such as silicon (Si).

This present thesis is a study on the feasibility of PBW in p-type GaAs, and compares experimental results with computer simulations using the Atlas© semiconductor device package from SILVACO. It has been established that hole transport is required for the electrochemical etching of GaAs using Tiron (4,5-Dihydroxy-m-benzenedisulfonic acid, di-sodium salt). PBW in GaAs results in carrier removal in the irradiated regions and consequently minimal hole transport (in these regions) during electrochemical etching. As a result the irradiated regions are significantly more etch resistant than the non-irradiated regions. The proton energy, proton fluence, beam current, etch current density, etch area, structural spacing, enclosed structures and post irradiated annealing were investigated. Successful three-dimensional micro structures were produced using PBW in GaAs and the simulation and experimental results are comparable which has helped to give a better understanding of the processes of PBW in GaAs and the subsequent electrochemical etching process.

Keywords: Proton Beam Writing, Gallium Arsenide, SILVACO
Dedication

I dedicate this thesis to Bhagawan Sri Sathya Sai Baba. Through his selfless love and compassion, he has been giving an ordinary guy, extraordinary opportunities. His friendship and guidance through the years have been a wonderful blessing. This chance to study for a Ph.D has enriched my life greatly, both academically, personally and spiritually. For all of this I am eternally grateful.
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Glossary of Terms

PBW: Proton Beam Writing
PMMA: Poly(methyl methacrylate)
FIB: Focused Ion Beam
EBL: Electron Beam Lithography
LIGA: Lithographie Galvanik Abformung (X-ray lithography Electroforming and Moulding)
keV: Kilo Electron Volts
MeV: Mega Electron Volts
SRIM: Simulations with Stopping and Range of Ions in Matter
GaAs: Gallium Arsenide
Si: Silicon
PIXE: Particle Induced X-Ray Emission
MEMS: Micro Electrochemical Systems
RBS: Rutherford Backscattering Spectroscopy
EOR: End of Range
UV: Ultra Violet
Ar: Argon
C: Carbon
S: Sulphur
Na: Sodium
O: Oxygen
Rs: Sheet Resistivity
HF: Hydrofluoric Acid
R: Range
Contents

Rp: Projected Range
IBA: Ion Beam Analysis
FWHM: Full Width Half Maximum
PL: Photoluminescence
a.u.: Arbitrary Unit
Chapter 1

1 Introduction

Throughout history techniques such as lithography and surface patterning have facilitated the transference of a master design onto a secondary substrate.

The term lithography originates from the combination of two Greek words: “lithos” meaning stone and “graphia” meaning to write. Thus lithography means “stone writing”.

The invention of modern lithography is credited to Alois Senefelder in 1798 in Munich, the Kingdom of Prussia (now Germany). He became interested in letterpress printing and worked with different printing plates, inks and surface treatments [1]. Plate material in these days consisted of copper, which was expensive. Senefelder found that natural limestone worked well as an inexpensive plate surface after grinding it smooth and treating with a special etching fluid.

Lithography remains a widely used technique in the world today and is regularly referred to many processes that involve transferring a master design onto a secondary substrate. Microchips and micro electrochemical systems (MEMS) are extensively fabricated using lithography techniques and with a growing demand for smaller micro-optical, micro-electronical and medical devices, lithography is a key for micro and nano-technology.

A comparison between the main lithography techniques will be shown in the next chapter and some of the factors that limit the application of existing lithography techniques such as aspect ratio, lateral resolution and structure depth will also be explained.

The present work deals with Proton Beam Writing (PBW). PBW is a new generation of direct write lithography that uses high energy protons to imprint a master design onto material without the need of masks. It was first developed in 1993 at Oxford University [2] and has been successfully used to produce high aspect, three dimensional structures at the micro and nano- scale in polymers [3, 4], etchable glasses [4, 5] and silicon [6-8].
1.1 Objectives

The main objective of this thesis is to investigate Proton Beam Writing (PBW) in GaAs which has never been undertaken in this material before, with the purpose of establishing the mechanisms involved. This will be done by:

- Studying the electrochemical etching process in GaAs in samples which have and have not been irradiated to determine the optimum etching parameters.
- Simulating the electrochemical etching process using the ATLAS© software package developed by SILVACO International Inc. (USA) [9] to help understand the mechanisms involved during electrochemical etching.
- A study to find the optimum fluence for proton beam writing.
- Using this optimum fluence to produce a range of structures, both simple and complex.

Having established the advantages and disadvantages of PBW in GaAs, the range of its application and potential can be explored.

1.2 Structure of Thesis

This thesis is divided into six chapters. Chapter One is used to give an introduction of the subject and the main objectives of the work. Chapter Two gives an overview of the key lithographic patterning techniques and provides a comparison. Chapter Three is a literature survey reviewing the key published literature of PBW performed in a range of materials. Chapter Four describes the main experimental techniques used in this work. Chapter Five relates the experimental details and their corresponding results. This chapter also provides a discussion on the outcomes. Chapter Six concludes the whole thesis and provides suggestions for further work in this field.
1.3 Novel Contributions of the Thesis

The main objective of this thesis is to perform an investigation into the feasibility of a new generation of direct write lithography called Proton Beam Writing (PBW) in the semiconductor material p-type gallium arsenide (GaAs). This is the first time that PBW has been investigated in GaAs and this work has the potential to have a range of applications in fields such as lithography and optoelectronics.

To date PBW has been performed in polymers, silicon and photosensitive glasses for the formation of three dimensional, high aspect ratio micro and nano scale structures.
Chapter 2

2 Overview of Patterning Techniques

2.1 Classifying Techniques

There are two types of lithographic processes. One uses masks whilst the other uses direct write techniques. These processes will be described in more detail in the following sections.

2.1.1 Mask Process

Patterned masks are used when electromagnetic radiation such as X-rays and UV light are used to expose a radiation sensitive material or a layer of sensitive material on a target material. The patterned mask needs to absorb radiation in certain regions and be transparent to it in others. It also requires good contrast being opaque to radiation in some areas and transparent in others. The pattern is transferred to the sensitive target material which is exposed in the transparent regions. The types of radiation used determine what material the mask is made out of. Figure 1 shows an example of the mask process where the X-ray or UV light gets absorbed by the opaque area of the mask and is transmitted through the transparent areas to expose the sensitive target material.

![Mask process in lithography](image)

**Figure 1** – *Mask process in lithography* [10].
2.1.2 Direct Write Process

There is no need for a mask when focused and scanned radiation such as an electron or ion beam is used to irradiate the sensitive target material. This is because the beam scans a computer generated pattern directly onto the sensitive target material. This can be seen in Figure 2.

![Diagram of Direct Write Process](image)

**Figure 2** – Direct Write Process in Lithography [10].

2.2 Photoresist and Mask Lithography Techniques

2.2.1 Photolithography

Photolithography, also known as optical lithography is one of the most widely used mask techniques. It is widely used in microelectronics and micromachining. It incorporates a pattern definition method which uses ultra-violet (UV) or visible radiation to expose the resist.
Figure 3 describes the basic steps of this technique.

Figure 3a [11] shows a thin film of a material, typically silicon dioxide on a substrate of another material (in this case, a silicon wafer). To selectively remove some of the silicon dioxide (figure 3f), the following process steps have to be undertaken.

Firstly a mask is produced. This will typically be a defined pattern on a glass plate. A polymer which is sensitive to ultraviolet light (called a photoresist) is used to coat SiO$_2$ layer on the Si wafer (figure 3b). Ultraviolet light is then shone through the mask onto the photoresist to expose it (figure 3c). The photoresist is then developed which transfers the pattern of the mask onto the substrate material (figure 3d).

There are two types of photoresist processes. These are referred to as the positive resist process and negative resist process. In a positive resist process, the ultraviolet light passes through the transparent regions of the mask and activates the photosensitive components of the resist, such that the areas of the resist are removed during the developing stage. In a negative resist process the unexposed areas are removed by the developer [12].

Hydrofluoric acid (HF) is then used to remove the oxide in the regions where it is not protected by resist (figure 3e). Finally the resist is removed using solvents leaving a patterned oxide on Si (figure 3f) [11].
Chapter 2 - Overview of Patterning Techniques

Figure 3 - Photolithography technique [11].

The feature size is limited by diffraction and depends on the wavelength of the electromagnetic radiation used to illuminate the mask. Current photolithography tools use Deep Ultraviolet (DUV) light with wavelengths of 248 and 193 nm, which are reported to allow minimum resist feature sizes down to 65nm [13-15].

2.2.2 X-ray Lithography (LIGA)

LIGA stands for lithographie, galvanomformung und abformung, which are the German acronym for lithography, electroplating and molding. LIGA is a fabrication process for high aspect ratio microstructures consisting of the following major process steps:
1. X-ray lithography (LI = Lithographie) using synchrotron radiation to generate deep primary microstructures (DXRL = deep x-ray lithography, UDXRL = ultra-deep x-ray lithography)

2. Electroforming (G = Galvanik) to produce a negative replica of the microstructures in metal

3. Molding (A = Abformung) of secondary microstructures in polymers, metals, and ceramics

X-rays are used to expose a pattern into a resist material such as PMMA which is normally supported on a metalised substrate. The PMMA is chemically developed to create a high aspect ratio, parallel wall mould. A metal or alloy, such as nickel, is electroplated onto the PMMA mould to create a metal microstructure. The PMMA is dissolved leaving behind a three-dimensional metal microstructure.

Even though LIGA requires a high-flux X-ray synchrotron source which is very expensive, repeated use of the final mould can make it an inexpensive microstructure replication technique, with the potential for mass fabrication [16-18]. However the production of the X-ray masks is very difficult and often requires another lithography technique such as electron beam lithography or proton beam writing to produce the original masks. A step by step graphic description of the basic LIGA process is given below in Figure 4 [19].
Chapter 2 – Overview of Patterning Techniques

Step 1
Deposition of Adhesion and Seed layer

Step 2
Resist coating

(Lithographie) Lithography

Step 3
Exposure (pattern transfer)

Step 4
Development of exposed resist

(Galvanoformung) Electroforming

Step 5
Metal Plating

Step 6
Removal of remaining resist
2.3 Direct Write Process

2.3.1 Electron Beam Lithography (EBL)

Electron beam lithography (EBL) is a technique used to fabricate extremely fine patterns that are used in some integrated circuits and bio sensors. The pattern is written by a beam of electrons scanned across the surface of a material (e.g. silicon wafer) that is covered with a resist film sensitive to those electrons. The advantage with EBL is that it is capable of producing sub-100nm features, however these can only be realized in very thin resist layers because electrons are easily scattered due to their low mass and therefore only capable of fabricating two-dimensional structures [20].

The EBL tool consists of four components: a column, a vacuum chamber, a substrate moving device and control electronics. The column is responsible for forming and controlling the electron beam. The electrons are accelerated close to the speed of light and are focused by electromagnetic lenses into an extremely fine probe, approximately 2nm at 20keV, that is used to write the patterns. The target, a flat substrate (e.g. a silicon wafer)
wafer) covered with electron sensitive material (resist), is placed on a moveable stage. The whole procedure is carried out in a vacuum chamber so that the electrons are not scattered by hitting any air molecules.

The main drawback to EBL is the rather slow way of creating patterns. This has lead to EBL being used for the fabrication of masks or imprint stampers. The scattering of electrons is also a major consideration because it prevents the formation of deep structures.

This can be seen in Figure 5 which shows a simulation of 50 keV electrons in PMMA from which it can be seen that the lateral scatter and the penetration depth of the electrons are of the same order of magnitude.

![50 keV electrons in PMMA](image)

**Figure 5** — *Simulation of electrons in PMMA [10].*

### 2.3.2 Focused Ion Beam Lithography (FIB)

The Focused Ion Beam (FIB) tool can be used to sputter material from a defined area. Sputtering is achieved by accelerating low / medium energy (up to 50 keV) heavy ions such as gallium at a specific site. This sputters the material at that site leaving a ‘hole’ in the surface. The equipment typically consists of a high brightness ion source (often a
liquid metal ion source) which produces a beam of ions which are accelerated and focused to a diameter of less than 100 nm using cylindrical electrostatic lenses [21].

The FIB is used for a whole range of applications such as fabrication of micromechanical tools [22], fabrication of diffractive optical elements [23-25], semiconductor device editing or modifications [26] and site-specific transmission electron microscopy (TEM) sample preparation [27].

An advantage of the FIB is that it is a direct etching process, with no need for pattern transfer from resist to substrate, as the required pattern is created directly on the substrate. It also has the potential to produce moulds with three-dimensional shapes.

However it can take a considerable time to produce three dimensional structures, e.g. several hours. This is because the material removal rate is typically of the order of 0.5μm³/s for PMMA [22]. This implies that FIB is essentially a surface milling technique. Figure 6 shows a Stopping and Range of Ions in Matter (SRIM) [28] simulation of 10KeV argon (Ar) ions penetrating into PMMA. The simulation indicates that the ions have a well defined path into PMMA for a depth of approximately 100 nm after which there is a considerable amount of scattering of ions inside the material.

![10 keV Ar ions in PMMA](image)

**Figure 6** – **SRIM simulation of 10 keV Ar ions in PMMA** [28].
2.3.3 Proton Beam Writing (PBW)

Proton Beam Writing is a technique that employs a focused MeV proton beam which is scanned in a predetermined pattern over a semiconductor material (e.g. Si or GaAs), etchable glass (e.g. Foturan\textsuperscript{TM}) or a resist (e.g. PMMA or SU-8), which is subsequently electrochemically or chemically etched and developed. The ultimate depth of the structure is determined by the range of the protons in the material and thus allows structures to be formed to different depths.

The equipment typically consists of a hydrogen ion source that produces negatively charged hydrogen ions. These ions are accelerated and stripped of their electrons in a Tandetron electrostatic accelerator to produce MeV H\textsuperscript{+} ions (protons) which are subsequently focused to a beam spot using magnetic quadrupole lenses. A beam spot with a focused spot size of $35 \times 75 \text{ nm}^2$ has been achieved [29].

Due to the low lateral spread compared with the deep penetration range and the straight trajectory of the proton beam, it is possible to produce three dimensional micro and nano structures with well-defined smooth side walls. These can be directly written into the materials. Recent reports have shown this technique is capable of writing high aspect ratio walls up to 160 and details down to 30 nm in width with sub-3 nm edge smoothness [29].

Figure 7 is a SRIM [28], simulation showing 2 MeV protons with a projected range ($R_p$) of 80\textmu m in PMMA. Projected range ($R_p$) is the average distance where the majority of ions come to a stop.

![2 MeV protons in PMMA](image)

**Figure 7** – SRIM simulation of 2 MeV protons in PMMA [28].

The simulation in Figure 7 shows that the protons have a well defined long range into the material and a small lateral spread making this technique very useful for fabricating high
aspect ratio structures. The lateral scattering is due to end of range stopping effects which is explained in Chapter 4. Therefore to obtain high aspect ratio structures, etching should stop short of the end of range of the protons. PBW can also be used to produce microstructures with complex geometry by using protons of different energies or changing the orientation of the material surface with respect to the incident proton beam.

2.4 Comparison

Proton beam writing offers significant advantages compared to other techniques, such as electron, photo, X-ray and focused ion beam lithography. This can be seen in Figure 8 which shows a diagrammatic comparison of these patterning techniques.

Electrons suffer from significant scattering on their way through matter due to their low mass. This produces a poor aspect ratio in the structures created by EBL. This means that sub 100nm structures can only be realized in very thin resist layers [20]. In thick films, the minimum feature size is comparable to the film thickness, making EBL essentially a two dimensional process.

LIGA uses highly collimated beams of X-rays (usually from a synchrotron or storage ring). This has the advantage of producing deep high aspect ratio structures, but requires the use of a mask which can be time consuming to prepare. It also requires access to a synchrotron light source which is expensive. Focused ion beams (FIB) use low energy heavy ions to erode the structure atom by atom (sputtering), and although this technique can be used to produce three dimensional structures it is relatively slow and there may be problems with the re-deposition of the sputtered atoms.

Photolithography also requires the use of a mask and the resolution depends upon the quality of the mask. Also problems with diffraction of the light with the edges of the mask patterns may lead to a lateral spread of UV light which would result in a loss of resolution.

A major advantage of PBW compared to these other techniques is the well-defined depth of the structures without the need of a mask. As there is no need for a mask, this technique is ideal for the prototyping of three-dimensional structures. Complex geometry
microstructures can also be produced using PBW by using protons of different energies or changing the orientation of the material surface with respect to the incident proton beam.

Some of the disadvantages of PBW is that, at the moment it is still considered a novel technique and the even though it can be associated with a range of applications such as masks, it has not yet established a main stream application that it is commonly used for. It also requires a different set up to that of the other forms of lithography so in order to implement this process a new experimental set up would be required.

![Patterning techniques comparison](image)

**Figure 8** – *Patterning techniques comparison [10].*

The 2006 International Technology Roadmap for Semiconductors (ITRS) recognises direct write and imprint technology as potential lithographic techniques for technology nodes of 45 nm and below and states that although these technologies are still very much in the research stage "**Breakthroughs in direct-write technologies that achieve high throughput could be a significant paradigm shift, eliminating the need for masks and resulting in cost and cycle-time reduction.**" [30].

The speed and compatibility of proton beams with ultra large scale integration (ULSI) makes PBW a very promising candidate for development in this field. Moreover, PBW
offers an attractive solution for the fabrication of X-ray masks which will be required if X-ray lithography is going to be used for future generations of devices.
Chapter 3

3 Literature Review of Proton Beam Writing

3.1 Introduction

It can be seen from the comparison in Section 2.4 that PBW appears to have a lot of advantages over the other types of lithography. I would now like to explore this in more detail. First of all, I will look at PBW in a positive resist called Polymethyl methacrylate (PMMA) and examine the literature. I will then look at the literature for PBW in a negative resist called SU-8. This will be followed by looking into PBW in a photosensitive glass called Foturan™. As PBW is possible in positive and negative resists and photosensitive glasses, I will then examine the literature of PBW in the semiconductor material silicon (Si). As PBW has never been performed in the semiconductor material under investigation, GaAs, the literature review will be concluded by looking at literature related to ion implantation and carrier removal in GaAs to aid the successful development of PBW in GaAs.

3.2 High Energy (MeV) Ion Beam Writing in Polymethyl methacrylate (PMMA)

PMMA was the first resist to be used in microlithography due to its sensitivity to UV light, electrons, ions and X-rays. In 1979, PMMA was first used in ion lithography [31], using protons with energies up to 250 keV in which a mask process was used, similar to X-ray lithography. A thin layer of PMMA was deposited on top of a substrate. The thickness of this layer of PMMA was chosen according to the energy used. The limiting factors for the structure resolution were found to be due to mask distortion and mask scattering. To avoid proton scattering by the mask membrane, the wafer and mask needed to be in contact with each other. This limited the minimum line width achievable. The use of open masks, where the absorber layer was not supported on a membrane, were also performed and sub-micron resolution was achieved.
However, PBW in PMMA was first developed by M.B.H. Breese et al. [2] in 1993 at Oxford University. In this work it was established that PMMA could be used with MeV protons in a maskless lithography process. In this process, the MeV proton beam was focused using magnetic quadrupole lenses to micron and sub-micron diameters. This focused beam of protons was then scanned following a pre-designed pattern, over the resist. In the exposure of PMMA, the MeV protons caused chain scissioning of the polymer chains. The resulting damaged resist, consisting of molecular chains with lower molecular weight, were then selectively removed using a suitable chemical developer at a specific temperature. PMMA therefore is a positive resist under proton irradiation. The procedure used to develop the structures in the PMMA depends on the type of PMMA used, the proton fluence and energy.

In 1997, S. V. Springham et al. [32] used a scanned 2 MeV proton beam of approximately 1 μm in diameter to produce micro structures in a high molecular weight PMMA resist. The development of the exposed resist followed the following procedure:

*Development:* One to two hours at 35 to 39°C, with mild agitation, in: 60% Diethylene Glycol Monobutyl Ether, 20% Morpholine, 5% Ethanolamine, 15% Water.

*First rinse:* 30 min at 35°C, with mild agitation, in 80% Diethylene Glycol Monobutyl Ether, 20% Water.

*Second rinse:* 30 min at 35°C, with mild agitation, in water.

The exposed resist was developed and the developer showed to be highly specific in removing exposed PMMA, while leaving unexposed and marginally exposed PMMA unaffected [33].

Test patterns were written with varying exposure and the most suitable range of exposures for 2 MeV protons was found to be $4.69 \times 10^{13}$ ions/cm$^2$ to $5.31 \times 10^{13}$ ions/cm$^2$ (75 to 85 nC/mm$^2$). Exposures much below $4.38 \times 10^{13}$ ions/cm$^2$ (70 nC/mm$^2$) resulted in incompletely removed resist, with exposures below $1.25 \times 10^{13}$ ions/cm$^2$ (20 nC/mm$^2$) being almost completely undeveloped. Exposures much above $5.63 \times 10^{13}$ ions/cm$^2$ (90 nC/mm$^2$) resulted in the formation of bubbles in the PMMA. Due to the peaking of the deposited energy density towards the end of the proton range, any overexposure of the
resist will be most pronounced close to this point in the material. An SEM image of a wall structure of varying thickness protruding from side of 400 X 400 μm square with a fluence of $5.5 \times 10^{13}$ ions/cm$^2$ (88 nC/mm$^2$) can be seen in Figure 9. Figure 9 shows the thinnest wall which remained fully attached to the underlying resist, having a thickness of 5.2 μm at the upper surface, but due to the lateral deviation of ion trajectories, tapering to ~1.4 μm near the point of contact. Barely visible in this SEM are the remains of a thinner wall which has been undercut and broken away from the side wall. These results demonstrates that microstructures can be produced in high molecular weight PMMA resist using a scanned 2 MeV proton microbeam and that a suitable range of exposures and development conditions have been established.

![SEM image of a wall of varying thickness protruding from side of 400 X 400 μm square](image)

**Figure 9** – SEM image of a wall of varying thickness protruding from side of 400 X 400 μm square, exposure $5.5 \times 10^{13}$ ions/cm$^2$ (88 nC/mm$^2$) [32]. The image in the referenced paper is of poor quality.

I. Gomez-Morilla [4] have described studies in PMMA using 2 MeV and 3 MeV protons. For fluences ranging from $3.75 \times 10^{14}$ ions/cm$^2$ to $6.25 \times 10^{14}$ ions/cm$^2$ (0.6 to 1 pC/μm$^2$), 3 MeV protons were used and the structures were developed using a solution consisting of 20% isopropanol and 80% methyl isobutyl ketone which was used for 2 minutes to develop the structures. Gomez-Morilla [4] found this development process to be effective in producing microstructures in PMMA over this fluence range and energy. Her studies also indicated that, when using protons of a different energy 2 MeV, if the irradiation fluence is much lower, ranging from $4.69 \times 10^{13}$ ions/cm$^2$ to $5.31 \times 10^{13}$ ions/cm$^2$ (0.075 to 0.085 pC/μm$^2$), another solution by T.M. Hall et al. [34] is more effective. This solution consists of 60% diethylene glycol monobutyl ether, 20% morpholine, 5%
ethanolamine and 15% water. The sample is placed in this solution at 35-39 °C for 1 hour and then placed in another solution of 80% diethylene glycol monobutyl ether and 20% water at 35 °C for 30 minutes. The lower fluence means that the total time of exposure of the sample to the beam is shorter, and therefore the probability of uneven exposure due to pixel to pixel statistical fluctuations, beam instabilities or other irradiation factors are reduced. However the development process takes longer.

Comparing the results of S. V. Springham et al. [32] and I. Gomez-Morilla [4], it appears that for S. V. Springham et al.’s [32] work, the optimum fluence, using 2 MeV protons, for producing structures in PMMA was between $4.69 \times 10^{13}$ ions/cm$^2$ to $5.31 \times 10^{13}$ ions/cm$^2$ (75 to 85 nC/mm$^2$). I. Gomez-Morilla [4] also found that, when using 2 MeV protons at this fluence range of $4.69 \times 10^{13}$ ions/cm$^2$ to $5.31 \times 10^{13}$ ions/cm$^2$ (0.075 to 0.085 pC/μm$^2$ (75 to 85 nC/mm$^2$)), microstructures were produced, however in her studies a different development process was used to reveal the structures. For larger fluences S. V. Springham et al. [32] reported that exposures much above $5.63 \times 10^{13}$ ions/cm$^2$ (90 nC/mm$^2$), resulted in the formation of bubbles in the PMMA, however Springham continued to use the same development process that he used for the lower fluences. I. Gomez-Morilla found that for higher fluences of $3.75 \times 10^{14}$ ions/cm$^2$ to $6.25 \times 10^{14}$ ions/cm$^2$ (0.6 to 1 pC/μm$^2$), using 3 MeV protons, an altogether different development process was required to effectively produce microstructures. These results indicate that the key parameters needed to produce microstructures in PMMA depends on the type of PMMA being used, the type of development process, the temperature, the fluence and the proton energy.

With regards to the scanning system used in PBW for PMMA, J. L. Sanchez et al. [35], reported that certain limitations occurred when using their existing scanning system (OMDAQ) for PBW. One of the limitations was that OMDAQ is limited to a 256 x 256 pixels raster scan. This system, while adequate for analytical applications, has limitations when machining high resolution structures using PBW. A new scanning system was developed in order to overcome this limitation. The new scanning system is based on a DAC PC-card that allows flexible scanning with a resolution of up to 4096 x 4096 pixels. As the scan resolution of the new system can be set up to 4096 x 4096 pixels this allows a much higher scan resolutions to be implemented, resulting in smoother edges. In addition to the simple raster mode scanning operation, a new scanning algorithm has been
implemented based on a 'turtle' scanning strategy [36]. Using raster scanning the beam rasters across the area to be scanned, remaining for a preset time on pixels that are to be exposed. In the raster mode, the beam is moved rapidly across regions not meant to be exposed, thereby exposing these regions to a small residual fluence. With the new 'turtle' algorithm the beam follows a meander path around the pattern in the area scanned so as to minimise the number of jumps over points that should remain unexposed. The new software also allows the outline of the figures to be scanned, to be drawn separately. This strategy improves the sharpness of the edges. The new system allows the beam to be scanned in specific patterns, which are designed to achieve optimal resolutions.

Using this system, a direct-write 2 MeV proton beam focused to 1 \( \mu \)m was used to expose a set of different patterns in a thick (2 mm) high density PMMA. The currents used ranged between 1 pA and 100 pA and the proton fluence was optimised at \( 5 \times 10^{13} \) ions/cm\(^2\) (80 nC/mm\(^2\)), [32]. After exposure, the PMMA was developed following the procedure given in [32]. A cross pattern was scanned using the 'turtle' mode over a square area of 400 \( \mu \)m at a scan resolution of 512 x 512 pixels. Figure 10 shows an electron micrograph of one of the corners of the developed structure. Both edges have the same level of smoothness, and the results are much superior to earlier machined structures [32]. The use of the new scanning system provides a mechanism for translating high resolution digital images into high resolution three dimensional microstructures.

![10.0 µm](image)

**Figure 10** - *SEM micrograph of a corner of a cross scanned. Both edges have the same level of smoothness. The small defect visible in the top edge is due to a fault in the bulk of the PMMA* [35].
This scanning system was further improved by A. A. Bettiol et al. [37], who designed and implemented the first version of a new PBW scanning software called Ionscan. This software has the ability to scan an arbitrary shape or a group of shapes up to a scan resolution of 16 bit per channel. Beam blanking and external dose normalisation have been implemented. Pixel, shape and figure normalisation can be used depending on the requirements of the exposure and the type of sample being used.

Using this Ionscan [37] system, J. A. van Kan et al. [38] performed PBW on PMMA to produce nanostructures. In his study a 350 nm thick PMMA film was spincoated on Si. He also states that the most suitable fluence to expose PMMA with 2 MeV protons is $5 \times 10^{13}$ ions/cm$^2$ (80 nC/mm$^2$). Parallel grooves and lines were written within an area 20 x 20 mm$^2$ in a 350 nm thick PMMA film spincoated on Si. The resulting damaged resist, was then selectively removed using a suitable chemical developer at 30°C [32]. Due to the difficulties in imaging sub-100 nm structures in polymer films, special sample preparation was required. The structures were written parallel with the edge of the sample and 30 mm from the edge. Using a precision diamond scriber/breaker the Si was cleaved along a crystal plane which encompassed the line structures, allowing the cross sectional profile to be imaged. The high aspect ratio walls, estimated to be 50 nm wide, are shown in Figure 11. These results indicate that the performance of PBW is dependent on how well the MeV protons are focused, and through advances in this area, proton beam spot dimensions down to the 35 nm level [38] have been achieved.
Figure 11 - *SEM image of parallel lines written in a 350-nm-thick PMMA layer* [38]. The structure was written with a focused 2 MeV proton beam. The photo indicates a wall width of 50 nm.

In 2005 A. A. Bettiol et al. [39], upgraded the existing PBW scanning software, version 1 of Ionscan, to encompass a new a suite of programs, collectively known as version 2 of Ionscan, that catered for the specific needs of PBW. The upgrades to the new version include the ability to perform combined stage and magnetic (or electrostatic) scanning, for fabrication of structures over the lengths of 2.5 cm. Other enhancements include the addition of the Ionutils program which gives the user the ability to design basic structures using an ASCII file format that was developed. This format contains basic information on the shape to be irradiated including the way in which it is scanned.

In relation to the scanning software for PBW, F. Menzel et al.[40], at the high energy ion nanoprobe LIPSION of the University of Leipzig has established a data acquisition system MICRODAS where a new scan program was developed and tested which is dedicated to the creation of arbitrarily shaped structures. Using this system they have discovered that the required ion dose for a special resist type 950 PMMA A15 was found to be $\sim 3.13 \times 10^{14}$ ions/cm$^2$ ($\sim 0.5$ pC/µm$^2$).

Other studies of PBW in PMMA include N. Uchiya et al. [41]. In this work, a 5µm layer of PMMA was spincoated onto an Si substrate and PBW with a beam spot size of 1µm was used to scan a grid pattern. The proton beam was scanned with a resolution of 8192 x 8192 pixels by an electrostatic deflection scanner without a beam blanking system [42-
After the PBW, the resists were developed using IPA-water (7:3) for 20 min and rinsed in deionised water. The grid structure can be seen in Figure 12. N. Uchiya et al. [41], observed that when scanning the same pattern using different fluences, the linewidth of the trench increases. This can be seen in Figure 13, which shows the linewidth of the trench as a function of fluence on PMMA with a thickness of 5 μm on silicon by PBW at 1.7 MeV after the development. The linewidth of the trench increases by only 1% for the change in the fluence by 10% around $6.25 \times 10^{13}$ ions/cm$^2$ (100 nC/mm$^2$). Therefore, the influence of the proton beam current fluctuation on the linewidth is quite small. These results indicate that by increasing the fluence, the structural width may also increase due to beam fluctuations.

Figure 12 - SEM image of 5 μm thick PMMA with grid pattern by PBW using 1.7 MeV protons with a fluence of $6.25 \times 10^{13}$ ions/cm$^2$ (100 nC/mm$^2$) [41].

Figure 13 - Dependence of the linewidth of 5 μm thick PMMA after development on the fluence of proton beam [41].
Several studies have investigated the fabrication of buried tunnels in PMMA using a single step ion irradiation process. This is possible by utilizing enhanced end-of-range damage in thick PMMA. Gonin et al. [46], have reported the production of a simple 3D cavity structures using single irradiation steps in PMMA polymers. The use of high-energy (MeV) ion irradiation to fabricate polymer waveguides with Si masks has been reported by Ruck et al. [47] and Hong et al. [48]. Recently, fabrication of symmetric Y-branch buried channel waveguides in PMMA were reported by Sum et al. [49]. Reviewing B. Rout et al.’s [50] work, he reports that the creation of the buried tunnels in PMMA with a single energy irradiation step was found to be strongly dependent on the ion fluence and chemical developing process. In order to find out the critical doses for the fabrication of buried tunnel structures, the PMMA was irradiated with a simple rectangular pattern with 3 MeV proton beam at different fluences $6.25 \times 10^{14}$ ions/cm$^2$ – $6.25 \times 10^{12}$ (1 pC/µm$^2$ – 0.01 pC/µm$^2$). In order to chemically develop the patterns easily the edges were irradiated with highest fluence. Figure 14 shows the SEM images of the irradiated PMMA sample with various fluences and subsequent chemical developments. It can be seen in Figure 14 that the irradiation of the PMMA sample with a fluence of $6.25 \times 10^{14}$ ions/cm$^2$ – $1.56 \times 10^{14}$ ions/cm$^2$ (1.0 pC/µm$^2$ – 0.25 pC/µm$^2$), shows the formation of channels with smooth sidewalls. The bottoms of the sidewalls are narrower, indicating the increase in the lateral straggling at the end of the range on the irradiating ion beam. Irradiating with a fluence of $6.25 \times 10^{13}$ ions/cm$^2$ (0.1 pC/µm$^2$), shows the formation of tunnels with some porous top surface layers while for the fluences between $1.56 \times 10^{13}$ ions/cm$^2$ and $4.69 \times 10^{13}$ ions/cm$^2$ (0.025 pC/µm$^2$ and 0.075 pC/µm$^2$), tunnels were formed at the end of the range. By selecting the right fluence for the proton beam, B. Rout et al. [50] have shown that it is possible to fabricate the micro-tunnel structures near the end of the ion range and because of the low fluence, not much damage occurs on surface layers above the tunnels. On further chemically developing of these tunnels, the porous material on the top surface layers gets removed, forming channels on top of the tunnels. Although it is possible with some other techniques like X-ray lithography to create very deep channels, PBW is the only technique able to create buried tunnels in a direct write mode. Also the depth of the tunnel can be easily controlled by varying the energy of the ion beam from the accelerator. The greatest advantages of this single energy irradiation step is the fabrication can be completed in a single step process,
without the need of refocusing of the ion beam, recalibration of the scanning sizes due to change of the ion energy, also not to mention the re-alignment of the sample.

Figure 14 - SEM image showing the results of varying exposures of 2.7 mm thick PMMA substrate using 2 μm x 2 μm, 3 MeV proton microbeam. Depth of penetration is 130 μm. The irradiation fluences are in units of pC/μm². The sample was chemically developed tunnels (~17 min) until the opening of the lowest fluence 0.025 pC/μm² (1.56 x 10¹³ ions/cm²) tunnel [50].

It is seen from the literature of PBW in PMMA that a critical fluence for proton irradiations exists, above which the irradiated regions start to swell and cracks appear inside the irradiated volume, due to the formation of gas bubbles of volatile products from chain scissioning [51]. Cracks also appear if the development process is carried out above a critical temperature. It has been seen that when using certain types of PMMA, specific development processes are required for specific fluences to reveal the structures produced by PBW. The formation of buried structures is also possible and the importance of the beam scanning has also been discussed. These critical proton fluences depends on the structure that is being produced, the specific type of PMMA, the proton energy, beam spot size and the developer used.

From the literature, PBW has been successfully performed in a positive resist PMMA. The next section describes PBW in a negative resist SU-8.
3.3 Proton Beam Writing in SU-8 Photo-resist

SU-8 is an epoxy-based, negative, chemically amplified, near-UV photoresist that is usually spin coated onto a substrate (typically Si). When the proton beam irradiates the SU-8, it causes cross-linking of the photoresist. A suitable chemical developer can then be employed at room temperature to selectively remove the unexposed areas [52], making SU-8 a negative resist under proton beam exposure.

J.A. van Kan et al. [52], reports that the PBW technique can be used to fabricate three dimensional structures in the SU-8 resist. He has performed studies into the sensitivity of SU-8 and the end of range energy deposition of a proton beam in SU-8. The microstructures in J.A. van Kan et al.'s study are all produced in thin resist layers in order to prevent the "end of range" broadening of the beam envelope in the resist layer. These resist layers were applied on Si wafers using the spin coating technique. After exposure the samples are developed in a chemical solution. The SU-8 was developed at room temperature using a common developer supplied by the manufacturers of the resists. Typical development times for these three resists are 3 to 7 min. In this study, currents ranging from 1 to 100 pA were used with a beam spot size close to 1 μm².

Figure 15 shows two perpendicular walls produced in a 36 μm layer of SU-8 resist using 2 MeV protons. Because SU-8 is a negative resist, the structures which remain are those which have been cross linked by the proton beam. The proton fluence used to expose the SU-8 was $1.38 \times 10^{13}$ ions/cm² (22 nC/mm²). It is clear from Figure 15 that smooth walls perpendicular to each other with a well-defined intersection can be produced using proton beam writing. The main advantage of the walls produced in the thinner SU-8 layer is the fact that the end of range spread of the proton beam occurs in the supporting Si wafer and not in the resist layer.
Due to the fact that protons have a relatively long and well defined range in resist materials, the penetration depth depends on the proton energy. This feature allows the production of slots and holes of well defined depth and the creation of multilevel structures in one resist layer. Further studies by J.A. Van Kan et al. report that by exposing the negative resist SU-8 to protons at different energies, novel structures can be produced in one layer of resist. These structures include cantilevers and buried micro-channels [53, 54].

An example of a cantilever structure written with a 1.0 MeV and 2.0 MeV proton beam is shown in Figure 16. This figure shows five cantilever structures produced in a single coated, 36 μm thick SU-8 layer applied on a Si wafer produced by J.A. van Kan et al [53, 54]. Two exposures were performed with 1 and 2 MeV protons. The 1 MeV protons have a range of about 22 μm in the SU-8 layer and therefore this exposure was used to produce the cantilevers. A fluence of $6.25 \times 10^{12}$ ions/cm$^2$ (10 nC/mm$^2$) was used for this 1 MeV exposure. The supporting anchor was exposed with a fluence of $2.19 \times 10^{13}$ ions/cm$^2$ (35 nC/mm$^2$) using 2 MeV protons. The cantilevers have a length between 70 and 260 μm, a width of 20 μm and a height of 22μm.
Figure 16 - SEM micrograph of a set of cantilevers produced in a 36 μm thick SU-8 layer. The suspended cantilevers were produced using a 1 MeV proton exposure and the anchor was exposed using 2 MeV protons [53, 54].

Figure 17 - SEM micrograph of a suspended multilevel grid produced in one 36 μm thick layer of SU-8 resist using three exposures at proton energies of 0.6, 1 and 2 MeV [53, 54].

Figure 17 shows an example of an intricate multilevel structure made by proton micromachining by J.A. van Kan et al [53, 54]. A 3D multilevel grid suspended by two anchors was assembled. This structure was produced using three different proton energies in one single layer of resist. In the centre two anchors can be seen, produced using 2 MeV protons (fluence $2.19 \times 10^{13}$ ions/cm$^2$ (35 nC/mm$^2$)). Protons with an energy of 600 keV have a range of less than 10 μm in SU-8; this energy was used to
produce the shallowest lines. The walls perpendicular to the first set were exposed with a 1 MeV proton beam; this resulted in 22 µm walls. This double layered grid was produced using an exposure of $6.25 \times 10^{12}$ ions/cm$^2$ (10 nC/mm$^2$). The individual lines have a width of 5 µm and a spacing of 20 µm. The grid is suspended by the two anchors, 50 x 200 µm$^2$ each. In a first attempt to produce high aspect ratio structures in SU-8, narrow walls were produced with a 2.2 MeV proton beam in a 36 µm SU-8 layer. The wall has a width of 1.5 µm. It should be noted that these preliminary performances were achieved with an unstable proton beam.

Besides simple square structures, J.A. Van Kan et al. [55] attempted more complex shapes using PBW in SU-8. Figure 18 shows circular pillars. They are written in a 20 µm thick Su-8 layer applied on a Cu coated Si wafer written with a 2 MeV proton beam (180 x 180 nm$^2$). This figure was produce using a spiral scanning algorithm. The smallest pillars have an aspect ratio of more than 10. The substrate here is metallic compared to a polymer used in previous studies. This shows that in PBW the type of substrate does not affect the quality of the written structures.

![Figure 18 - SEM image of circular pillars of 2 µm and 1.5 µm diameter, written in a 20 µm thick Su-8 layer which was applied on a Si wafer. These structures were written with a focused 2 MeV proton beam [55].](image-url)
Several studies have investigated the fabrication of three dimensional structures in SU-8 using PBW. N. Uchiya et al. [41] reports that the following structure seen in Figure 19 is an SEM image of SU-8 developed after the irradiation by proton beam at 1.7 MeV with a dot pattern (fluence: \(6.25 \times 10^{13} \text{ ions/cm}^2\) \((100 \text{ nC/mm}^2)\)). Since the irradiated area remains for the negative resist after development, the structure of pillars was formed. The width of the pillar was 1.1 \(\mu\text{m}\) at the top and 2.2 \(\mu\text{m}\) at the bottom on the silicon substrate with a height of 21 \(\mu\text{m}\). The increasing width of the pillars along the depth is ascribed to the lateral scattering and inhomogeneous depth distribution of the electronic stopping power, as predicted by SRIM 2003 (data not shown in the paper). This result shows that PBW is suitable for the micromachining of high aspect ratio structures. Comparing this structure with that produced by J.A. Van Kan et al. [55], seen in Figure 18, it is observed that the diameter of the structures are smaller and they are taller as well. This indicates that high performance results for PBW can be achieved using different setups and different types of suppliers and development processes of SU-8, showing the versatility of PBW.

![Figure 19 - SEM image of 21 \(\mu\text{m}\) height SU-8 pillars by PBW at 1.7 MeV with a fluence of \(6.25 \times 10^{13} \text{ ions/cm}^2\) \((100 \text{ nC/mm}^2)\) [41].](image)

Figure 20 is a SEM image of the grid patterns formed on a 50 \(\mu\text{m}\) thick SU-8 film by PBW at 3 MeV by N. Uchiya et al. [41] . Taking into account the smaller electronic stopping power for 3 MeV, the fluence was increased to \(9.38 \times 10^{13} \text{ ions/cm}^2\) \((150 \text{ nC/mm}^2)\), by a factor of 1.5. The self-standing grid SU-8 patterns on silicon in Figure 20 were obtained by post exposure bake for the self-standing rigid structure. Meanwhile, the
post exposure bake is not necessary for the case of PBW as previously reported [56], such as for the 21 μm SU-8 pillars shown in Figure 19, though the baking process is required for the case of UV and X-ray [57]. The feature such as vertical sidewall with smooth surface for the positive and negative resists confirmed that the PBW technique is useful for the micro-machining of thick resists with several tens of micrometers. For better homogeneity in the linewidth along the depth direction, the PBW at higher energy is desirable for less scattering of protons for resists with the same thickness.

**Figure 20** - SEM image of structure of 50 μm thick SU-8 wall with grid pattern by PBW at 3 MeV with a fluence of 9.38 x 10^{13} ions/cm² (150 nC/mm²) [41].

F.Menzel et al. [40] reports that the new scanning program linked to the new MICRODAS data acquisition system was able to produce arbitrarily shaped structures by PBW in SU-8. He also reports that the feature size of structures written in SU-8 at the LIPSION beam line was lowered to 130 nm.

Further studies by J.A. Van Kan et al. [55], to determine the potential of p-beam writing in obtaining high aspect ratio, test structures were written using a 2 MeV proton beam in a 10 μm thick layer of Su-8, spin-coated onto a Si wafer. In this experiment 2 MeV protons were focussed down to a spot size of 60 x 120 nm² and scanned in a matrix of circular pillars seen in Figure 21. During the exposure, extra lines were written through the centre of the cylinders forming a high aspect ratio nano grid. As can be seen in the SEM
pictures in Figure 21, the single written lines are 60 and 120 nm in width, which is believed to, currently be the smallest written single line in Su-8 [58]. The support given by the adjacent cylindrical pillars ensures that the structural integrity of the narrow walls is not degraded during the development procedures. The narrow wall structure exhibits an aspect ratio of more than 160. Only Bogdanov and Peredkov [58], have reported similar aspect ratios for SU-8 structures, but with a structural width of 4 µm or more.

Figure 21 - *SEM image of 2 µm diameter circular pillars written in a 10 µm thick Su-8 layer. Linking the cylinders are high aspect ratio walls of width 60 nm. The structures were written with a 2 MeV proton beam [55].*

Since the proton beam has a well defined range in both positive (PMMA) and negative (SU-8) resists, the depth of structures can be easily controlled by using different proton energies enabling the construction of slots, channels and holes, with a well defined depth. The depth can be different for these slots, channels or holes in one single resist layer and complex shapes can be machined with very well defined sharp edges. Arbitrary shapes can be fabricated, high-aspect-ratios (more than 100) can be achieved in PMMA and SU-8 resist, and the smallest single line achieved so far in a PMMA layer is 30 nm [38]. In the exposure of PMMA, the protons cause chain-scissioning of the polymer chains. The resulting damaged resist, consisting of molecular chains with lower molecular weight, are
 Chapter 3 — Literature Review

then selectively removed using the required developer. PMMA therefore is a positive resist under proton irradiation. On the other hand SU-8 cross-links under proton beam exposure. A suitable chemical developer can then be employed at room temperature to selectively remove the unexposed areas, making SU-8 a negative resist under proton beam exposure. From these studies, the most suitable fluence to expose PMMA with 2 MeV protons is $5 \times 10^{13}$ ions/cm$^2$ (80 nC/mm$^2$). In the case of SU-8 only $1.88 \times 10^{13}$ ions/cm$^2$ (30 nC/mm$^2$), is needed for full cross-linking [55].

Seeing from the literature that PBW has been successfully performed in both a positive and negative resist, the next section investigates PBW in a non polymer material, photosensitive glass.

### 3.4 Proton Beam Writing in Photosensitive Glass

Several materials have been investigated for the fabrication of lab-on-a-chip devices with integrated optics. These materials include photosensitive glasses. One such material is Foturan™. Foturan™ is a photosensitive glass that becomes etchable after irradiation with UV light and subsequent heat treatment. Studies show that it can be readily modified using lasers [59-61] or MeV protons [4, 5, 62, 63]. Upon heat treatment, the exposed regions of the sample undergo a phase change from glass into a crystalline form of Lithium-metasilicate. Lithium-metasilicate has a 20 times higher etch rate in hydrofluoric acid (HF) than the surrounding glass, hence microstructures can be formed by etching the post heat treated sample [64]. The ability to directly form microstructures in this glass along with its resistance to high temperature and corrosion has made it an attractive material for microfluidic applications such as microelectrochemical reactors [65, 66]. In addition to this etch contrast, irradiated and heat treated Foturan™ has also a higher density and refractive index. The ability to selectively modify the refractive index of this material on a micron scale allows for the possibility to fabricate embedded photonic structures such as waveguides [67, 68] and gratings [60].

I. Gomez-Morilla performed investigations [4, 5, 62, 63] into PBW on the photosensitive glass, Foturan™. Gomez-Morilla's work investigated whether high energy protons induce the same effects as ultraviolet light. It was found that the etch rate increases
significantly when the Foturan™ has been both irradiated with protons and annealed therefore it exhibits positive behaviour to radiation. These results demonstrate that MeV protons induce a phase change from glass into a crystalline form of Lithium-metasilicate in the Foturan™ and that this phenomenon can be exploited to create structures in the glass. Following exposure and heat treatment, the exposed regions have a red colouration, demonstrating that the silver ions in the glass have been left in an optically active state.

I. Gomez-Morilla’s results indicate that when irradiating with low currents, up to ~0.5 pA and low fluences, up to ~1.56 x 10^{11} ions/cm^2 (~0.25 nC/mm^2), shallow buried channels were etched in the sample and some damage on the samples surface could be observed. This can be seen in Figure 22.

![Figure 22 - SEM image of Foturan™ with shallow etching due to low dose (2 MeV, 0.5 pA, 1.56 x 10^{11} ions/cm^2 (0.25 nC/mm^2)) [4].](image)

With intermediate currents (~0.8 pA) and fluences of ~3.13 x 10^{11} ions/cm^2 (~0.5 nC/mm^2), as well as the shallow etching observed with smaller fluences, buried channels could also be etched at the end of the proton range when some path was provided for the etchant to reach that depth – for example, by irradiating the sample over an edge.

Figure 23 (a) and (b) are SEM images of gratings done by irradiation with a 3 MeV proton beam with a total fluence of 3.13 x 10^{11} ions/cm^2 (0.5 nC/mm^2), and current of 0.8 pA over the edge of the sample. Channels a few micrometers deep have been etched, as well as 80 μm deep channels, coinciding with the end of range of protons.
Figure 23 – (a) SEM image of buried channels in Foturan™ etched after irradiation with 3 MeV protons (current 0.8 pA, fluence $3.13 \times 10^{11}$ ions/cm$^2$ (0.5 nC/mm$^2$)). (b) Close up of Figure 24. Buried channels (82 μm deep) as well as shallow channels (<5 μm deep) can be observed [4].

With higher currents ($\geq 1.1$ pA) and fluences $\geq 3.13 \times 10^{11}$ ions/cm$^2$ (0.5 nC/mm$^2$), the glass was etched all the way from the surface, down to the end of range of protons as seen in Figure 24.

Figure 24 – SEM image of walls etched in Foturan™ with 1.5 MeV protons (3 pA, $6.25 \times 10^{11}$ ions/cm$^2$ (1 nC/mm$^2$)) [4].
The threshold fluence for patterning Foturan™ (approximately $10^4$ protons/µm$^2$) is much smaller than for PMMA and SU-8 [4, 35, 38, 55], and the beam currents required are so low that it is difficult to measure them accurately. Foturan™ is very sensitive, and therefore problems of reproducibility can be encountered.

I. Gomez-Morilla states that structures etched in Foturan™ glass show an absence of end of range roughness due to low levels of beam power density being deposited at the end of range. This can be seen in Figure 25.

![Figure 25](image)

**Figure 25** – SEM image of grid structure made in Foturan™ with 2.5 MeV protons (SRIM range ~61 µm, actual depth 60.9 µm) [4, 5].

Reviewing the literature, it has been seen that PBW has been successfully performed on both the positive and negative resists as well as on Foturan™ glass. The next section investigates PBW in the semiconductor material silicon (Si).

### 3.5 High Energy (MeV) Ion Beam Writing in Silicon

One of the major limitations of conventional lithography and silicon (Si) etching is the multiple processing steps required to fabricate free standing multilevel structures [69, 70]. Polesello et al. [71] demonstrated the possibility of patterning silicon as a resist material with MeV protons, however the resulting micromachined structures lacked edge definition and height due to the poor beam stability and spatial resolution.
E. J. Teo et al. [6], reports that the PBW technique can be used to fabricate multilevel free-standing microstructures in bulk Si using a single etch step, after irradiating the sample with protons of different energies. In E. J. Teo et al.’s [6] work (100) p-type Si with normal resistivity of 15 Ωcm was used for micromachining. An etch stop technique which relies on the localized damage created by a high fluence of focused MeV proton irradiation for three dimensional microfabrication is employed. As a 2 MeV proton penetrates the material, it loses energy and eventually comes to a rest after traversing approximately 48μm below the surface. Silicon vacancies and interstitials are created along the ion path, with most of the damage produced at the end of range. The resistivity of the irradiated regions is expected to increase by 3-4 orders of magnitude [72]. This significantly reduces the current flow through the silicon electrolyte interface, preventing the formation of porous Si in the irradiated regions patterned by the proton beam.

The electrochemical etching process for the Si irradiated sample uses an electrolyte mixture of hydrofluoric acid:water:ethanol (1:1:2). An electrical current of 40 mA/cm² is passed through the silicon (which forms the anode) which causes the formation of ‘porous silicon’ at the surface [73, 74]. The damage, caused by the proton irradiation, inhibits the formation of porous Si [73, 74]. After electrochemical etching, the porous Si is removed using a dilute potassium hydroxide (KOH) solution, leaving the final patterned structure on the wafer surface as a 3D representation of the scanned pattern area. This process is diagrammatically shown in Figure 26.
E. J. Teo et al. [6] have shown that it is possible to obtain structures with vertical side walls, due to the fact that the MeV proton beam follows an almost straight path in the material with little straggling except at the end of range. This overcomes the undercutting effect encountered when a surface mask is used [75]. This can be seen in Figure 27 which shows a square structure produced by 2 MeV proton irradiation with a fluence of $5 \times 10^{15}$ ions/cm$^2$ in p-type Si.
Figure 27 - (a) Diagram showing the reduced current flow (dashed lines) through a damaged region created by the ion beam. (b) SEM image of a square structure produced by 2 MeV proton irradiation with a fluence of $5 \times 10^{15}$ ions/cm$^2$ in p-type Si [6].

E. J. Teo et al. [8], have shown that it is possible to produce a uniform array of closely packed, high aspect-ratio pillars obtained by single spot irradiations of a focused proton beam in (100) p-type Si with normal resistivity of 15 $\Omega$cm. A scanning electron micrograph (SEM) of this can be seen in Figure 28. Each spot has an accumulated dose of $5 \times 10^{16}$ ions/cm$^2$. The sample was then etched for 15 minutes with a current density of 40mA/cm$^2$. The pillars are 4.5 $\mu$m high with a diameter of 0.6 $\mu$m, and a periodicity of 2 $\mu$m. The profile of the pillar reveals vertical and smooth sidewalls with slight broadening at the base. A longer etching time may be used to increase the height and aspect-ratio of the silicon pillars. Such a periodic array of sub-micron diameter pillars is potentially important for the fabrication of photonic crystals [76].

By aligning the incident ion beam with an axis or set of crystal planes, the ion beam becomes channeled, which reduces the probability of nuclear collisions with silicon atoms [77]. This results in a significant reduction of the damage caused by the channeled ion beam close to the surface. Figure 28 (b) shows the structure obtained with a similar irradiation pattern and dose as for the random structure in Figure 28 (a) but with the beam channeled along the $<$100$>$ axis of the sample. The reduced damage created near the surface regions results in much sharper and thinner tips, with a radius of curvature of about 15 nm at the tip.
There has been work performed by F. Menzel et al. [78] also looking at producing micro and nano structures in Si using PBW. In his studies he has produced arrays of Si pillars by single spot irradiation. In his results the pillar diameter depends on the fluence applied to the spots using a 2.25 MeV proton beam of about 1.2 μm diameter. An exposure with 40 pC/spot (2.5 x 10^{16} ions/cm^2 (35 pC/μm^2)), results in 2.1 μm pillar diameter, while 12
pC/spot ($6.88 \times 10^{15}$ ions/cm$^2$ (11 pC/$\mu$m$^2$)), leads to a 1.2 $\mu$m pillar diameter as shown in Figure 29(a) and (b), respectively. The crystal structure of the Si seems to influence the pillar shape as can be seen in a top view on the pillars (Figure 29(c)). However, the pillar shape also is affected by the beam spot shape or fluctuations of the beam spot position. The egg like shape of the pillar base area in Figure 29(d) may therefore be caused by the non circular beam spot shape due to an imperfectly focused ion beam or by fluctuations of the beam position. Comparing these results to those of E. J. Teo et al [6], it can be seen that fluctuation in the beam spot and its shape have a significant effect on the structures produced.

Figure 29 – Pillar structures created in Si by single spot proton irradiation with (a) 40 pC/spot and (b) 12 pC/spot showing the increase of the pillar diameter with irradiation
dose. The pillar shape seems to be influenced by the crystal structure (c) as well as by the beam spot shape (d) [78].

It has been demonstrated in E. J. Teo et al.'s [6], work that three dimensional multilevel free-standing bridge structures in bulk silicon is possible. They found that after prolonged etching beyond the end of range, the isotropic etching process starts to undercut the structure. This means that multilevel structures can be created by exposing the sample with two different proton energies. Since the structure irradiated with lower energy has a shorter range, it will begin to undercut at a shallower etch depth while the structure with higher energy irradiation continues to increase in height. This was performed by exposing the silicon to different proton energies of 0.5 MeV and 2 MeV. The implanted depth and hence structure height can be precisely controlled to obtain freestanding multilevel microstructures using a single etch step by the electrochemical etch. This can be seen in Figure 30.

The much smoother surface of the irradiated structures compared with the unirradiated regions suggests that porous Si is strongly restricted from forming in the irradiated regions.

**Figure 30** - 3D multilevel free-standing bridge structures in bulk silicon by p-beam writing [6].
Teo, E.J. et al. [7], have also produced multilevel structures by multiple fluence exposures in a single irradiation step in bulk silicon using an MeV single focused helium beam and subsequent electrochemical etching. This multilevel structure, seen in Figure 31 was generated by using a helium beam and irradiating $6 \times 10^{14}$, $2.5 \times 10^{15}$ and $1.9 \times 10^{16}$ ions/cm$^2$ fluences of 2 MeV helium ions. The raised portions of the structure were produced using higher beam fluences than the surrounding large cross. Undercutting of the structure can be seen around the outer edge of the cross as the sample is etched beyond the end of range, enabling the formation of cantilever structures.

![Figure 31 - Multilevel cross structures irradiated with multiple fluences of He ions [7, 8].](image)

3.6 Comparison

From the literature, it has been seen that PBW has successfully been performed to produce micro and nano high aspect ratio, three dimensional structures in PMMA, SU-8, Foturan™ and Si. Table 1 shows a comparison of the required fluence and the smallest feature size with respect to the materials investigated in this literature review for PBW [79]. This information will be used to help with the experimental preparation for PBW in GaAs.
Table 1 – Fluence and smallest feature size with respect to the materials investigated in the literature review [79].

As the aim of this Ph.D is to perform PBW in GaAs it would be beneficial to look into the literature regarding ion implantation and carrier removal in GaAs. The next part of this section aims to describe some of the literature in this area to aid the development of PBW in GaAs.

3.6.1 Implant Isolation

Initially, ion implantation was developed for doping the semiconductor elements of integrated circuits. When compared to growth or diffusion techniques, it has several advantages such as:

- Minimal lateral spread of dopants beneath a mask.
- Accurate dose and depth control.
- Several dopants may be added.
- Good uniformity and reproducibility of doping.
- Low temperature or room temperature implantation.
The introduction of dopants is often possible which cannot be introduced by diffusion. It
has become the standard for this type of work due to its speed, cleanliness, accuracy and
controllability of the process.

The introduction of disorder to the crystal during the implantation process is one of the
disadvantages of ion implantation. Therefore, much of the early research was directed
towards the problem of finding out the optimum implant conditions and annealing
sequence needed to remove damage, and therefore allow the implant to dope the
semiconductor. However, it was found that this type of damage can be used in
semiconductors to form high resistivity layers. Ion implantation has also become strongly
recognised as a technique for selectively modifying the resistivity of semiconductors
through the introduction of implantation induced deep level trap charge carriers [81].
Implant isolation is also referred to as isolation by ion irradiation. It provides insulating
device isolation for integrated circuits.

In III-V semiconductors, radiation induced defects are observed to generate effective
compensating centres that are stable at room temperature. When light ions such as N+ and B+
are implanted into GaAs at 1 MeV, 200 carriers are removed per implanted ion [82]. Therefore when implanting dopant ions, even if all of the implanted ions become
electrically active, one residual defect per implanted ion is sufficient to compensate all of
the doping effect. Therefore, for device isolation applications, this damage technique is
valuable. For creating implant isolated regions in III-V semiconductors there are two
types of mechanism:

- Damage induced isolation: This occurs when the target is implanted with neutral
  ion species to create damage related deep levels in the material. The isolation is
  caused from the induced lattice damage and is dependent on a variety of
  parameters such as energy, dose, ion mass and substrate temperature during
  implantation.

- Chemical induced isolation: This occurs when ion species are implanted into the
  material and combine with impurities or dopants already present in the material to
  generate chemically active deep level state. For this type of compensation to
  occur, it requires the ion species to be substitutional, and hence annealing may be
  required to promote the ion into a substitutional site. The behaviour of iron in InP
  is an example of this model.
Damage induced isolation is effective to a temperature at which the damage anneals out, however, chemically induced isolation requires substitutionality of the implanted species through annealing. In this respect the two methods are somewhat complementary.

3.6.1.1 Proton Implant Isolation

Hydrogen implantation has been used successfully to reduce electrical conductivity in selected areas of III-V compound semiconductors for device isolation and definition [83-90]. The mechanism by which proton implantation produces carrier compensation is mainly through the introduction of damage, that is, damage induced isolation. Crystal damage of the GaAs is the primary mechanism by which proton implantation produces carrier removal. Point defects and traps in the crystalline material are created during the proton implantation. This leads to deep levels in the band gap which can trap the charge carriers. A conducting doped layer becomes electrically isolated when the concentration of traps is high enough to capture all the carriers.

The irradiation for electrical isolation purposes is usually performed with light mass ions. This provides penetration depths that are similar or larger than those of the doped layers. The electrical isolation or carrier removal technique, was first applied in the early 1970’s, and is now used for a range of applications such as integrated circuits, lasers and LEDs [84].

3.6.1.1.1 Annealing Effects

S. Ahmed et al. [91, 92] investigated the formation of electrical isolation in Si-doped GaAs layers using 500 keV hydrogen ions at three different substrate temperatures (room temperature (RT), 100°C and 200°C) during implantation. The effects exhibited by elevated temperature implants as compared to room temperature implants were studied in terms of the annealing characteristics of the sheet resistivity for all three substrate temperatures. After implantation with $3 \times 10^{14}$ protons cm$^{-2}$, the sheet resistivity increased from about 130 $\Omega$/sq to 2.6 $\times 10^4$ $\Omega$/sq for RT implanted samples, from 106 $\Omega$/sq to 4.1 $\times 10^6$ $\Omega$/sq for 100°C implants and from 85 $\Omega$/sq to 6.0 $\times 10^6$ $\Omega$/sq for 200°C
implants. It is interesting to note that the sheet resistivity for RT implanted samples is more than two orders of magnitude lower than those implanted at either 100°C or 200°C.

After the proton implantation, these samples were then annealed. As the RT-implanted samples are annealed at progressively higher temperatures, the resistivity increases, reaching a maximum of about $2.3 \times 10^7 \, \Omega$/sq at 350°C, with continued annealing leading to restoration of the initial resistivity of about $126 \, \Omega$/sq at 450°C. This is a classical feature observed in previous implant-isolation studies [81], where the annealing treatment causes extensive hydrogen diffusion and accumulation at particular interfaces. It is well established that hydrogen is attached to any deformation in a semiconductor lattice and actually may force its way to weakened bonds [93]. But the case for those samples implanted at elevated temperatures is somewhat different. For an implant temperature of 100°C, the maximum resistivity ($R_s = 7 \times 10^7 \, \Omega$/sq) is achieved again at 350°C but the restoration of initial resistivity is obtained only after a 550°C anneal. At an annealing temperature of 450°C, the sheet resistivity is still quite high ($R_s = 2.1 \times 10^7 \, \Omega$/sq) as compared to RT-implanted samples where restoration of initial resistivity occurred at this post-implant annealing temperature. The samples irradiated at 200°C also have resistivities that increase with increasing temperature, reaching a maximum ($R_s = 8.1 \times 10^7 \, \Omega$/sq) at 350°C. With continued annealing at 450, 550 and 600°C, the resistivity decreases only from $3.2 \times 10^7 \, \Omega$/sq to $4 \times 10^6 \, \Omega$/sq. The value of sheet resistivity after annealing at 450°C is almost five orders of magnitude higher than those achieved at the same annealing temperature but with samples implanted at RT. Similarly at 550°C, $R_s$ for implants at 200°C is more than four orders of magnitude higher than those samples annealed at 550°C after irradiation at 100°C. The restoration of initial sheet resistivity in this case is achieved when the samples are annealed at 850°C. Figure 32 shows the evolution of sheet resistivity in the proton-implanted n-type GaAs layers used in S. Ahmed et al.'s studies [91, 92].
3.7 Electrochemical Etching of Gallium Arsenide

The electrochemical etching is used to drive an oxidation reaction at the anode (the GaAs sample) and a reduction reaction at the cathode in a direction in which does not occur spontaneously. The oxide is then chemically stripped resulting in the etching of the sample.

3.7.1 n-type Gallium Arsenide

T. Ambridge et al. [94] describes the process that is involved to electrochemically etch n-type GaAs using the commercially available PN4300PC Electrochemical C-V Profiler from BIO-RAD [95]. His studies indicate that a suitable combination of electrolytic conductivity and behaviour can be met by using 0.1M Tiron (4,5-Dihydroxy-m-benzenedisulfonic Acid, Disodium Salt), for the electrochemical etching of GaAs.
The electrochemical etching of GaAs depends on the presence of holes. For n-type materials, in which electrons are the majority charge carriers, holes have to be created for etching to take place. By illuminating the semiconductor/electrolyte junction with light of a short enough wavelength, electrons can be promoted from the valence band into the conduction band, leaving holes behind [94]. For p-type semiconductors holes are plentiful and electrochemical etching can be readily achieved without the need for illumination [95-97].

Their findings state the importance of using illumination during etching for n-type GaAs. A narrowband filter at 550 nm was used in conjunction with the quartz iodine tungsten light source to provide light which is strongly absorbed within a region much narrower than the depletion width. This ensures that in almost all cases, a similar number of minority carriers are available for the dissolution reaction. The results indicated an improvement in smoothness at the base of the etched area when using the 55nm narrowband filter [96]. They also describe how increasing the current density in the electrochemical etch results in a faster etch of the material at the expense of increased surface roughness and pitting [98]. If on the other hand the current density is reduced the etching of the material is considerably slower but the surface of the remaining material is smoother.

W. C. Niehaus et al. [99] have used a different set up for the electrochemical etch. They used an electrolytic bath system where the electrodes consist of a platinum cathode and the GaAs sample as the anode held totally immersed in the electrolyte solution by tweezers made of a readily oxidized material such as aluminium. The bath electrolyte consists of a H₂O:H₃PO₄ (pH 2.0-2.6) solution. With this setup the electrolytic tailoring of the breakdown voltage depends on two basic features of anodization:

1) The thickness of anodic oxide grown depends on the voltage \( V_{ox} \) available for anodisation

2) \( V_{ox} \) in turn is essentially the applied voltage \( V_a \) diminished by the breakdown voltage \( V_b \) of the solution semiconductor junction.

This system anodises the sample with the voltage applied \( V_a \) which is set equal to the desired breakdown voltage \( V_b \) followed by the chemical removal of the anodic oxide, the anodisation proceeds at each step until the breakdown voltage everywhere has risen to
the uniform value $V_a = V_b$. At this point there is no further anodisation because $V_{ox}$ has dropped to zero. It was found that this oxide is soluble in NH$_4$OH or HCl but is insoluble in organic solvents. In this study it was recognised that anodic current in the semiconductor is carried out by electrons created by the avalanche process at the oxide-semiconductor interface which is a Schottky barrier in reverse bias. The results indicate that successful etching occurred using a 50V applied voltage but due to material defects with low breakdown voltages resulting in locally thicker oxides, non uniform etching occurred.

3.7.2 p-type Gallium Arsenide

T. Ambridge et al. [97] have also reported that with a little modification, the PN4300PC Electrochemical C-V Profiler from BIO-RAD [95] is suitable for the etching of p-type GaAs. This etch is possible without illumination as holes are plentiful p-type semiconductors and electrochemical etching can be readily achieved without the need for illumination.

N. F. Jackson et al. [100] have performed studies of pulsed anodic etching of III-V semiconductors. One of the materials that they have investigated is p-type GaAs. They have used ammonium pentaborate (APB) as the anodising component and aqueous ammonia (NH$_3$) as the oxide agent. The paper describes that when a current of 50mA/cm$^2$ was used, rapid etching produced a course and uneven surface texture. Studying the effects of lower currents such as 6.2mA/cm$^2$ and 4.8mA/cm$^2$ with different concentrations of electrolyte solution results indicated that the surface finishes were smooth, bright and featureless, but the dissolved areas were not flat. This was thought to be due to inadequate electrolyte circulation, however when magnetic stirring was applied the surface finish was unchanged suggesting that effective circulation was not occurring in the whole system. Their study has demonstrated that the problem can be circumvented by using a pulsed process. This achieves a separation of anodisation and dissolution, the latter largely occurring in the interval between the pulses.
Chapter 4

4 Experimental Theory and Techniques

4.1 Introduction

In order for PBW to occur in the GaAs samples, several processes need to be performed. The aim of this chapter is to explain the fundamental theory underlying the major techniques used in this dissertation for PBW in GaAs. This will include the initial proton irradiation, scanning and the electrochemical etching.

4.2 Microbeam

Although the techniques of ion beam analysis (IBA) have been performed for many years with broad beams (5 -10 mm diameter), it was only in the early 1980’s that the technology for focusing high-energy ion beams was developed to the point where beam diameters of 1μm were achievable [101, 102]. Recent advances in focusing systems allow 50-100nm to be the state of the art.

4.2.1 Surrey Ion Beam Centre Stephens Laboratory

The PBW experiments were performed in the ‘Stephens Laboratory’ at the University of Surrey, Ion Beam Centre. Figure 33 shows a schematic floor plan of this laboratory. The microbeam line was used for PBW in the experiments.
A very brief overview of the ‘Stephens Laboratory’ has been described below, however the following pages describe selected parts of the ‘Stephens Laboratory’ in more detail.

- **Ion Source** - Produces negatively charged Hydrogen ions
- **Analysing Magnet** - The negatively charged ions pass through the field of an energy analysing magnet and an aperture, where they are mass analysed to select the required ion species
- **Tandem Accelerator** - The selected negatively charged ions are accelerated and stripped of electrons in the 2MV Tandetron electrostatic accelerator to produce MeV energy H$^+$ ions (protons).
- **Selector Magnets** - It is used to select which beam line the ions will be used in.
- **Microbeam Line** - Used for proton beam writing and elemental analysis
- **Quadrupole Lens** - Used to focus the beam onto the sample
• Microbeam Line End Stage - Where the samples are mounted in the target chamber under vacuum
• External-beam Line - Used for elemental analysis of large or vacuum sensitive samples
• Rutherford Backscattering Spectroscopy (RBS) Chamber - Used for depth measurements of the elements within a sample

4.2.2 Accelerator

The major component of the proton microprobe facility at Surrey is the particle accelerator [103]. An electrostatic type accelerator is used, in which a static voltage is generated, and the particles are accelerated in two steps.

4.2.2.1 Tandetron Accelerator

A duoplasmatron plasma source for gases is used as the ion source. When hydrogen ions are desired, hydrogen gas is used in the ion source. An extraction voltage of 20 kV is applied to the source. This will lead to an extraction of negative ions. The Einzel lens help to focus the beam.

The extracted ions should have a very small energy distribution before being accelerated.

To get ions of uniform mass and energy an analysing magnet is used. This ensures that only ions of the correct mass and energy will be selected.

These negative ions are accelerated up the accelerating tube towards the positively charged terminal where they enter a stripping canal with a gas stripper. A schematic drawing of this can be seen in Figure 34. For the accelerator at Surrey, the gas stripper is nitrogen, which removes $n + 1$ electrons, where $n$ is the total number of electrons and hence makes them positively charged. They emerge as an ion with a charge of $ne$ (where e is the charge of an electron) and are now repelled and accelerated towards the ground.
potential. Thus the final energy is twice the terminal potential, and the net result is an ion with the kinetic energy of \((n + 1)eV\) [104, 105].

**Figure 34** - *Schematic diagram of Tandem electrostatic accelerator [103].*

Figure 35 shows a picture of the accelerator with the parts labelled.

**Figure 35** - *Tandetron accelerator capable of producing up to 4MeV protons at Surrey University.*
4.2.3 Focusing System

After acceleration, the MeV ions have a high momentum. This makes them difficult to focus. Magnetic quadrupole lenses were used to focus the ion beam. The quadrupole lenses have four magnetic poles arranged N-S-N-S around the beam axis, seen in Figure 36. They have a strong focusing action on charged particle beams but, because of the antisymmetry, a single quadrupole lens converges the beam in one plane only and diverges in a plane normal to this. For this reason two or more quadrupoles of alternating polarity are required to form a point focus [103]. G.W. Grime and F. Watt [106] have performed studies using two power supplies on quadrupole lens systems of two, three and four lenses. Their findings indicated that the ‘Oxford triplet’ CDC (C = convergence, D = divergence, top line indicates the power supply is shared) system to be favourable. This ‘Oxford triplet’ system has been used in this project.

![Magnetic poles arrangement for quadrupole lens](image)

**Figure 36** – *Magnetic poles arrangement for quadrupole lens [103]*.
4.2.4 Beam Scanning

The standard microprobe scanning system which controls the proton beam in the microbeam line uses the Oxford Microbeam data acquisition software OMDAQ [107], which was originally designed for ion beam analysis. The OMDAQ software can be used to define a pattern as a matrix formulation. A binary file which contains information about beam on / off is loaded into the OMDAQ and the software creates a table to store the required pixel coordinates in the order they would appear in a zigzag raster. The two components of the full raster scan are a slow horizontal and a fast vertical sweep. The original OMDAQ software has a limited resolution of 256 x 256 pixels and the focused beam jumps sequentially from one pixel to the next. Thus the size of the scan area needs to be chosen so that the beam spot size approximates to the pixel size. In 2007 an
upgraded version of this system called OMDAQ++ is available which has a pixel resolution of 1024x 1024.

Figure 38 shows a frame pattern and the path of the beam in raster mode. The dashed lines indicate the beam jumping from one point to another and it can be seen that this occurs over the blank spaces of the pattern. For very sensitive materials such as PMMA this would produce residual exposure on the blank areas.

![Figure 38](image.png)

**Figure 38 - Raster mode frame pattern followed by the beam. The dashed lines indicate jumps where residual exposure occurs [4].**

Bettiol, A.A et al.[37] have developed scanning software called Ionscan which has a pixel resolution of up to 64 k x 64 k. The main function of the Ionscan program is to scan the focused ion beam in a vector style pattern which first traces the contours of the pattern and then raster scans the rest of the area that needs to be exposed. This is called “turtle mode scan”. This reduces the number of jumps in the beam path which results in greater scanning resolution. Due to this, curved structures will have smoother edges and more complicated patterns can be designed. With controlled beam blanking the proton beam would not expose the selected regions of the target material. This would reduce residual exposure on the blank areas. This is particularly useful for very sensitive materials such as PMMA.
Figure 39 shows the same frame pattern as in Figure 38 and the path of the beam in turtle mode, with the jumps indicated by the dashed lines. It can be seen that the beam is scanned around the blank spaces of the pattern which leads to better structural definition.

Figure 39 – Turtle mode frame pattern path followed by the beam [4].

4.3 Ion Interactions with Matter

To help understand what occurs when GaAs is irradiated with ions (protons in this study), we need to look at how the energy is transferred from the ion to the solid.

4.3.1 Ion Stopping and Range

On entering the target material the energetic ions lose kinetic energy by two processes before eventually coming to rest. These two processes are:

- Electronic stopping, where the ion loses energy, inelastically, by interacting with the electrons of the target atoms.
- Nuclear stopping, where the ion loses energy, elastically, by collisions with the target nuclei.

At high energies electronic stopping predominates. The resulting lattice damage is small as electronic stopping involves considerably smaller energy losses per collision than nuclear stopping. As the energy transferred to a target atom is lower than its
displacement energy [108], the atom vibrates resulting in an increase in local lattice temperatures.

It is only after the ion velocity has slowed down sufficiently that nuclear stopping starts to occur more frequently. Towards the end of range nuclear stopping becomes the dominant mechanism. As the energy transferred to a target atom is higher than its displacement energy, the atom will be displaced from its lattice site. As a result, a vacancy-interstitial (Frenkel) pair is formed. If the displaced atom has enough energy, it could displace other nearby atoms. This would result in a cascade of defect-generating collisions. As a result, a damaged layer is formed due to the overlapping collision cascades as the ions are implanted in to the target material.

The range (R) is the total path length of an ion travelling within the target material before losing all of its original kinetic energy. The mean projected range \( (R_p) \) is the average distance where the majority of ions come to a stop. By adjusting the energy of the ions the \( R_p \) can be controlled. Each ion has a random path as it moves through the target, losing energy by electronic and nuclear stopping. Due to this beam straggling occurs. This straggling is not only present in the beam’s direction of travel (longitudinal straggling), but it is also present in the transverse direction. This causes the beam to broaden because the ions undergo multiple small angle collisions one after the other. This results in different trajectories of the ions. This can be seen in Figure 40 which shows a SRIM [28, 109] simulation of 2MeV protons in GaAs.

In lithography applications, lateral straggling leads to reduced beam resolution beneath the surface of the target material. This could lead to undercutting of the developed structures.

**Figure 40** – SRIM simulation of a 2MeV proton beam in GaAs. The direction of travel is from left, (where the beam enters the GaAs) to right [28, 109].
4.3.2 Simulations with the Stopping and Range of Ions in Matter (SRIM)

Since the process of ion implantation has a statistical nature, statistical models have been used to simulate the range profile. The Stopping and Range of Ions in Matter (SRIM) [28, 109], can be used to obtain the atomic depth distribution and damage profile. SRIM is a group of programmes which calculate the stopping and range of ions in matter using a quantum mechanical treatment of ion-atom collisions. SRIM can simulate energies from 10eV to 2GeV. It provides rapid calculation of values for the ion range and straggle as well as the nuclear and electronic stopping over a wide range of energies. The SRIM [28, 109], programmes provide the damage distribution and atomic profile inside the target material. The programmes use a Monte-Carlo calculation. The calculation follows the ion into the target, making detailed calculations of the energy transferred to every target atom through collisions. The target material is considered to be amorphous with atoms at random locations. This means that the directional properties of the crystal lattice are ignored. The end result of the simulations is based on the summation of the nuclear and the electronic scattering events occurring in a large number of simulated ion trajectories.

4.4 Theory of Electrochemical Etching

For electrochemical etching an anode, a cathode, an electrolyte and a current source are needed. The experimental setup is shown below in Figure 41 where the anode is the sample and the cathode is the electrode.
The etching of semiconductor material depends on the presence of holes. For p-type materials holes are plentiful and etching is readily achieved by forward biasing the semiconductor/electrolyte junction.

The electrochemical etching is used to drive an oxidation reaction at the anode and a reduction reaction at the cathode in a direction in which does not occur spontaneously. Reduction means to add an electron or to take away oxygen. Oxidation means to take away an electron or to add oxygen.

The current source is driving electrons into the cathode so that there is current flow. In this setup the cathode is formed by a graphite electrode. The electrolyte used is a 0.1 mol solution of Tiron (4,5-Dihydroxy-m-benzenedisulfonic acid, di-sodium salt) $\text{C}_6\text{H}_4\text{O}_5\text{S}_2\text{Na}_2$. 

**Figure 41** - Electrochemical etching for p-type GaAs [95].
The electrolyte allows charge exchange to take place [110]. The positively charged ions in the electrolyte migrate towards the cathode and that is where they will react. \( \text{Na}^+ \) ions migrate towards the cathode as shown in Figure 41. Two reactions can occur at the cathode. These are the reduction of \( \text{Na}^+ \) to \( \text{Na} \) and the reduction of water to hydrogen.

**Cathode (-):**

\[
\begin{align*}
\text{Na}^+ + e^- & \rightarrow \text{Na} \\
2 \text{H}_2\text{O} + 2 e^- & \rightarrow \text{H}_2 + 2 \text{OH}^- 
\end{align*}
\]

It is much easier to reduce water than \( \text{Na}^+ \) ions because the energy required to make \( \text{Na} \) is greater than the energy required to make hydrogen. Therefore the only product normally formed at the cathode is hydrogen gas.

**Cathode (-):**  \( 2 \text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 + 2 \text{OH}^- \)

At the anode, which in this setup is formed by the GaAs sample, oxidation of GaAs by the sulphonic groups occur and this oxide is then immediately dissolved in the etchant solution leading to the removal of the GaAs.

As the electrochemical etching process in GaAs depends on the flow of charge, the etching rate is, for the ideal case proportional to the current flowing between the anode and cathode. The amount of material removed and consequently the etched depth \( W_r \) is given by Faraday's first law of electrolysis as follows [95]:

\[
W_r = \frac{M}{z F \rho a} \int_0^t I dt \quad \text{Eq. 1}
\]

Where \( M \) = molecular weight, \( a \) = etch area, \( \rho \) = density of the semiconductor (5.32gcm\(^{-3}\)), \( z \) = the number of charge carriers transferred per molecule dissolved (= 6 for GaAs in this work), \( F \) = the Faraday (9.64 x 10\(^4\)C), \( I \) = instantaneous dissolution current [95].

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It is to be noted that the damage caused by the proton irradiation of selected areas of the GaAs sample reduces the carrier mobility in the material and creates centres, which trap free carriers. Therefore, these irradiated regions exhibit a higher resistance. This results in the proton irradiated regions being resistant to the etchant. So as the holes move down the sample, it is only where they meet the proton irradiated regions that the holes can not move and therefore they move around those areas. Consequently the non-irradiated regions are preferentially etched [95]. This can be seen in Figure 42.

![Diagram](image)

**Figure 42— Basic steps of electrochemical etching of GaAs [111, 112].**

### 4.5 SEM

Scanning electron microscopy (SEM) is used to detect and display high resolution images of the composition and morphology of conductive surfaces with magnifications up to $10^5$.

The SEM operates by generating a beam of electrons in the electron gun, which is at the top of the column. The electrons are emitted from a cold field emission tip which functions as the cathode. The cold field emission tip and its heating supply are maintained at a high negative potential using the high voltage supply during operation of the SEM. At the operating temperature, electrons are accelerated towards the anode. As the anode is positive in relation to the filament, powerful attractive forces for the electrons are formed. A hole in the anode allows a fraction of these electrons to continue down the column towards the lenses and onto the sample.
As this beam is accelerated through the anode, it is condensed by the condenser lens to a spot size and focused on the sample using the objective lens [113]. When the electron beam hits the sample, backscattered and secondary electrons are produced from the sample. By using a backscattered electron or a secondary electron detector, these electrons can be detected, converted to a current and amplified to produce a stronger signal for better imaging.

Figure 43 – Schematic drawing representing components of the SEM [114].

4.6 Nomarski Microscopy

To enhance the contrast of an image in relation to the topography of the sample a Nomarski optical microscope is used. This helps with the imaging of structures produced by PBW in GaAs.
A schematic diagram showing the set up of the Nomarski microscope can be seen in Figure 44. A tungsten-halogen light source is used to provide collimated light which is linearly polarised using the polarizer, and deflected by 90° by the half mirror. The light then passes through a Nomarski prism which is formed by two pieces of optical quartz that are wedge shaped and joined together. As the quartz has a birefringent nature, the light splits as it enters the Nomarski prism. Two orthogonally polarised rays are formed which become spatial separated. The two rays are focused at slightly different lateral locations on the sample using the objective lens. These rays become slightly out of phase with reference to the topography of the sample due to the fact that they traverse different optical paths. The objective lens collects the reflected rays which then recombine as they pass through the Nomarski prism for a second time. As the ray exits the Nomarski prism, they pass through the half mirror. They encounter the analyser which is another polarizer. Components of the two orthogonal rays that are parallel to the analyser transmission vector are able to pass through the analyser, and consequently interfere with one another. An image is then formed which shows the fluctuations in amplitude that vary according to the topography differential of the sample.
4.7 Taylor Hobson Mark V Talystep Instrument

The instrument used to measure the height/depth of the structures and etch steps was the Taylor Hobson Mark V talystep instrument. The talystep instrument can measure the height/depth by traversing the sapphire tipped stylus across the sample. The vertical movement of the stylus is amplified electronically and recorded as a graphical representation of the difference in levels on the sample.

Calibration of the talystep instrument was performed by traversing the stylus over several different test groves on the standard sample which was supplied with the unit. This measurement was repeated twenty times over the same sample.

The error when measuring the test groove on the sample standard was ± 2.5 %

4.8 SILVACO Simulations

4.8.1 Simulation of PBW in p-type GaAs

In various different areas of research, computer simulations have shown that they are a valuable tool for increasing the understanding of device and systems knowledge. The simulation software used in this study is the commercially available ATLAS software package developed by SILVACO International Inc. (USA) [9]. It is a two and three dimensional simulator used to predict the physics of semiconductor devices for complex device modelling, process simulation and device performance simulation. Atlas has a modular architecture that includes several licensable tools and is designed to be used in conjunction with the VWF Interactive tools. The VWF interactive tools include DECKBUILD (Run time environment), TONYPLOT (Visualisation tool), DEVEDIT (Structure and mesh editor) [9]. The process flow can be seen in Figure 45. The device structure is designed in DEVEDIT and source code is written in DECKBUILD where the structure file is included. The simulation is running in ATLAS module. The Output, Log and Solution files are visualised in the TONYPLOT module.
The ATLAS software package is a physically-based device simulator. Physically-based device simulators predict electrical characteristics that are associated with specified physical structures and bias conditions. This is achieved by approximating the operation of a device onto a two or three dimensional grid, consisting of a number of grid points called nodes. By applying a set of differential equations, derived from Maxwell's laws and by providing the solution of Poisson's equations which are numerically solved for this grid it is possible to simulate the transport if carries through a structure [9]. This means that the electrical performance of a device can be modelled in DC, AC or transient modes of operation.

The ATLAS software package was used to explore the electrochemical etching of the p-type GaAs samples that had undergone proton beam writing (PBW). Because the electrochemical etching is based upon the movement of holes and etching only occurs at the surface of the GaAs samples where the electrolyte is in contact with the material, hole current density simulations were conducted. This was done to better understand the mechanisms occurring in this etch.

The software allowed us to simulate the electrochemical etching process for several different structures produced by PBW. Hole current density simulations were displayed which indicated the hole movement during the etch process. These simulations in
comparison with experimental results can be seen in Section 5 - Results and Discussion. In Appendix A, an example of the simulation code can be seen.

### 4.9 Annealing

The Jipelec Rapid Thermal Annealer (RTA) was used to anneal the GaAs samples in this study. This annealer uses halogen lamps to heat the sample and reaches the target temperature in few seconds. The sample is placed between two silicon carbide coated graphite plates which act as the sample holder. A pyrometer, focused at the underside of the sample holder, and two thermocouples, one at the base of the sample holder and the other embedded within it are used to monitor the temperature of the sample. A feedback loop using the thermocouple embedded within the silicon carbide coated graphite is used to control the temperature of the anneal.

### 4.10 Photoluminescence (PL) Measurements

Photoluminescence (PL) measurements were performed using the Spectra Physics 2025 cw argon ion laser to optically excite the sample. In all measurements the samples were cooled close to liquid nitrogen temperature approximately 80 K by suspending the samples in an Oxford Instruments CF1204 cryostat with a continuous flow of nitrogen vapour. This was performed to prevent thermal quenching of spectral features and to reduce the thermal broadening of the emission lines. Previous studies in the literature report that the cooling of the semiconductor samples result in narrower line-width, sharper and more readily identifiable peaks [116]. The argon ion laser was used as a source because it can deliver watts of power from the ultraviolet to the green end of the spectrum. The visible 514nm line from the laser was used for the PL measurements which operated at continuous output power ranging from 150 mW. The beam passed through an optical chopper which was used to provide a reference signal which was fed back to a phase sensitive amplifier. The chopper had an operating frequency of around 32 Hz. The beam was then directed into a line pass filter to discriminate any unwanted plasma lines. Lenses were then used to focus the beam onto the sample. Luminescence was excited at near normal incidence to the sample surface plane and was then adjusted to
an angle of approximately 60°. This was done so that the direct reflection of the laser was not collected by the collimating lens. Lenses were used to collimate and focus the dispersed luminescence from the sample upon the entrance of the Spec 1740 spectrometer. In accordance to the resolution required, the slit width was adjusted. The signal was collated and spectrally analysed with the spectrometer equipped with a liquid nitrogen cooled germanium PIN diode which was used to detect the output signal from the spectrometer. The detection was limited to a certain wavelength window by the response of the detector. The reference signal from the chopper was modulated and the detector output signal was processed with the lock-in amplifier in order to improve the signal to noise ratio.

A computer program written in Microsoft QuickBasic language was used to automate the data acquisition on an IBM compatible personal computer. This system enabled the data to be acquired from the lock-in amplifier via an IEEE-488 bus and also regulated the temperature controller in addition to driving the spectrometer.

4.11 Measuring the Beam Spot

The proton beam was focused to dimensions ranging from 1.5μm x 3μm up to 6μm x 7μm for individual irradiations. The actual beam spot size on target was measured by scanning the proton beam in a raster scan over a copper grid with spacings of approximately 25μm and copper bars of approximately 8μm thick. This was followed by a vertical and a horizontal line scan (‘L shape scan) over the individual crossbars of the copper grid shown in Figure 46.
Figure 46 – Beam spot measurement on copper grid.

Figure 47 – Elemental map of the copper grid produced by the PIXE detector. Scan size is 100μm².

A particle induced x-ray emission (PIXE) detector is used to detect the x-rays emitted as the proton beam is scanned across the copper. The PIXE detector will detect almost zero counts of copper characteristic x-rays when it is not on the copper and detect copper characteristic x-rays as it is scanned over the copper. This can be seen in Figure 47 which
is an elemental map of the copper grid produced by the x-rays detected using the PIXE detector.

As the beam is scanned across the copper, the slope of the transition between zero counts of the copper characteristic x-rays to 100% of the copper characteristic x-rays will indicate the thickness of the beam in the x and y directions with respect to whichever edge we are scanning across. This is indicated by the full width half maximum (FWHM) graph seen in Figure 46. A 10% and 90% measurement from the FWHM graph are used to calculate the beam spot size and to compensate for noise interferences.

The copper grid is used because it has horizontal and vertical bars with sharp edges which enable both the x and y dimensions of the beam to be measured. Also, the beam scans completely over the bars of the copper grid so that we can obtain an average reading of the measurement.

4.12 p-type GaAs Sample

This study is based on the investigation of the feasibility of PBW on p-type GaAs. The p-type GaAs had the following parameters:

- Orientation <100>
- Doped with Zinc
- Carrier concentration $4.8 - 6.1 \times 10^{18}$ ions/cm$^3$
- Resistivity $1.1 - 1.3 \times 10^{-2}$ Ωcm

The GaAs wafers were produced using the Liquid Encapsulated Czochralski (LEC) growth technique.
Chapter 5

5 Results and Discussion

5.1 Introduction

This section begins with a description of the two electrochemical etching configurations used. Both etch setups were used to etch a GaAs sample that had undergone PBW in order to test whether the electrochemical etch would work. Both setups etched the GaAs samples that had undergone PBW however one setup was more effective than the other. To show the development of the electrochemical etch process, I will show the investigations for both etch setups, however it should be noted that there were several inconsistencies in the performance with etch setup 1 and due to these inconsistencies in performance, etch setup 2 was chosen as the method of electrochemical etching.

This will be followed by an investigation of the use of PBW in p-type GaAs which will begin with studies into the optimum fluence for the structures. The experimental results will then be compared with SILVACO simulations and more complex structures will be investigated.

The error bars that can be seen in the graphical results have all been estimated by taking into account the errors in the experimental setup, which include, temperature change, equipment resolution, electrochemical set-up, environmental and vibrational effects, equipment performance, human error, statistical errors and other variables that could induce error which will effect the results.
5.2 Electrochemical Etch Setup 1

As mentioned in Section 4.4, for the electrochemical etching of p-type GaAs, an anode, a cathode, an electrolyte solution and a current source are needed. In the electrochemical setup diagram shown in Figure 49, it can be seen that GaAs sample acts as the anode and the platinum wire acts as the cathode. The electrolyte allows charge exchange to take place.

The first electrochemical etch setup used to etch the p-type GaAs samples in this study was based on the studies by T. Ambridge et al. [94] and the commercially available BIO-RAD unit [95]. These studies indicated that p-type GaAs can be etched electrochemically using a 0.1M Tiron (4,5-Dihydroxy-m-benzenedisulfonic acid, di-sodium salt) solution as the electrolyte in the electrochemical cell. Using this information, a solution of one part Tiron and 30 parts deionised water (5.5g of Tiron and 165ml of deionised water) was used to give the 0.1M Tiron electrolyte solution.

The electrochemical etching process of GaAs depends on the presence of holes. For p-type materials the majority carriers are holes. This means that when the p-type GaAs sample is connected to the electrochemical etching cell (seen in Figure 48) the parts of the sample that are exposed to the Tiron electrolyte solution are etched when the current source is switched on.

During proton irradiation, carriers within the GaAs material are removed which results in increased resistivity in the irradiated areas. These proton irradiated regions are resistant to the electrochemical etching process. Figure 48 shows a schematic drawing if the hole movement within GaAs sample during the electrochemical etch. It is only where they meet the proton irradiated regions that the holes can not move and therefore they move around those areas. Consequently the non-irradiated regions are preferentially etched.
Figure 48 - Schematic diagram showing the electrochemical process of p-type GaAs irradiated with protons.

Figure 49 - Experimental electrochemical etch setup 1 for p-type GaAs.
Figure 50 is a photograph of the actual electrochemical etch setup which was performed inside a fume cupboard in a clean room.

![Diagram of electrochemical etch setup]

**Figure 50** – (a) *Digital picture of the experimental electrochemical etch setup 1 for p-type GaAs*

Each of the GaAs samples has a thickness of 500μm and they have been cleaved to an approximate size of 1cm x 1cm. Only three quarters of the GaAs sample is immersed in the Tiron electrolyte solution. This unetched region acts as a reference point to measure how deep the etch is. The next section will describe the etching effects.
5.2.1 Etching Effects

The electrochemical etch setup as described in Section 5.2 was tested using unirradiated p-type GaAs samples of an approximate size of 1cm x 1cm x 500μm (thickness) from the same wafer. In each etch, approximately three quarters of the sample was immersed in the Tiron electrolyte solution. Therefore the total area of the sample immersed in the electrolyte was approximately 1.625cm².

Figure 51 shows a diagram of the immersed part of the sample. After each etch, a new 0.1M solution of the Tiron electrolyte was produced to be used for the next one.

It was decided that a range of etch currents would be investigated to determine the optimum etch current for the electrochemical etch with the p-type GaAs samples. The etch currents investigated were, 0.5 mA, 5 mA, 10 mA and 15 mA. shows a comparison of the etch rates when using these currents. The etch area was kept constant at approximately 1.625 cm². A talystep device was used to measure the etch depths. Table 2 shows the current density and etch rates with respect to the etch currents investigated.
Chapter 5 – Results and Discussion

Figure 52 – Graph of etch depth versus etch time for un-irradiated GaAs using etch currents of 0.5 mA, 5 mA, 10 mA and 15 mA using the electrochemical etch setup.

Table 2 – Table showing the current density and etch rates for the etch currents investigated. The etch area was kept constant at approximately 1.625 cm².

<table>
<thead>
<tr>
<th>Etch Current (mA)</th>
<th>Current Density (mA/cm²)</th>
<th>Etch Rate (µm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mA</td>
<td>0.31 mA/cm²</td>
<td>0.01 µm/min</td>
</tr>
<tr>
<td>5 mA</td>
<td>3.08 mA/cm²</td>
<td>0.05 µm/min</td>
</tr>
<tr>
<td>10 mA</td>
<td>6.15 mA/cm²</td>
<td>0.11 µm/min</td>
</tr>
<tr>
<td>15 mA</td>
<td>9.23 mA/cm²</td>
<td>0.16 µm/min</td>
</tr>
</tbody>
</table>

The etch rate for the different currents investigated have been calculated by averaging the etch rates at different times.

It can be observed in and Table 2 that:

1) The etch depth increases with time

2) The etch depth increases with the applied etch current
3) Increasing the applied current leads to an increase in etch rate

These results indicate that when the etch area is kept constant and individual etch currents are investigated, the etch rates have a linear trend.

As expected, this implies that the resistivity of the material, up to the etch depth of 30μm is uniform.

From Figure 52, the average etch rate when using the individual etch currents can be calculated. When using an etch current of 0.5mA, the average etch rate was calculated to be 0.01μm/min. The advantage of using this etching current is that the etched surface is not as rough as it is when using a higher etch current. The major disadvantage is that because the etch rate is so slow, it is not practical to use this current to etch any deeper than 0.5μm (which would take 50 min).

When using etch currents of 5mA, 10mA and 15mA, the average calculated etch rates increase to 0.05μm/min, 0.11μm/min and 0.16μm/min respectively. However, one of the effects noticed was that the roughness of the etched region also increases as the current is increased. Using the information gained from this etch study, it was decided that the etch currents of 0.5mA and 5mA were not practical for the deep etching of the irradiated p-type GaAs samples as the etch rate was too slow. This left the etch currents of 10mA and 15mA. It was decided that the best etch current to use for the electrochemical etch was 10mA. Even though it had a slower etch rate than when using the etch current of 15mA, its surface roughness was smoother. This was the deciding factor.

One of the major problems that was found when using the electrochemical etch setup was that it was very difficult to maintain the same etch area for each etch. As the p-type GaAs sample was inserted into the Tiron electrolyte with only three quarters of the sample being immersed, as soon as the current source was turned on, the electrolyte solution rose up on the sample to touch the tweezers and immerse the majority of the sample. This occurred very randomly throughout the etch study and even for different currents.

An example of this rising of the Tiron electrolyte during the etch can be seen in Figure 53. The etch was meant to cover three quarters of the sample as shown in Figure 53,
however as soon as the current source was turned on, the Tiron solution rose up on the sample to touch the tweezers.

![Diagram showing the position of Tiron electrolyte before and after the current source was turned on.]

**Figure 53 – Image of the effect of the rising Tiron electrolyte near the tweezers on an unirradiated p-type GaAs sample electrochemically etched using an etch current of 10mA.**

Several methods were used in order to combat this but the one with the most success was using a three stage clean to clean the samples prior to the etch. A description of this three stage clean can be seen in Table 3.

<table>
<thead>
<tr>
<th>Stage 1</th>
<th>Acetone on heated hotplate for 2 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 2</td>
<td>Methanol on heated hotplate for 2 min</td>
</tr>
<tr>
<td>Stage 3</td>
<td>Isopropanol at room temperature for 5 min</td>
</tr>
<tr>
<td></td>
<td>Dry using nitrogen air gun</td>
</tr>
</tbody>
</table>

**Table 3 – Three stage cleaning process.**

It is important that only the region that was to be etched was allowed to be immersed. The rest of the sample had to remain completely dry. If the sample was accidentally immersed completely in the Tiron electrolyte then the three stage clean would need to be performed again. Due to the fact that it was very easy to accidentally, completely immerse the sample, special care needed to be taken when setting up this electrochemical etch.
5.2.2 Etch Area Investigation

An investigation into the effects of the etch area was conducted using four equally sized unirradiated p-type GaAs samples from the same wafer. Using the 3 stage cleaning technique ensuring that the sample was dried completely, as well as careful setup of the electrochemical etch, it was possible to etch different area sizes on these samples. This can be seen in Figure 54.

Each of the samples were etched for a duration of 10 min using the same etch current of 10 mA. A new Tiron electrolyte solution was used for each etch. The first sample was almost completely immersed in the electrolyte solution so that it had the largest etch area of 1.94 cm$^2$. The second sample was three quarters (1.63 cm$^2$) immersed in the electrolyte solution so that the etch area was reduced. The third sample was immersed up to half way (1.10 cm$^2$) in the electrolyte solution, further reducing the etch area. The fourth and final sample was only one quarter (0.58 cm$^2$) immersed in the electrolyte solution so that it had the smallest etch area. A diagrammatic version of this can be seen in Figure 54.

Figure 54 – The different etch areas of the p-type GaAs samples.
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Figure 55 - Graph of etch rate versus etched area for p-type un-irradiated GaAs samples.
An etch current of 10 mA was used for an etch of 10 min for these samples.

It can be seen in Figure 55 and Table 4, that when the etch area is decreased the etch rate increases. A constant etch current of 10 mA was used for these etches.
Chapter 5 – Results and Discussion

Figure 56 - Graph of etch rate versus current density for p-type un-irradiated GaAs samples of different etch areas linked with Table 4. An etch current of 10 mA was used for an etch of 10 min for these samples.

<table>
<thead>
<tr>
<th>Etch Area (cm²)</th>
<th>Current Density (mA/cm²)</th>
<th>Etch Rate (μm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.94 cm²</td>
<td>5.16 mA/cm²</td>
<td>0.085 μm/min</td>
</tr>
<tr>
<td>1.63 cm²</td>
<td>6.14 mA/cm²</td>
<td>0.11 μm/min</td>
</tr>
<tr>
<td>1.10 cm²</td>
<td>9.09 mA/cm²</td>
<td>0.17 μm/min</td>
</tr>
<tr>
<td>0.58 cm²</td>
<td>17.24 mA/cm²</td>
<td>0.25 μm/min</td>
</tr>
</tbody>
</table>

Table 4 - Table showing the current density and etch rates for the etch areas investigated. The etch current for these etches was 10 mA.

The results seen in Figure 56 and Table 4 are broadly in agreement with those in Table 2 and show that when the current density increases, the etch rate increases. A constant etch current of 10 mA was used for these etches.
It can be seen that the etch rate does not remain constant for the samples with different etch areas, when keeping current and time constant. The sample with the largest etch area of 1.94 cm$^2$ has the slowest etch rate of 0.085 μm/min while the sample with the smallest etch area of 0.58 cm$^2$ has the fastest etch rate of 0.25 μm/min. Figure 55 shows the trend of how the etch rate is increased with a decrease in etch area. The relationship shows a linear trend.

This data indicates the importance of maintaining a constant size for the etch area in order to keep a consistent etch rate. Changing the etch area will cause the current density to change. Figure 56 shows the effect that changing the current density has on the etch rate. Because it is very difficult to constantly maintain the same etch area using this electrochemical setup, the current density is not always constant. This is thought to be the reason for the variation in etch rates in the etch study seen in Figure 52. Due to this problem, another electrochemical etch setup was investigated. Further details can be seen in Section 5.3.

5.2.3 Etch Uniformity

After etching the first set of unirradiated GaAs samples over an etch area of 1.625 cm$^2$, using etch currents of 0.5 mA, 5 mA, 10 mA, and 15 mA, a talystep profile was taken over the etched region to check the etch uniformity of samples. It was observed that the etch was not uniform. The talystep profiles indicated that more etching occurred towards the edges of the sample than at the middle. This can be seen in Figure 57. This effect was initially thought to be due to no circulation of the electrolyte solution. After conducting the same etches on a new set of samples using a magnetic stirrer which was set to the maximum stirring speed of 1500 rpm to circulate the electrolyte, an improvement in etch uniformity was noticed. However, deeper etching still occurred towards the edges of the sample than at the middle. This can be seen in Figure 57 which shows the talystep profiles across an unirradiated sample etched using a current of 10 mA when using the etch setup 1. Due to this non uniform etch, the etch step measurements for the etch studies were taken at the centre of the unirradiated samples, which is the same position where the PBW will occur on the irradiated samples. This gives an indication of the etch rate where the samples will be irradiated.
Figure 57 — Talystep profiles across unirradiated sample etched using an etching current of 10 mA using etch setup 1. Variations in etch depth across sample were observed.

5.2.4 Etch rate of Irradiated Samples

Figure 58 shows a comparison of etch rates for an unirradiated GaAs sample and a proton irradiated GaAs sample. This sample was irradiated with one raster scan that covers an area of 0.01 cm$^2$ and was etched for set time periods to match with that of the unirradiated sample. The etch depth and structure height was measured using a talystep after each of these periods. As the total etch area of 1.625 cm$^2$ is considerably larger than the irradiated region of 0.01 cm$^2$, an irradiation of such a small area would not show a considerable difference in the etch rate. This can be seen in the fact that the average etch rate for both of the etches are the same at 0.11 μm/min. It can be noticed in Figure 58, that the sample’s etch steps are fractionally different to that of the unirradiated sample. This difference is thought to be due to the etch area not being constant for both etches.
5.3 Electrochemical Etch Setup 2 - using Biorad PN4300

5.3.1 Setup

The second electrochemical etch setup used to etch the unirradiated p-type GaAs samples in this study was the commercially available PN4300PC Electrochemical C-V Profiler from BIO-RAD [95].

As with the previous setup, this unit uses the GaAs sample as the anode and a counter-electrode as the cathode in the electrochemical cell. The same solution of 0.1 M Tiron (4,5-Dihydroxy-m-benzenedisulfonic acid, di-sodium salt) was used as the electrolyte in this etch. A diagram of the electrochemical cell can be seen in Figure 59.
The ohmic contacts to the sample consist of four pins that are connected to the plunger. When the sample is placed onto the sealing ring and the plunger is released, the pins apply a constant pressure to the back of the sample. This forms the ohmic contact to the sample as well as ensures that the sample is secure against the sealing ring. The ease with which the sample can be loaded and immediately contacted enables better precision for etching. It is possible to check these ohmic contacts using the PN4300PC Electrochemical C-V Profiler. This is important because the contact formation procedure occasionally produces less than adequate contacts due to dirt and other impurities, which would necessitate removal of the sample from the cell. This is why it is very important that the electrolyte is not inserted into the cell until these ohmic contacts are formed and checked.

Prior to etching, the GaAs sample needs to be cleaned using the three stage clean (described in Table 3) to remove any dirt that could have built up on the sample. Apart from this, no pre-treatment of the sample is required. Special care is needed, however, in
relation to the area of electrolyte contact with the sample. A moulded plastic sealing ring of diameter 0.35 cm, is used to define the area of contact. A graduated syringe is used to inject 7 ml of the electrolyte into the access duct at the top of the cell. The electrolyte should almost fill the cell chamber however it should not reach the filling hole of the access duct to prevent spillage. When the cell chamber is filled with electrolyte, a bubble is normally trapped between the ring and the sample. These bubbles can be removed by partly refilling the syringe with electrolyte in the cell and directing the syringe at the bubbles before releasing the electrolyte. They can also be removed by the pump which directs a pulse of electrolyte from the pump chamber of the cell to the inside of the sealing ring during the preparation for a run. When the bubbles are removed, the front of the sample should appear as a metallic disk with a distinct circular edge which can be seen through the cell window. The pump is also used in a more continuous mode to assist in generated gas removal during etching. The pumping cycle involves the creation of a vacuum at the pump chamber of the cell. Approximately 1 ml of the cell's volume of electrolyte is sucked into the pump chamber by the pump jet. A pressure pulse forces this 1 ml volume of electrolyte back through the pump jet, and onto the sample surface. The jet of electrolyte swirls into the sealing ring orifice, sweeping out any trapped bubbles. This pump cycle takes between 4 to 8 seconds.

5.3.2 Etch Rate

Etch rate studies using the PN4300 were conducted to determine the optimum etch current density for the electrochemical etching for the p-type GaAs samples. In all of these etch studies, an unirradiated p-type GaAs sample was used. A fresh 0.1 M Tiron electrolyte solution was used for each etch and the electrolyte contact area was $0.10 \text{ cm}^2$ using a moulded plastic sealing ring of diameter 0.35 cm.

Etch currents of 0.05 mA, 0.3 mA and 0.5 mA were investigated.

Figure 60 shows a graph of etch depth in µm versus etch time in minutes for un-irradiated GaAs using etch currents of 0.05 mA, 0.3 mA and 0.5 mA.
Figure 60 - Graph of etch depth in μm versus etch time in minutes for un-irradiated GaAs with etch currents of 0.05 mA, 0.3 mA and 0.5 mA using the Biorad PN4300.

<table>
<thead>
<tr>
<th>Etch Current (mA)</th>
<th>Current Density (mA/cm²)</th>
<th>Etch Rate (μm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 mA</td>
<td>0.5 mA/cm²</td>
<td>0.01 μm/min</td>
</tr>
<tr>
<td>0.3 mA</td>
<td>3 mA/cm²</td>
<td>0.06 μm/min</td>
</tr>
<tr>
<td>0.5 mA</td>
<td>5 mA/cm²</td>
<td>0.11 μm/min</td>
</tr>
</tbody>
</table>

Table 5 – Table showing the current density and etch rates for the etch currents investigated.

The etch rate has been calculated by averaging the etch rates at different times.

It can be observed in Figure 60 and Table 5 that:

1) The etch depth increases with time
2) The etch depth increases with applied current
3) Increasing the applied current leads to an increase in etch rate

Figure 60 indicates that when electrochemically etching the unirradiated p-type GaAs with etch currents of 0.05 mA, 0.3 mA and 0.5 mA, they all have a linear trend. This would imply that the resistivity of the material, up to the etch depth of 30 μm is uniform. This linear etch rate trend is also seen when using the previous etch setup (etch setup 1).
It is to be noted that etch setup 2 has a better linear fit in all of the results produced, that of etch setup 1. One of the main factors for this is due to etch setup 2 having a better ability at keeping the etch area the same for each etch via the “O” sealing ring and the fact that only one side of the sample is being etched. This further supports the importance of maintaining the same size of the etch area to keep the etch rate consistent. Another factor is that even though etch setup 2 is using lower etch currents than that used in etch setup 1, the etch rates are similar. This is due to the fact that the etch area of etch setup 2 is smaller than that of etch setup 1. This results in similar current density values for some of the investigations performed for both etch setups which would produce similar etch rates for the corresponding current density values. Therefore, the determining factor for the etch rate is not the etch area, it is the current density.

The advantage of using the 0.05 mA etch current is that the etched region does not become as rough as it is when using a higher etch current. An optical image of the sample etched to a depth of 1μm using an etch current of 0.05mA can be seen in Figure 61. The major disadvantage is that because the etch rate is so slow at 0.01 μm/min, it is not practical to use this etch current to etch any deeper than 0.5 μm (which would take 50 min).

![Etch step (“O” ring seal) / Etched region / Unetched Region](image)

**Figure 61 - An optical image using a Nomarski Microscope of the sample etched to a depth of 1μm using an etch current of 0.05mA.**

When using etching currents of 0.3 mA and 0.5 mA the etch rates increase to 0.06 μm/min and 0.11 μm/min respectively. However, one of the effects noticed was that the roughness of the etched region marginally increases as the etch current is increased from
0.3 mA to 0.5 mA. This can be seen in Figure 62 which shows optical images of the sample etched to a depth of 1 μm using an etch currents of 0.3 mA and 0.5 mA.

![Etch Current 0.3 mA](image1)

![Etch Current 0.5 mA](image2)

**Figure 62** - An optical image using a Nomarski Microscope of the sample etched to a depth of 1 μm. (a) An etch current of 0.3 mA was used. (b) An etch current of 0.5 mA was used.

Using the information gained from this etch study for etch setup 2, it was decided that the etch currents of 0.05 mA and 0.3 mA were not practical for the deep etching of the irradiated p-type GaAs samples as the etch rates were too slow. Even though there is a slight increase in the surface roughness, it was decided that the most practical etch current to use for the electrochemical etch was 0.5 mA.

### 5.3.3 Etch Uniformity

In order to investigate the etch uniformity, talystep profiles were conducted on the etched unirradiated p-type GaAs samples after etches of 1 μm, 5.6 μm, 10.5 μm and 12 μm. The talystep has a maximum depth measurement of 12 μm so the etch depth measurements after this depth were conducted using an SEM.

Figure 63 shows the talystep profiles of a 1 μm, 5.6 μm, 10.5 μm and 12 μm etch steps in the p-type GaAs samples. It can be seen that all of these etches have an etch step but the surface roughness can be seen to increase as the etch depth increases.
Figure 63 – Replication of Talystep profiles indicating etch depth and etch uniformity.

Figure 64 – Optical Image using a Nomarski Microscope showing a comparison in surface roughness of a 1μm etch and a 10.5μm etch when using an etch current of 0.5 mA. It is to be noted that the etch overlap was purposefully done to enable an image with two different etch depths to be taken. For the studies in Figure 63 there was no etch overlap as this would affect the etch uniformity.

5.3.4 Etch Rate of Irradiated Samples

Figure 65 shows a comparison of etch rates for an unirradiated GaAs sample and a proton irradiated GaAs sample. The irradiated sample has been irradiated with one scan that covers an area of 0.01 cm\(^2\) with a fluence of 1.25 \( \times 10^{17} \) ions/cm\(^2\). This area covers 10% of the etched area of 0.1 cm\(^2\). The irradiated sample was etched for set time periods to match with that of the unirradiated sample. The etch depth and structure height were measured using a talystep after each of these periods. It can be seen that the etch rates are different. The irradiated sample has a faster etch rate of 0.12 μm/cm\(^2\) than that of the unirradiated sample whose etch rate is 0.11 μm/cm\(^2\). The reason for this increase in etch
rate is due to the fact that the irradiated area covers 10% of the total etch area. Because no etching occurs at the irradiated regions, the etch area has been reduced by 10%, increasing the current density from 5 mA/cm$^2$ to 5.6 mA/cm$^2$, thereby resulting in a faster etch rate.

Figure 65 - Graph of etch time (min) versus etch depth (μm) for un-irradiated GaAs and irradiated GaAs samples. An etch current of 0.5 mA was used.
5.4 Etch Rate Comparison between Etch Setup 1 and Etch Setup 2

A comparison between the etch setup 1 and the etch setup 2 can be seen in Figure 66.

![Figure 66 - Etch rate comparison between Etch Setup 1 and Etch Setup 2.](image)

It has already been stated in the previous sections that etch setup 1 was conducted using an etch current of 10 mA over an etch area of 1.625 cm$^2$ which gives a current density of 6.15 mA/cm$^2$, whilst etch setup 2 was conducted using an etch current of 0.5 mA over an etch area of 0.1 cm$^2$ which gives a current density of 5 mA/cm$^2$. It can be seen in Figure 66 that the average etch rates for both etch setups 1 and 2, at these current densities, are the same at 0.11 μm/min. Comparing the current densities of 6.15 mA/cm$^2$ for etch setup 1 and 5 mA/cm$^2$ for etch setup 2, it was expected that etch setup 1 would have a faster etch rate due to its larger current density. However this was not the case as the results indicate the same etch rate for both setups. One possibility for this is due to the non uniform etch of setup 1 and the central position used to measure the etch step. 1.

However, another possibility is that for etch setup 1, there is no control measure for the area of the sample that is exposed to the electrolyte except that of human ability in setting up the etch. It has already been stated that the current density is the main factor in
determining the etch rate. With this in mind, if the etch area is larger than the expected 1.625 cm², this would lead to a reduction in the current density and hence a slower etch rate. Because of this, human error needs to be considered as the etch area will vary, when using etch setup 1.

Combining these errors for etch setup 1, it is not surprising that there are differences between the two etch setups. This is why etch setup 2 was chosen over etch setup 1.

### 5.5 Bar Structures

#### 5.5.1 Single Bar Structure

A simple single bar pattern was scanned onto the p-type GaAs sample with the Ionscan scanning software.

The irradiation parameters are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Energy</td>
<td>2 MeV</td>
</tr>
<tr>
<td>Beam Current</td>
<td>1 nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>4 μm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>5 μm</td>
</tr>
</tbody>
</table>

**Table 6 – Irradiation parameters for single bar structure.**

Because the optimum fluence for the structure is unknown for this material, the same single bar pattern was scanned six times at different locations on the GaAs sample with different fluences. These fluences were:

<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>Time for Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.56 x 10¹⁶</td>
<td>8 min 30 sec</td>
</tr>
<tr>
<td>3.13 x 10¹⁶</td>
<td>16 min 45 sec</td>
</tr>
<tr>
<td>4.69 x 10¹⁶</td>
<td>25 min</td>
</tr>
<tr>
<td>6.25 x 10¹⁶</td>
<td>33 min 30 sec</td>
</tr>
<tr>
<td>9.38 x 10¹⁶</td>
<td>50 min</td>
</tr>
<tr>
<td>1.25 x 10¹⁷</td>
<td>1 hour 6 min 45 sec</td>
</tr>
</tbody>
</table>

**Table 7 – Fluence and time parameters for single line structures.**

The irradiated sample was then cleaned using the three stage clean (described in section 5.2.1) prior to etching. The electrochemical etch setup 2 was used to etch this sample using a current of 0.5 mA over an area of 0.1 cm². All six scans were positioned within the etching area of 0.1 cm² so they could be etched together to directly compare the
results. Figure 67 shows an SEM image of the six single line structures at different fluences. The line on the far left of the Figure 67 was irradiated with a fluence of $1.56 \times 10^{16}$ ions/cm$^2$ followed by lines with fluences of $3.13 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$, $6.25 \times 10^{16}$ ions/cm$^2$, $9.38 \times 10^{16}$ ions/cm$^2$ and $1.25 \times 10^{17}$ ions/cm$^2$. The six bar structures can be seen, proving that this electrochemical etch technique is effective in revealing the PBW structures.

(i) SEM Images

(ii) Diagrammatic Representation of SEM Images

Figure 67 – (i) SEM image of single bar structures of different fluences. From left $1.56 \times 10^{16}$ ions/cm$^2$, $3.13 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$, $6.25 \times 10^{16}$ ions/cm$^2$, $9.38 \times 10^{16}$ ions/cm$^2$ and $1.25 \times 10^{17}$ ions/cm$^2$. (ii) Diagrammatic representation of SEM images.

This sample was etched using the electrochemical setup 2 explained in Section 5.3. The etch rate for this particular irradiated sample was $0.11 \, \mu$m/min. As the scanned irradiated area for all of the line structures is small (< 2% of etch area) compared to the total etch area, the etch rate remains constant with that observed for the unirradiated samples seen in Section 5.3.

As all of the structures have been etched together, it is expected that they would all have the same heights. However, this is not the case. Looking at the bar structure with the smallest fluence of $1.56 \times 10^{16}$ ions/cm$^2$ (Figure 67(a)), talystep and SEM measurements indicate that this structure does not form at the surface of the sample. Instead there is a
certain depth that needs to be etched before the structure is revealed. This is called the critical depth and is diagrammatically described in Figure 68. The critical depth was measured by performing a layer by layer exposure and comparing the depth of the etch step with the height of the structure using the talystep. If the etch does penetrate past the critical depth then the structure could not be seen. This can be diagrammatically seen in Figure 68 which shows the structure is not revealed until after the critical depth has been etched.

![Diagram of critical depth](image)

**Figure 68 — A diagrammatic image of critical depth.**

For the bar structure with a fluence of $1.56 \times 10^{16}$ ions/cm$^2$, the critical depth was 0.18 μm. This critical depth region is also seen for the bar structures with fluences of $3.13 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$, $6.25 \times 10^{16}$ ions/cm$^2$, $9.38 \times 10^{16}$ ions/cm$^2$. However, as the fluence is increased, the critical depth after which the structure is formed is reduced. At a fluence of $1.25 \times 10^{17}$ ions/cm$^2$, the critical depth is zero and the structure has the same height as the etch depth. Table 8 shows the figures of the critical depth and structure width with respect to fluence. These measurements were taken using both the talystep profiler and the SEM images.

The results indicate that the critical depth remains constant over a range of etch depths. This indicates that no etching occurs to the structures produced by PBW. Figure 68 is a schematic diagrammatic of how the critical depth remains constant when etching to different etch depths.
Chapter 5 – Results and Discussion

<table>
<thead>
<tr>
<th>Dose (pC/μm²)</th>
<th>Fluence (ions/cm²)</th>
<th>Critical Depth (μm)</th>
<th>Structure Width (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>After a 1μm etch (9min etch)</td>
<td>After a 5μm etch (46min etch)</td>
</tr>
<tr>
<td>25</td>
<td>1.56 x 10¹⁶</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>50</td>
<td>3.13 x 10¹⁶</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>75</td>
<td>4.69 x 10¹⁶</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>100</td>
<td>6.25 x 10¹⁶</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>150</td>
<td>9.38 x 10¹⁶</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>200</td>
<td>1.25 x 10¹⁷</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 8 – Table showing critical depth and structure width with respect to fluence in the p-type GaAs samples that have undergone PBW.

Figure 69 – Schematic diagram showing that critical depth is constant when etching to different etch depths. For this diagram a the bar structure with a fluence of 6.25 x 10¹⁶ ions/cm² was represented.

It can be observed in Figure 70, as the fluence of the bar structures increase, the critical depth decreases until it reaches a fluence of 1.25 x 10¹⁷ ions/cm². At the fluence of 1.25 x 10¹⁷ ions/cm², the critical depth is zero and the structure is formed at the surface of the sample.
It has already been mentioned in Chapter 3 that nuclear stopping creates defects through the creation of point defects. This in turn leads to carrier removal in the GaAs.

The energy lost by the protons through electronic collisions cause disruptions in the electronic system of the GaAs, but there is insufficient energy to cause physical displacement of either the Ga, As from their lattice sites. The damage caused by nuclear stopping is harder to repair than that caused by electronic stopping.

The critical depth region occurs because not enough damage, through nuclear collisions, occurs at the surface of the material. Even though there are some nuclear collisions at the sample surface, these are not enough to remove all of the carriers so enough carriers are still available to allow conduction to occur at this surface region, which results in this area being etched. In other words, there is not enough damage at the surface of the sample. This phenomenon has also been observed in PBW in Si [7].
To help explain this, SRIM simulations for 2 MeV protons in GaAs were conducted. The data from these simulations were used to plot the percentage of atoms that have been permanently disordered in the GaAs material resulting from the energy lost by the protons directly to the atoms of the GaAs material through nuclear collisions. This has been labelled as “% Disorder” on the graphs. The “% Disorder” has been plotted against the depth (µm) into the sample. This was conducted for the respective fluences investigated which can be seen in Figure 71.

It is to be noted that experimental measurements of stopping powers is a difficult task, and there is wide variation in the results. Since the stopping calculations are based in great part on theory, the interpolation of stopping powers between various ions and targets is often more accurate than individual measurements, especially for difficult targets. But basically, the stopping of ions in matter can not be calculated from first principles. Within stopping theories are parameters which normalize calculated stopping powers to existing data [28]. Some examples of the major parameters are shell corrections, mean ionization potentials, the effective charge of ions and the Fermi velocity of solids. Shell Corrections and Mean Ionization Potentials are used in Bethe-Bloch stopping for high velocity ions [117]. In SRIM, these ions are considered to have energies above 1 MeV/amu [28, 117].

Shell corrections (usually noted using the symbol C/Z2) constitute a large correction to proton stopping powers in the energy range of 1-100 MeV, with a maximum correction of about 6%. It corrects the Bethe-Bloch theory requirement that the particle’s velocity is far greater than the bound electron velocity. As a particle velocity decreases from relativistic energies, the particle-electron collisions need to be considered with detailed evaluation of each target electron’s orbital bonding in order to obtain accurate stopping powers. Many authors have contributed to the theoretical definition of non-relativistic shell corrections [117-124].
Figure 71 (a) – Graph of % disorder versus depth from SRIM data for fluences of $1.56 \times 10^{16}$ ions/cm$^2$, $3.13 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$, $6.25 \times 10^{16}$ ions/cm$^2$, $9.38 \times 10^{16}$ ions/cm$^2$ and $1.25 \times 10^{17}$ ions/cm$^2$ using 2 MeV protons.

Figure 71 (b) – Zoomed in image of graph of Figure 71(a), % disorder versus depth from SRIM data for fluences of $1.56 \times 10^{16}$ ions/cm$^2$, $3.13 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$, $6.25 \times 10^{16}$ ions/cm$^2$, $9.38 \times 10^{16}$ ions/cm$^2$ and $1.25 \times 10^{17}$ ions/cm$^2$ using 2 MeV protons.
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It can be seen in Figure 71 (a) and (b) that:

1) As the fluence is increased, the % disorder increases.

The simulations suggest that for the bar structure formed with a fluence of $1.25 \times 10^{17}$ ions/cm$^2$ a 1.94% disorder results. The experimental results indicate that the bar structure with this fluence forms at the surface of the material. This means that the damage is reaching the sample surface and consequently, the critical depth is zero. This would imply that a % disorder of 1.94% is needed to form the structure. However, if we look at the % disorder for the bar structure formed with a fluence of $9.38 \times 10^{16}$ ions/cm$^2$, the SRIM simulation indicates that a 1.94% disorder does not occur until the protons reach a depth of 9µm into the material. This would imply that the critical depth after which the structure with a fluence of $9.38 \times 10^{16}$ ions/cm$^2$ will form is 9µm. Experimental results for a bar structure with this fluence of $9.38 \times 10^{16}$ ions/cm$^2$ show that the critical depth is actually 0.05µm. This does not fit the SRIM simulation and suggests that a 1.47% disorder produces a structure with a critical depth of 0.05µm.

For the fluences of $6.25 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$, $3.13 \times 10^{16}$ ions/cm$^2$ and $1.56 \times 10^{16}$ ions/cm$^2$, the simulations indicate that a 1.94% disorder occurs at 20µm, 25µm, 29µm and 32µm into the sample for the respective fluences. The experimental results for the bar structures with these fluences show that the critical depths are 0.1µm, 0.13µm, 0.15µm and 0.18µm for these respective fluences. Once again the experimental results do not fit the SRIM simulation. Comparing the simulations with the experimental results it appears that, for each fluence, an individual % disorder occurs.

Relating these critical depth results to the data from the SRIM simulations, Table 9 shows the critical depth values in relation to the % disorder at the critical depth of the different bar structures for the respective fluences.
Chapter 5 – Results and Discussion

<table>
<thead>
<tr>
<th>Fluence (ions/cm²)</th>
<th>Critical Depth (µm)</th>
<th>% Disorder from SRIM data at critical depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.56 x 10¹⁶</td>
<td>0.18</td>
<td>0.25</td>
</tr>
<tr>
<td>3.13 x 10¹⁶</td>
<td>0.15</td>
<td>0.52</td>
</tr>
<tr>
<td>4.69 x 10¹⁶</td>
<td>0.13</td>
<td>0.86</td>
</tr>
<tr>
<td>6.25 x 10¹⁶</td>
<td>0.1</td>
<td>1.03</td>
</tr>
<tr>
<td>9.38 x 10¹⁶</td>
<td>0.05</td>
<td>1.47</td>
</tr>
<tr>
<td>1.25 x 10¹⁷</td>
<td>0.00</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Table 9 - Table showing critical depth and % disorder at the critical depth from SRIM data with respect to fluence.

These results show that the % disorder at the sample surface is considerably less than it is towards the end of range. This corresponds with the fact that, as the protons lose energy and slow down within the material, nuclear collisions become more probable.

It is also observed that as the fluence increases, the % disorder at the sample surface also increases which would result in more carriers being removed. This would result in less and less conduction occurring at the sample surface as the fluence in increased, until the point is reached where enough carriers have been removed at the surface to completely stop conduction.

From the experimental results, it was found that for fluences below 1.25 x 10¹⁷ ions/cm² there was a critical depth of material which could be removed during etching as the amount of damage near the surface was not sufficient to prevent it being etched. As the fluence is increased up to 1.25 x 10¹⁷ ions/cm², the depth of this region decreases and at 1.25 x 10¹⁷ ions/cm², the damage extends up to the surface.
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Figure 72 - Graph of critical depth versus % Disorder at critical depth using the data from the SRIM simulations and in accordance with data in Table 9.

It can be seen in Figure 72 that, as the % disorder increases, the critical depth decreases until the % disorder reaches a value of 1.94 % disorder which corresponds with a fluence of $1.25 \times 10^{17}$ ions/cm$^2$ and the structure extends up to the surface. This implies that 1.94 % disorder is enough to stop conduction right up to the surface of the sample which leads to the formation of structures produced by PBW at the surface of the p-type GaAs sample.

It was also observed that the width of the structures increase as the fluence increases as seen in Figure 67 and Table 8. The intended width for the structure was 10$\mu$m. The line structure with the smallest fluence of $1.56 \times 10^{16}$ ions/cm$^2$ (on the far left of the Figure 67 ) can be seen to have rounded edges at the top corners of the line structure so no distinct edge can be seen. The width of this structure was measured to be 13.8$\mu$m and this width is smaller that those of the larger fluences. For the other bar structures produced using larger fluences, this rounding of the corners was not observed. As the fluence is increased, the % disorder increases towards the surface of the sample removing more carriers and an improvement in structural definition is observed.
Figure 73 - Graph of the width of the bar structures versus the corresponding fluence.

It can be seen in Figure 73 that as the fluence is increased, the width of the bar structures increase.

The effect of the structural width increase when the fluence is increased is thought to be due to the Gaussian profile of the proton beam.

It has already been stated in Section 4.10 that the proton beam has a Gaussian profile instead of a sharp square profile. This Gaussian profile of the proton beam is due to the fact that the beam current density is not uniform. The periphery of the proton beam has a lower beam current density than at the centre.

As the fluence is increased, a wider Gaussian profile of the proton beam is observed. This can be seen in Figure 74 which shows two Gaussian profiles. One profile represents a general fluence (X) which the other profile represents double the original fluence (2X). This profile implies that the width of the structure would also increase. Therefore critical fluence required to achieve isolation will be achieved in a wider base area for a high fluence than it will for a low fluence.
Another effect that is observed on the high fluence bar structures with fluences of $9.38 \times 10^{16}$ protons/cm$^2$ and $1.25 \times 10^{17}$ protons/cm$^2$ was semicircular grooves at the centre of these structures. This was unexpected. One explanation for this could be that these structures are overdosed. If a structure is given too high a fluence, hopping conduction occurs because the band structure becomes heavily populated with levels, some of which are reasonably shallow so holes can actually jump between the states.

One reason why the edges of the structure do not appear to be affected is because they may have a lower fluence than that of the centre of the structure, alternatively a current could just flow though the centre of the structure due to the hopping conduction mechanism.

Based on the information gathered from this study, it was decided that the most practical and optimum fluence for the structures produced by PBW in the p-type GaAs samples is $10^6$. 

Figure 74 — Gaussian distribution indicating behaviour of the thickness of the structures when the fluence is doubled
6.25 \times 10^{16} \text{ ions/cm}^2. \text{ Even though this fluence does not form the structure at the surface of the material, it has a better structural definition than the other fluences investigated. This is why this fluence was chosen for the rest of the study.}

5.5.1.1 Single Bar Simulation Comparison

The Atlas© semiconductor device package from SILVACO was used to model the hole concentration during the electrochemical etch. A comparison of two dimensional simulations for the single line structure with the experimental results from the same structure with a fluence of \( 6.25 \times 10^{16} \text{ ions/cm}^2 \) can be seen in Figure 75.

![Image of Atlas© simulation showing the hole current density zones in the GaAs sample during the electrochemical etch.](image)

**Figure 75** — (a) Atlas© simulation showing the hole current density zones in the GaAs sample during the electrochemical etch. (b) Atlas© simulation showing the hole current density profile at the surface of the GaAs sample during the electrochemical etch (region...
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between the dotted lines in (a)), (c) SEM image of a single bar structure produced by 2MeV protons in GaAs, (d) Diagrammatic representation of SEM image, (e) Replication of Talystep profiles indicating etch dip at base of structure.

Figure 75 (a) and (b) are two-dimensional computer simulations using the Atlas® semiconductor device package from SILVACO. The simulations are two dimensional cross-sections of the irradiated GaAs sample and they show the hole current density zones in the sample during the electrochemical etching process. The GaAs sample has been irradiated with 2 MeV protons scanned in a single bar structure. The irradiated regions are indicated by the purple rectangular area in Figure 75 (a). At 2 MeV, the protons have a range of approximately 32 μm in the GaAs which was put in as one of the input parameters for the simulation. The simulation seen in Figure 75 (a) shows the different zones of hole current density during the electrochemical etching process in the GaAs sample after PBW, whilst Figure 75 (b) is a cut line through the simulation at the point indicated showing how the hole current density varies across the surface, where the etching occurs. It is observed that in the irradiated regions, the hole current density is zero which is expected due to the removal of carriers by the protons. This was another of the input parameters in the simulation. Because the electrochemical etching is based upon the hole conduction therefore no etching is expected to occur in these regions. An interesting observation from these simulations is that there is a slight increase in hole current density next to the edges of the irradiated areas. As there are a larger concentration of holes in this region, more conduction is expected to occur due to the increased hole movement which would lead to a faster etch rate around these regions. This agrees with the results where talystep profiles indicate small dips around the structure edge.

Figure 75 (c) is a scanning electron micrograph (SEM) image of single bar structure produced in p-type GaAs. This structure was produced using a proton beam with an energy of 2 MeV and a fluence of 6.25 x 10^{16} ions/cm^2. As stated previously, this sample was etched using the electrochemical setup 2. The etch rate was 0.11μm/min and the wall heights of the structure are 15.8μm. Comparing this structure with the simulations seen in Figure 75 (a), (b) and (c) it can be seen that:

The protons remove the carriers in the irradiated regions
This leads to reduced hole current density in the regions that have been irradiated. This results in the formation of structures in the irradiated regions which is supported by both the simulations and the SEM images.

During talystep measurements of this structure, a small dip is noticed around the structure edge as expected from the simulation. This dip was measured using the talystep to be 0.01 μm after a 1 μm etch, then 0.05 μm for the 5 μm etch, 0.1 μm for the 10 μm etch and 0.16 μm after a 15.9 μm etch for this structure. This indicates that for each etch, the dip around the structure etches approximately 1% more than the total etch depth of the rest of the structure. Figure 75 (e) shows a replication of talystep measurements for the 0.16 μm etch dip after a 15.9 μm etch which corresponds with the SEM image seen in Figure 75 (c). Due to the fact that the talystep has a maximum vertical resolution of 12 μm, the top of the structure is not in the talystep profile. At the corners of the structure, this dip is more pronounced.

An increase in hole current density around the edges of the structure is seen in the Figure 75 (b) simulation. This supports the experimental results. An explanation for this 1% increase in etch rate at the edges of the structure is that the field lines are more concentrated at changes in geometrical shape, especially points. The geometrical change in the sample caused by the structure leads to a higher concentration of field lines at the walls of the structure during the etch, resulting in a higher hole current density in this area. Due to the larger movement of holes in this area, a faster etch rate is observed.

5.5.2 Equally Spaced Bars

In order to investigate the effects of having equally spaced bar structures next to each other, four bar structures were scanned onto the GaAs sample using 2 MeV protons with the Ionscan software. The bar structures were the same as that of Section 5.5.1, except four bars were scanned instead of the one. Simulations using the Atlas© semiconductor device package from SILVACO were performed for this four bar structure to help understand the mechanisms involved during the electrochemical etch.

The irradiation parameters are as follows:
Proton Energy 2 MeV
Beam current 1 nA
Horizontal Beam Spot Size 4 µm
Vertical Beam Spot Size 5 µm
Time 133 mins
Fluence $6.25 \times 10^{16}$ ions/cm²

Table 10 - Irradiation parameters for four bar structure

![Proton Beam](image)

Figure 76 - (a) Atlas© simulation showing the hole current density zones in the GaAs sample during the electrochemical etch for a four equally spaced bar structure, (b)
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Atlas© simulation showing the hole current density profile at the surface of the GaAs sample during the electrochemical etch for a four equally spaced bar structure, (c) SEM image of a the four equally spaced bar structure produced by 2MeV protons in GaAs (d) Zoomed in SEM image of the four equally spaced bar structure, (e) Replication of Talystep profiles indicating etch dip at base of structure, (f) Diagrammatic representation of SEM image.

Figure 76 (a) shows the different zones of hole current density during the electrochemical etching process in the GaAs sample after PBW, whilst Figure 76 (b) is a line cut showing simulated hole current density at the surface, where the etching occurs.

The irradiated regions were simulated as being regions of zero doping and from the simulation in Figure 76 (a) it is observed that at these regions, the hole current density is zero, indicated by the purple region.

The simulations seen in Figure 76 (a) and (b) show symmetrical hole current density characteristics between the equally spaced bar structures. This is expected due to the fact that the spacings and dimensions of the structures are the same.

As seen in the Atlas© simulations in Section 5.5.1.1, an increase in hole current density is observed at the edges of the structures. This would suggest that an increase in the etch rate occurs at these regions due to the larger hole movement.

Figure 76 (c) is a scanning electron micrograph (SEM) image of the four bar structure with equal spacings produced in p-type GaAs. This structure was produced using a proton beam with an energy of 2 MeV and a fluence of $6.25 \times 10^{16}$ ions/cm². This sample was etched using the electrochemical setup 2. The depth to which the sample was etched before the structure was observed (critical depth) for all four bar structures, was measured at 0.1μm. This supports the results of Section 5.5.1 which indicates that structures with a fluence of $6.25 \times 10^{16}$ ions/cm² have a critical depth of 0.1μm. The wall heights for the four bar structure was 15.8μm.

The etch rate for this irradiated sample was 0.11μm/min. Comparing this etch rate to that of the unirradiated sample in Section 5.3, the same etch rate of 0.11μm/min is observed.

It can be seen at the bottom of Figure 76 (c) that a horizontal bar structure connects all of the vertical bar structures. This horizontal structure is the result of the beam jumping
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from one vertical bar structure to another very quickly during the scan, resulting in a lower fluence across the horizontal bar. It was observed that the corners of this structure were rounded as those seen for the $1.56 \times 10^{16}$ ions/cm$^2$ bar structure in Figure 67 in Section 5.5.1. The critical depth for the horizontal bar structure was measured to be $8.1\mu$m and the height difference between the vertical bar structures and the horizontal bar structure was measured to be $8\mu$m. The total fluence of this horizontal bar structure is approximately $\sim3.13 \times 10^{15}$ ions/cm$^2$ and the formation of this structure implies that at low fluences:

- Structures can be formed using PBW.
- The corners of the structures are rounded.
- Formation of buried structures is possible by varying the fluence.
- The critical depth of the structure increases at an increased rate as the fluence decreases.

Comparing this data with the previous data obtained from the studies looking into the relationship between fluence and critical depth in Section 5.5.1 and Figure 70, it can be seen that the critical depth for the $\sim3.13 \times 10^{15}$ ions/cm$^2$ bar structure does not follow the same trend as the critical depths seen for the $1.56 \times 10^{16}$ ions/cm$^2$, $3.13 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$, $6.25 \times 10^{16}$ ions/cm$^2$, $9.38 \times 10^{16}$ ions/cm$^2$ and $1.25 \times 10^{17}$ ions/cm$^2$ fluence bar structures. At a fluence of $\sim3.13 \times 10^{15}$ ions/cm$^2$, a critical depth of $8.1\mu$m is observed for the structure. This critical depth is significantly larger than that seen for a fluence of $1.56 \times 10^{16}$ ions/cm$^2$ at $0.18\mu$m. From this result it appears that between the $\sim3.13 \times 10^{15}$ ions/cm$^2$ and $1.56 \times 10^{16}$ ions/cm$^2$ fluence range, the critical depth for the structures produced by PBW in GaAs increases significantly. It is thought that this effect occurs because not enough damage, through nuclear collisions, has occurred at the surface region of the material at this lower fluence. Even though there are some nuclear collisions at the sample surface, these are not enough to remove all of the carriers so enough carriers are still available to allow conduction to occur at this surface region. This results in this area being etched. In other words, there is not enough damage at the surface of the sample until a depth of $8.1\mu$m, for the structure produced with a fluence of $\sim3.13 \times 10^{15}$ ions/cm$^2$, at which the damage is sufficient to stop conduction and the structure is formed.
The effect of the horizontal bar structure can be solved by installing a beam blanking system which deflects the beam off the sample at gaps in the scanned pattern.

Comparing the simulations seen in Figure 76 (a) and (b) with this structure Figure 76 (c), it can be seen that the simulations indicate zero hole current density in the irradiated regions which results in no etching in these areas. This leads to the formation of the structures in the irradiated regions due to carrier removal by the protons. Both the simulations and SEM images support each other.

It was noticed during talystep measurements of these structures that a small dip occurs around the edges of the structures. This indicates that for each etch, the dip around the structure etches approximately 1% more than the total etch depth of the rest of the structure. Figure 76 (e) shows a replication of talystep measurements for the 0.16 \( \mu \text{m} \) etch dip after a 15.9 \( \mu \text{m} \) etch which corresponds with the SEM image seen in Figure 76 (c) and (d). Due to the fact that the talystep has a maximum vertical resolution of 12 \( \mu \text{m} \), the top of the structure is not in the talystep profile. This dip at the base of the structure is also observed in Section 5.5.1.1 and is of the same order of magnitude. This also agrees with the SILVACO simulations.

### 5.5.3 Influence of Distance Between Structures

Using the same bar structure seen in Section 5.5.1, an investigation into the effects of reducing the distances between the bar structures was conducted.

The Ionscan software was used to develop a twelve single bar pattern with decreasing spacings between the bars. Twelve bars were chosen to investigate a range of varying distances between the structures. This pattern was scanned onto the p-type GaAs sample using 2 MeV protons.
In order to understand the mechanisms involved during the etch of this structure, the Atlas© semiconductor device package from SILVACO was used.

The irradiation parameters are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Energy</td>
<td>2 MeV</td>
</tr>
<tr>
<td>Beam Current</td>
<td>1.65 nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>5.4 μm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>5.4 μm</td>
</tr>
<tr>
<td>Time</td>
<td>243 min</td>
</tr>
<tr>
<td>Fluence</td>
<td>$6.25 \times 10^{16}$ ions/cm$^2$</td>
</tr>
</tbody>
</table>

Table 11 – Irradiation parameters for decreasing spaced bar structure.
Figure 77 – (a) Atlas© simulation showing the hole current density zones in the GaAs sample during the electrochemical etch for a decreasing spaced bar structure, (b) Atlas© simulation showing the hole current density profile at the surface of the GaAs sample during the electrochemical etch for a decreasing spaced bar structure, (c) SEM image of a decreasing spaced bar structure produced by 2MeV protons in GaAs (d) Zoomed in SEM image of the decreasing spaced bar structure, (e) Replication of Talystep profiles indicating etch dip at base of structure.
A simulation of the hole current density concentrations during the electrochemical etch are shown in figure Figure 77 (a). Figure 77 (b) shows a cut line simulation showing hole current density values at the surface, where the etching occurs. As with the previous simulations, the irradiated regions are represented by regions of zero doping. This would imply that no hole movement would occur in these regions and therefore, no etching would occur in these areas. This is supported by the experimental results seen in Figure 77 (c) and (d).

The simulations for the twelve bar structures, seen in Figure 77 (a) and (b), indicate that as the distance between the structures gets smaller, the hole current density increases in the spaces between the bar structures.

This would imply that a faster etch rate would occur between structures with the smallest spacing.

Figure 77 (c) is a SEM image of the twelve bar structure with decreasing spacings produced in p-type GaAs. This structure was produced using a proton beam with an energy of 2 MeV and a fluence of $6.25 \times 10^{16}$ ions/cm$^2$. This sample was etched using the electrochemical setup 2. The critical depth for this structure was measured to be is 0.1 µm. This supports the results of Section 5.5.1 and 5.5.2 which indicate that structures with a fluence of $6.25 \times 10^{16}$ ions/cm$^2$ have a critical depth of 0.1 µm. The wall heights of the vertical bar structures are approximately 16.7 µm. The etch rate for this particular sample was 0.11 µm/min. This etch rate is the same as observed as for the unirradiated samples in Section 5.3 of 0.11 µm/min.

A horizontal bar structure connecting all of the vertical bar structures can be seen at the bottom of Figure 77 (c). As explained in Section 5.5.2, this horizontal structure is the result of the beam jumping from one vertical bar structure to another very quickly during the scan, resulting in a lower fluence across the horizontal bar of $\sim 3.13 \times 10^{15}$ ions/cm$^2$. As a result, the critical depth for this structure is deeper than those of the vertical bars which have higher fluences of $6.25 \times 10^{16}$ ions/cm$^2$. The critical depth for this horizontal structure is $\sim 8.1$ µm and the height difference between the vertical bar structures and the horizontal bar structure is $\sim 8$ µm. It was also observed that the corners of this horizontal structure were rounded as those seen for the other low fluence structures such as the $1.56 \times 10^{16}$ ions/cm$^2$ bar structure in Figure 67 and the $\sim 3.13 \times 10^{15}$ ions/cm$^2$ horizontal line.
structure in Figure 76 (c). These results support the fact that at low fluences the structural edge definition reduces and the critical depth increases. They also support the previous results seen in Figure 76 (c) that buried structures can be formed ~8 μm within the GaAs sample with a fluence of ~3.13 x 10^{15} ions/cm².

Comparing the simulations for this structure seen in Figure 77 (a), with the experimental results, Figure 77 (b), (c) and (d) it can be seen that over the large spacings of 101 μm to 61 μm the simulations indicate only a marginal hole current density increase. This would suggest that the etch rate between the line spacings would be similar. The results indicate that they are and the structure heights are the same. As the spacings between the structures continue to decrease from 49 μm to 8 μm, the simulations suggest that a faster etch rate would occur, however the experimental results do not agree with this. Instead, the heights of all the vertical bar structures remain the same apart from the structures with the two smallest spacings of 12 μm and 8 μm. Figure 77 (c) and (d) show that these two bar structures at their ends have the same height as all of the bar structures but moving closer to the centre of the structure the etch depth decreases until only 1.3 μm and 0.9 μm are etched. This reduced etch depth in the smaller spacings of 12μm and 8μm are thought to be due to chemical crowding which means that the etch products cannot get in and out of these small spacings. This is supported by the fact that at the end of the structure the etch depth is approximately 16.7 μm as there is more access for the chemicals to the spacings in this area. The simulations suggest a larger hole current density in the smaller spacings which would lead to a faster etch rate. This is not seen as all of the structures can be seen to be etched to the same depths at their edges. A possible explanation for this is that the combination of the increased etch rate and the effects of the chemical crowding in these small spacings result in the same etch depth for all the structures.

Another effect noticed during the Talystep measurements was that a small dip occurs around the edges of the bar structures. These dips have also been noticed in the previous structures investigated and are caused by high hole current densities at the base of the structure because a larger concentration of field lines occur at geometrical changes in shape. This leads to a faster etch rate in these areas as observed by this dip effect. After a 1μm etch this dip was measured to be 0.01 μm. for the 5 μm etch the dip was measured to
be 0.05 μm, for the 10 μm etch the dip was measured to be 0.1 μm and for the 16.8 μm etch the dip was measured to be 0.17 μm. This indicates that for each etch, the dip around the structure etches to 1% of the total etch depth. Figure 77 (e) shows a replication of talystep measurements for the 0.17 μm etch dip after a 16.8 μm etch which corresponds with the SEM image seen in Figure 77 (c) and (d). Due to the fact that the talystep has a maximum vertical resolution of 12 μm, the top of the structure is not in the talystep profile. The results corresponds with the previous results where the dip was also 1% of the total etch depth. At the ends of the structures, this dip, is more pronounced where the corners are visible.

This dip effect is supported, to a certain degree, by the simulations which show an increase in hole current density around the walls of the structures seen in Figure 77 (b). As the spacing between the structures reduces to 49 μm and below, the simulations indicate that this dip does not occur. The experimental results show that this dip is constant for all of the bar structures where the etch depth is the same thereby conflicting with the simulations.

### 5.5.4 Etching of Enclosed Features

In order to test if PBW could produce enclosed structures in p-type GaAs, a single hollow circle pattern was scanned onto the p-type GaAs sample using 2 MeV protons with the Ionscan scanning software.

The irradiation parameters are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Energy</td>
<td>2 MeV</td>
</tr>
<tr>
<td>Beam Current</td>
<td>0.77 nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>3.1 μm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>4.7 μm</td>
</tr>
</tbody>
</table>

**Table 12** – Irradiation parameters for hollow circle structure.

From the results in the previous sections, it has already been stated that the optimum fluence for the single bar structures is $6.25 \times 10^{16}$ ions/cm$^2$. It is not known if the formation of a hollow circle is possible in this material, so a fluence study was again conducted to determine if this structure was possible and what the optimum fluence for this type of structure would be. It is noted that the scanning area for these structures was 300 μm x 300μm. This was chosen so that different fluences for this structure could be
scanned during the same experimental run on the microbeam. If the size is reduced, the desired fluence is reached in a faster time. This was done in order to keep as many variables constant as possible.

The same hollow circle pattern was scanned six times at different locations on the GaAs sample with different fluences. These fluences were:

<table>
<thead>
<tr>
<th>Fluence</th>
<th>Time for Irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.56 \times 10^{19}$ ions/cm²</td>
<td>6 min 36 sec</td>
</tr>
<tr>
<td>$3.13 \times 10^{16}$ ions/cm²</td>
<td>13 mins</td>
</tr>
<tr>
<td>$4.69 \times 10^{16}$ ions/cm²</td>
<td>19 mins 30 sec</td>
</tr>
<tr>
<td>$6.25 \times 10^{16}$ ions/cm²</td>
<td>26 mins</td>
</tr>
<tr>
<td>$1.25 \times 10^{17}$ ions/cm²</td>
<td>51 mins 48 sec</td>
</tr>
<tr>
<td>$1.88 \times 10^{17}$ ions/cm²</td>
<td>1 hour 17 mins 36 sec</td>
</tr>
</tbody>
</table>

Table 13 – Fluence and time parameters for hollow circle structures.

The irradiated sample was then cleaned using the three stage clean (described in section 5.2.1) prior to etching. The electrochemical etch setup 2 was used to etch this sample using a current of 0.5 mA over an area of 0.1 cm². All six scans were positioned within the etching area of 0.1 cm² so they could be etched together to directly compare the results. Figure 78 shows an SEM image of the six hollow circle structures labelled with their corresponding fluences. The six hollow circle structures can be clearly identified, proving that this technique is effective in producing enclosed structures.
(i) SEM Images

(ii) Talystep

Figure 78 – (i) From left $1.56 \times 10^{16}$ ions/cm$^2$, $3.13 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$, $6.25 \times 10^{16}$ ions/cm$^2$, $9.38 \times 10^{16}$ ions/cm$^2$ and $1.25 \times 10^{17}$ ions/cm$^2$. (ii) Replication of Talystep profiles indicating groove at top of structure and etch dip at base of structure for Figure 78 (e) - structure with fluence $9.38 \times 10^{16}$ protons/cm$^2$ and (f) - structure with fluence $1.25 \times 10^{17}$ protons/cm$^2$.

The etch rate for this irradiated sample was 0.11µm/min. Comparing this etch rate to that of the unirradiated sample in Section 5.3 and the irradiated samples in Section 5.5, the same etch rate of 0.11µm/min is observed.
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It has already been observed in Section 5.5.1-3 that at different fluences, structures have different critical depths. Based on these results it is expected that the hollow circles will have corresponding critical depths for their respective fluences.

Observing these hollow circle structures with different fluences, it can be seen that the height and the width of the structures vary with fluence. Along with this, there appears to be some sloping etch effects at the walls of the circles in the horizontal direction. This effect occurs for all of the circle structures. Looking at the hollow circle structure with the smallest fluence of $1.56 \times 10^{16}$ ions/cm$^2$ (Figure 78(a)), talystep and SEM measurements indicate that this structure does not form at the surface of the sample. Instead there is a critical depth of 0.18 μm after which the structure is formed.

This critical depth region is also seen for the circle structures with fluences of $3.13 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$ and $6.25 \times 10^{16}$ ions/cm$^2$. However, as the fluence is increased, the critical depth is reduced. At a fluence of $1.25 \times 10^{17}$ ions/cm$^2$ and $1.88 \times 10^{17}$ ions/cm$^2$, the critical depth is zero and the structure has the same height as the etch depth. Figure 79 shows the figures of the critical depth and structure width with respect to fluence. These measurements were taken using both the talystep profiler and calculations using the SEM images at 1 μm, 5 μm and 10 μm etches. As the talystep has a maximum measurement of 12 μm, all measurements after etching this depth were conducted using the SEM images.
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<table>
<thead>
<tr>
<th>Dose (pC/µm²)</th>
<th>Fluence (ions/cm²)</th>
<th>Critical Depth (µm)</th>
<th>Structure Width (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>After etching for 9 min to an etch depth of 1 µm</td>
<td>After etching for 48 min to an etch depth of 5 µm</td>
</tr>
<tr>
<td>25</td>
<td>$1.56 \times 10^{16}$</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>50</td>
<td>$3.13 \times 10^{16}$</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>75</td>
<td>$4.69 \times 10^{16}$</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>100</td>
<td>$6.25 \times 10^{16}$</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>200</td>
<td>$9.38 \times 10^{16}$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>300</td>
<td>$1.88 \times 10^{17}$</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 14 – Table showing critical depth and structure width with respect to fluence for hollow circles.

The results from the critical depth analysis of the enclosed hollow circle structures are comparable with those of the bar structures seen in Section 5.5.1. Figure 79 shows a comparison of the critical depth versus the corresponding fluence for the single bar structures and the hollow circle structures. The results are very similar and they indicate that at a fluence of $1.25 \times 10^{17}$ ions/cm², the structures are formed at the surface of the sample as sufficient holes have been removed so that no etching occurs at the sample surface. The larger increase of fluence to $1.88 \times 10^{17}$ ions/cm² for the hollow circle structure indicates that beyond $1.25 \times 10^{17}$ ions/cm² the critical depth remains at zero. This effect was expected as it was observed for the bar structures with the corresponding fluences.

An interesting effect is observed for the hollow circle structures with the larger fluences of $1.25 \times 10^{17}$ ions/cm² and $1.88 \times 10^{17}$ ions/cm². It can be seen that a semi-circular groove is etched at the top of the circle walls. This can be seen in Figure 78 (ii) which shows a replication of talystep measurements performed at the top of the circle walls.

This effect also occurs for the bar structure with fluences of $9.38 \times 10^{16}$ ions/cm² and $1.25 \times 10^{17}$ ions/cm² seen in Figure 67 in Section 5.3.1. As stated previously, this effect is thought to occur due to hopping conduction. It is interesting that etching only occurs at the centre of the circular wall structures. At the edges no etching is apparent which is supported by the critical depth measurements being constant for the two structures. One reason why the edges of the structure do not appear to be affected is because they may
have a lower fluence than that of the centre of the structure, alternatively a current could just flow though the centre of the structure due to the hopping conduction mechanism. This effect is also noticed for in the bar structures with a fluence of $9.38 \times 10^{16}$ ions/cm$^2$ and above.

Another observation for these structures was the variations in the width as the fluence increased. This can be seen in Figure 78. The hollow circle structure with the smallest fluence of $1.56 \times 10^{16}$ ions/cm$^2$ (Figure 78 (a)) can be seen to have rounded edges at the top corners of the structure so no sharp edge can be seen. The width of this structure was measured to be 9\mu m and this width is smaller that those of the larger fluences where the structure width increases to 26.9\mu m. The Gaussian profile of the beam is thought to be responsible for this effect of structural width increase as explained in Section 5.5.1.

As the fluence is increased, the % disorder increases towards the surface of the sample removing more carriers and an improvement in structural definition is observed.

**Figure 79** - Graph showing the critical depth until the structure is revealed versus the corresponding fluence for the bar and hollow circle structures.
Talystep measurements of this structure indicated the occurrence of a small dip around the edges of the structures. The dip around the structures etches to 1% of the total etch depth. This effect was also observed in the previous results for the bar structures in the earlier sections.

The similarities between the fluence studies of the bar and hollow circle structures regarding the critical depth, structure width and groove formation at high fluences, indicate reproducible effects occurring for PBW conditions. It is interesting to note that the enclosed region inside the circle structures etch at the same rate as the regions outside the circle.

As with the bar structures, the information gathered from this study of the hollow circle structures, indicates that the fluence of $6.25 \times 10^{16}$ ions/cm$^2$ is the most practical and optimum fluence for the structures produced by PBW in the p-type GaAs samples.

Even though this fluence does not form the structure at the surface of the material, it has a better structural definition than the high fluences of $1.25 \times 10^{17}$ ions/cm$^2$ and $1.88 \times 10^{17}$ ions/cm$^2$. This is why this fluence was chosen.
5.5.4.1 Hollow Circle Simulations Comparison

In order to accurately simulate the hollow circle structure, a three dimensional simulation was performed using the Atlas© semiconductor device package from SILVACO which took into account the enclosed area. Hole concentration simulations during the electrochemical etch for the hollow circle structure were performed to better understand the mechanisms involved during the etch. As with the previous simulations, the irradiated region was simulated as regions of zero doping, 32 μm into the material, to represent the removal of carriers by the protons and the proton range.

![Diagram of Proton Beam and Sample Surface](image)

**Figure 80** - (a) Atlas© simulation showing the hole current density zones in the GaAs sample during the electrochemical etch for a hollow circle structure, (b) Atlas© simulation showing the hole current density profile at the surface of the GaAs sample during the electrochemical etch for a hollow circle structure, (c) SEM image of a hollow circle structure produced by 2MeV protons in GaAs.
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Simulations showing the different zones of hole current density during the electrochemical etching process in the GaAs sample after PBW can be seen in Figure 80 (a), whilst Figure 80 (b) is a cut line simulation showing hole current density values at the surface, where the etching occurs.

The simulations indicate that etching would occur both inside and outside of the enclosed regions of the structure. The hole current density profile seen in Figure 80 (b) appears to increase marginally at both, the outer and enclosed edges of the hollow circle structure. The enclosed edges appear to have a marginally higher hole current density profile than the outer edges but this does not appear significant enough to affect the etch rate.

Comparing this simulation with the experimental results seen in Figure 80 (c) it can be seen that:

- The removal of carriers in the irradiated areas by the protons leads to reduced hole current density in these regions.
- As the electrochemical etch is based on conduction of holes, structures are produced in the irradiated regions as seen in the SEM images.
- Talystep measurements indicate that the etch depth outside and inside the hollow circle structure are the same which correspond with the simulations.
- The sloping etch effect at the horizontal side walls of the structure and the dips occurring around the edges of the structure are not seen in the simulations.
5.6 Effects of Energy

It has already been stated in previous sections, that the optimum fluence for PBW in the GaAs samples investigated in this work is $6.25 \times 10^{16}$ ions/cm$^2$. In order to investigate the effects of energy with PBW in GaAs, a single bar structure was scanned on the GaAs samples using four different energies. The results from previous work in this Chapter 5, indicate that by reducing the scanning area to 300 $\mu$m x 300 $\mu$m, the time required for a particular fluence reduces and does not appear affect the PBW process unless the spacings between the structures are 12$\mu$m or less. The Ionscan software was used to scan a single bar structure using a scan size of 300 $\mu$m x 300 $\mu$m. The energies of 1 MeV, 1.5 MeV, 2 MeV and 2.5 MeV were used. SRIM [28, 109] simulations, seen in Figure 81, indicate that as the energy is increased, the protons travel further into the material. These simulations also indicate that the end of range lateral straggle of the protons also increases with increase in energy. This would imply that we would get taller structures with continued etching. It is noted that when changing the beam energy, the irradiation parameters change as a result due to the beam focusing. With this in mind, every attempt was made to keep these variations to a minimum.

![Figure 81 - SRIM simulations of 1 MeV, 1.5 MeV, 2 MeV and 2.5 MeV protons in GaAs.](image)
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The irradiation parameters for these structures can be seen in Table 15.

<table>
<thead>
<tr>
<th>Proton Energy</th>
<th>1.0 MeV</th>
<th>1.5 MeV</th>
<th>2.0 MeV</th>
<th>2.5 MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam Current</td>
<td>0.6 nA</td>
<td>1.0 nA</td>
<td>0.8 nA</td>
<td>1.0 nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>2.5 μm</td>
<td>4.1 μm</td>
<td>5.1 μm</td>
<td>3.5 μm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>5.0 μm</td>
<td>7.0 μm</td>
<td>4.7 μm</td>
<td>6.7 μm</td>
</tr>
<tr>
<td>Scan Size</td>
<td>300μm x 300μm</td>
<td>300μm x 300μm</td>
<td>300μm x 300μm</td>
<td>300μm x 300μm</td>
</tr>
<tr>
<td>Fluence</td>
<td>6.25 x 10^{16} ions/cm^{2}</td>
<td>6.25 x 10^{16} ions/cm^{2}</td>
<td>6.25 x 10^{16} ions/cm^{2}</td>
<td>6.25 x 10^{16} ions/cm^{2}</td>
</tr>
<tr>
<td>Time</td>
<td>5min</td>
<td>3min</td>
<td>3min 54sec</td>
<td>3min</td>
</tr>
</tbody>
</table>

Table 15 – Irradiation parameters for multiple energy bar structures.

The irradiated sample was then cleaned using the three stage clean prior to etching. The electrochemical etch setup 2 was used to etch this sample at an etch current of 0.5mA and an etch area of 0.1cm^{2}. Four samples were irradiated. One for each energy containing the bar structures that were scanned. All four samples were etched to the same depths to directly compare the results.

Figure 82 shows an SEM image of the bar structures formed with the four different energies:
Figure 82 – (i) SEM images of Bar structures with a fluence of $6.25 \times 10^{16}$ ions/cm$^2$ formed with different energies, (a) 1 MeV, (b) 1.5 MeV, (c) 2 MeV, (d) 2.5 MeV. (ii) Diagrammatic Representation of SEM Images.

An etch rate of 0.11 μm/min was observed for all four samples which is consistent with the previous etch rates for the other experiments.

As seen with the previous results in this chapter, the talystep measurements indicated a small dip which is observed at the edges of the bar structures for all the energies and this dip is once again 1% of the total etch depth which is consistent with the previous results.

The SEM images indicate that at the energies of 1 MeV and 1.5 MeV, the bar structures have an increase in surface roughness and pitting. At the 2 MeV irradiation, the pitting is
reduced and the structure surface appears smoother. For the structure produced using 2.5 MeV protons, the structure surface smoothness is improved.

Investigating these structures irradiated with the same fluences, but different energies, it is observed that the critical depth at which the structure is formed varies. The critical depth region occurs because not enough damage, through nuclear collisions, occurs at the surface of the material. Even though there are some nuclear collisions at the sample surface, these are not enough to remove all of the carriers so enough carriers are still available to allow conduction to occur at this surface region, which results in this area being etched. In other words, there is not enough damage at the surface of the sample. These results can be seen in Table 16 and Figure 83.

<table>
<thead>
<tr>
<th>Dose (pC/µm²)</th>
<th>Fluence (ions/cm²)</th>
<th>Energy (MeV)</th>
<th>Critical Depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>After etching for 9 min to an etch depth of 1 µm</td>
</tr>
<tr>
<td>100</td>
<td>6.25 x 10^{16}</td>
<td>1.0</td>
<td>0.02</td>
</tr>
<tr>
<td>100</td>
<td>6.25 x 10^{16}</td>
<td>1.5</td>
<td>0.06</td>
</tr>
<tr>
<td>100</td>
<td>6.25 x 10^{16}</td>
<td>2.0</td>
<td>0.10</td>
</tr>
<tr>
<td>100</td>
<td>6.25 x 10^{16}</td>
<td>2.5</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 16 — Table showing critical depth with respect to fluence and energy for bar structures produced at different energies of 1 MeV, 1.5 MeV, 2 MeV and 2.5 MeV.
Figure 83 — Graph corresponding with
Table 16 showing critical depth with respect to energy for the bar structures produced at different energies of 1 MeV, 1.5 MeV, 2 MeV and 2.5 MeV.

These results show that at lower energies of 1 MeV, the critical depth after which the structure is formed was measured to be 0.02 µm. As the energy is increased the critical depth also appears to increase. For the structure produced by 2.5 MeV protons, the critical depth was measured to be 0.16 µm. This can be seen in Figure 83. To compare these results with the data from SRIM simulations, protons with energies of 1 MeV, 1.5 MeV, 2 MeV and 2.5 MeV and fluences of $6.25 \times 10^{16}$ ions/cm$^2$ in GaAs were simulated using SRIM. The data from these simulations were used to plot the percentage of atoms that have been permanently disordered in the GaAs material resulting from the energy lost by the protons directly to the atoms of the GaAs material through nuclear collisions. This has been labelled as “% Disorder” on the graphs. The “% Disorder” has been plotted against the depth (µm) into the sample and can be seen in Figure 84 for the respective energies.
Figure 84 - Graph of % disorder versus depth from SRIM data for fluences of $6.25 \times 10^{16}$ ions/cm$^2$ using proton energies of 1 MeV, 1.5 MeV, 2 MeV and 2.5 MeV.

From the results of the data from the SRIM simulations for % Disorder, seen in Figure 84, it can be seen that:

1) At the surface of the material, protons with lower energies have a larger % disorder than protons of higher energies.

2) The % disorder at the sample surface is considerably less than it is towards the end of range. This corresponds with the fact that, as the protons lose energy and slow down within the material, nuclear collisions become more probable.

3) As the proton energy is increased, the % Disorder at the end of range decreases.

The simulations suggest that for a bar structure formed with 1 MeV protons and a fluence of $6.25 \times 10^{16}$ ions/cm$^2$, a 1.51 % disorder results at the critical depth. The experimental results for the bar structure produced by 1 MeV at a fluence of $6.25 \times 10^{16}$ ions/cm$^2$ (seen in Figure 82 (a)) indicates that this bar structure has a critical depth of 0.02μm.
However, if we look at the % disorder for the bar structure formed with 1.5 MeV protons and a fluence of $6.25 \times 10^{16}$ ions/cm$^2$, the SRIM simulation indicates that a 1.51 % disorder does not occur until the protons reach a depth of 7 μm into the material. This would imply that the critical depth after which the structure formed with 1.5 MeV protons and a fluence of $6.25 \times 10^{16}$ ions/cm$^2$ will form is 7μm. Experimental results for a bar structure formed with 1.5 MeV protons and a fluence of $6.25 \times 10^{16}$ ions/cm$^2$ show that the critical depth is actually 0.06 μm. This does not fit the SRIM simulation and suggests that a 1.36 % disorder produces a structure with a critical depth of 0.06μm.

Looking at the $6.25 \times 10^{16}$ ions/cm$^2$ bar structures produced by 2 MeV and 2.5 MeV protons, the simulations indicate that a 1.51 % disorder occurs at 15 μm and 18 μm for the respective proton energies. The experimental results for the $6.25 \times 10^{16}$ ions/cm$^2$ bar structures produced by 2 MeV and 2.5 MeV protons show that the critical depths are 0.1 μm, 0.16 μm, for these respective proton energies. Once again the experimental results do not fit the SRIM simulation as they suggest that a 1.03 % disorder produces a structure with a critical depth of 0.1μm for the 2 MeV protons and a 0.86 % disorder produces a structure with a critical depth of 0.16μm for the 2.5 MeV protons.

Comparing the simulations with the experimental results it appears that structures produced with the same fluence but using different proton energies have individual % disorders that relate to the formation of the structures and their respective critical depths. What appears to be in agreement from the simulations are that the as the proton energy decreases, the % disorder at the critical depth increases. At the lower energies more nuclear collisions occur at the material surface as the protons are travelling slower and as they lose energy and slow down within the material, nuclear collisions become more probable. This is also supported by the fact that as the proton energy increases, the critical depth also increases.

Relating these critical depth results to the data from the SRIM simulations, Table 17 and Figure 85 shows the critical depth values in relation to the % disorder at the sample surface.
Table 17 – Table showing critical depth and % Disorder at critical depth from SRIM data with respect to Energy for single bar structures with a fluence of $6.25 \times 10^{16}$ ions/cm$^2$.

<table>
<thead>
<tr>
<th>Energy (MeV)</th>
<th>Critical Depth (μm)</th>
<th>% Disorder from SRIM data at Critical Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.02</td>
<td>1.51</td>
</tr>
<tr>
<td>1.5</td>
<td>0.06</td>
<td>1.36</td>
</tr>
<tr>
<td>2.0</td>
<td>0.10</td>
<td>1.03</td>
</tr>
<tr>
<td>2.5</td>
<td>0.16</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Figure 85 - Graph of critical depth versus % Disorder at critical depth using the data from the SRIM simulations and in accordance with data in Table 17.

Comparing the critical depth versus % disorder for the bar structures produced by 1 MeV, 1.5 MeV, 2 MeV and 2.5 MeV proton with a fluence of $6.25 \times 10^{16}$ ions/cm$^2$, it can be seen in Figure 85 that, as the % disorder at the critical depth increases, the critical depth decreases.
These results indicate that:

- At low energies, more nuclear collisions occur at the sample surface than at higher energies.

- Structures are formed closer to the surface of the material at low energies than at high energies when irradiating with the same fluence, (The critical depth is smaller at low energies).

A comparison of these results with previous SRIM % disorder simulations and experimental results seen in Section 5.5.1, Table 9 and Figure 71 which investigated producing bar structures by varying fluences between $1.56 \times 10^{16}$ ions/cm$^2$ and $1.25 \times 10^{17}$ ions/cm$^2$ using 2 MeV protons, can be seen in Table 18.

<table>
<thead>
<tr>
<th>% Disorder</th>
<th>Critical Depth (μm)</th>
<th>Energy (MeV)</th>
<th>Fluence (ions/cm$^2$)</th>
<th>Dose (pC/μm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.94</td>
<td>0.00</td>
<td>2.0</td>
<td>$1.25 \times 10^{17}$</td>
<td>200</td>
</tr>
<tr>
<td>1.51</td>
<td>0.02</td>
<td>1.0</td>
<td>$6.25 \times 10^{16}$</td>
<td>100</td>
</tr>
<tr>
<td>1.47</td>
<td>0.05</td>
<td>2.0</td>
<td>$9.38 \times 10^{16}$</td>
<td>150</td>
</tr>
<tr>
<td>1.36</td>
<td>0.06</td>
<td>1.5</td>
<td>$6.25 \times 10^{16}$</td>
<td>100</td>
</tr>
<tr>
<td>1.03</td>
<td>0.10</td>
<td>2.0</td>
<td>$6.25 \times 10^{16}$</td>
<td>100</td>
</tr>
<tr>
<td>1.03</td>
<td>0.10</td>
<td>2.0</td>
<td>$6.25 \times 10^{16}$</td>
<td>100</td>
</tr>
<tr>
<td>0.86</td>
<td>0.13</td>
<td>2.0</td>
<td>$4.69 \times 10^{16}$</td>
<td>75</td>
</tr>
<tr>
<td>0.86</td>
<td>0.16</td>
<td>2.5</td>
<td>$6.25 \times 10^{16}$</td>
<td>100</td>
</tr>
<tr>
<td>0.52</td>
<td>0.15</td>
<td>2.0</td>
<td>$3.13 \times 10^{16}$</td>
<td>50</td>
</tr>
<tr>
<td>0.25</td>
<td>0.18</td>
<td>2.0</td>
<td>$1.56 \times 10^{16}$</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 18 – Comparison of the % disorder SRIM simulations and critical depth experimental results seen in this section with respect to $6.25 \times 10^{16}$ ions/cm$^2$ fluence bar structures produced by 1 MeV, 1.5 MeV, 2 MeV and 2.5 MeV protons against the results seen Section 5.5.1, Table 9 and Figure 71 which investigated producing bar structures by varying fluences between $1.56 \times 10^{16}$ ions/cm$^2$ and $1.25 \times 10^{17}$ ions/cm$^2$ using 2 MeV protons.
protons. The black text indicates the results in this section and the red text indicates the results from Section 5.5.1, Table 9 and Figure 71.

The comparison table in seen in Table 18 shows the results in this section in black text and the results from Section 5.5.1, Table 9 and Figure 71 in the red text. By comparing these results it can be seen that when the proton energy and fluence of the structures are the same, the critical depth and the respective % disorder are constant. This can be seen when comparing the bar structures produced using 2 MeV protons with a fluence of $6.25 \times 10^{16}$ ions/cm$^2$ for results both in this section and from Section 5.5.1 and Figure 71 where the % disorder is the same at 1.03 % disorder and the critical depths are also the same at 0.1μm.

However when comparing the results of the bar structures that were produced with same % disorder of 0.86 % disorder but with different proton energies of 2 MeV and 2.5 MeV and different fluences of $4.69 \times 10^{16}$ ions/cm$^2$ and $6.25 \times 10^{16}$ ions/cm$^2$, it can be seen in Table 18 that the critical depth for these two structures are different. It appears that a bar structure produced with a lower fluence and at a lower energy has a shorter critical depth than a bar structure produced using a higher fluence and energy even though the % disorders for both are the same at 0.86 % disorder.

These results indicate that it appears that structures produced with different fluences and different proton energies have individual % disorders that relates to the formation of the structures and their respective critical depths.

5.7 Free Standing Structure by Varying the Energy

Previous studies of PBW in SU8 and Si show that free standing structures can be produced by scanning at different energies. With this in mind, two different bar structures were produced in GaAs using 2 MeV (Bar (a)) and 1 MeV (Bar (b)) protons. An etch rate of 0.11 μm/min was observed which is consistent with the previous etch rates for the other experiments in Sections 5.3, 5.5. and 5.6. Figure 86 shows an SEM image of this structure that has been etched to a depth of 20.1 μm. It can be seen that the
1 MeV (Bar (b)) structure has been undercut and is standing 10.5 µm clear of the bottom of the sample. The end of range effects, where the beam broadens can also be seen in this undercut 1 MeV bar structure.

SRIM simulations [28, 109], indicate that 1 MeV protons have a projected range of 10.9 µm in GaAs. Comparing these results to the SRIM simulations for 1 MeV protons it can be seen that they are comparable.

**Figure 86** - SEM image of a free standing structure in GaAs produced by varying the energy. Horizontal bar (Bar (a)) produced by 2 MeV protons. Vertical bar (Bar (b)) produced by 1 MeV protons.

### 5.8 Multi-Level Structure by Varying Fluence

The next complex structure occurred by accident. It has already been explained in Section 5.5.3 that whilst scanning 2 MeV protons in a twelve vertical bar pattern a horizontal bar structure was formed as the beam jumps from one part of the scan to the next. The fluence in the horizontal bar (~3.13 x 10^{15} ions/cm^2) is much less than that of the vertical bars (6.25 x 10^{16} ions/cm^2) and this is confirmed by its formation, ~8 µm below that of the other structures. One of the interesting effects of this structure is that a step can clearly be seen between the bars with the larger fluence and the bar with the lower fluence. This indicates that multi-level, buried structures can be produced by varying the fluence. This can be seen in Figure 87.
The irradiation parameters for this structure are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Energy</td>
<td>2 MeV</td>
</tr>
<tr>
<td>Beam Current</td>
<td>1.65 nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>5.4 μm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>5.4 μm</td>
</tr>
<tr>
<td>Time</td>
<td>243 min</td>
</tr>
<tr>
<td>Fluence</td>
<td>6.25 x 10^{15} ions/cm²</td>
</tr>
</tbody>
</table>

Table 19 – Irradiation parameters for decreasing spaced bar structure.

Figure 87 - SEM image of part of the decreasing bar structure produced by 2 MeV protons in GaAs using the Ionscan scanning software.

5.9 Rings

5.9.1.1 Concentric Rings

The next complex structure is the concentric rings seen in Figure 88. This structure was selected in order to find out if multiple enclosed structures could be produced for applications such as ring resonators in optical devices. The Ionscan software was used to scan this pattern.

The irradiation parameters are as follows:
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Proton Energy 2 MeV  
Beam Current 1.65nA  
Horizontal Beam Spot Size 5.45 μm  
Vertical Beam Spot Size 5.47 μm  
Time 203min  
Fluence $6.25 \times 10^{16}$ ions/cm²  

<table>
<thead>
<tr>
<th>Table 20</th>
<th>Irradiation parameters for University of Surrey logo structure.</th>
</tr>
</thead>
</table>

This structure was produced using a proton beam with an energy of 2 MeV and a fluence of $6.25 \times 10^{16}$ ions/cm². The critical depth for this structure was measured to be 0.1 μm. This supports the results from the previous sections of Section 5.5.1 and 5.5.2 which indicate that structures with a fluence of $6.25 \times 10^{16}$ ions/cm² have a critical depth of 0.1μm. The structure height is 17.7 μm. The etch rate for this sample was 0.11μm/min, the same as that observed for previous samples.

It can be seen that as each ring has a spacing of 45μm to each other and a uniform etch occurs in all of the spacings of structure. A line structure can be seen joining up all of the rings. This is due to the beam jumping very quickly from one ring pattern to another whilst scanning. This gives the line structure a lower fluence of $\sim 3.13 \times 10^{15}$ ions/cm². The critical depth of this line structure was measured to be 8.1 μm and its height difference to the circle structures is 8 μm shorter. This result also agrees when compared to Figure 76 and Figure 77 where the structures produced by the beam jumping from one part of the scan to the other also have a critical depth of 8.1μm. This supports the fact that buried structures can be produced with a fluence of $\sim 3.13 \times 10^{15}$ ions/cm².

This structure indicates that several enclosed structures with widths of 45μm can be produced as long as adequate spacing is available between the structures so that chemical crowding does not occur.
5.9.1.2 Olympic Rings

The final complex structure investigated is the Olympic rings structure seen in Figure 89. This structure was selected in order to find out the effects of overlapping structures with the same fluence and observe the effects of the etch on the enclosed structures. The Ionscan software was used to scan this pattern.

The irradiation parameters are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Energy</td>
<td>2 MeV</td>
</tr>
<tr>
<td>Beam Current</td>
<td>1.65nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>5.45 µm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>5.47 µm</td>
</tr>
<tr>
<td>Time</td>
<td>203min</td>
</tr>
<tr>
<td>Fluence</td>
<td>$6.25 \times 10^{16}$ ions/cm$^2$</td>
</tr>
</tbody>
</table>

Table 21 – Irradiation parameters for University of Surrey logo structure.

This structure was produced using a proton beam with an energy of 2 MeV and a fluence of $6.25 \times 10^{16}$ ions/cm$^2$. The critical depth for this structure was measured to be 0.1 µm. This supports the results from the previous sections of Section 5.5.1 and 5.5.2 which indicate that structures with a fluence of $6.25 \times 10^{16}$ ions/cm$^2$ have a critical depth of 0.1µm. The etch rate for this sample was 0.11µm/min, the same as that of the previous samples investigated in this study, and the structure height is 12.7 µm.
Talystep measurements and SEM imaging indicate that the etch depth inside and outside of the structures is constant. Two horizontal line structures can be seen joining up all of the rings. As explained before, these structures are due to the beam jumping very quickly from one ring pattern to another whilst scanning. This gives the line structure a lower fluence of $\sim 3.13 \times 10^{15}$ ions/cm$^2$. The critical depth of this line structure was measured to be 8.1 $\mu$m and its height difference to the circle structures is 8 $\mu$m shorter.

This result agrees when compared to Figure 76, Figure 77 and Figure 88 where the structures produced by the beam jumping from one part of the scan to the other also have a critical depth of 8.1 $\mu$m. Another interesting effect observed in Figure 89 (b) is the small groove seen in the structure at the point where two parts of the circle structures overlap. This groove is seen at all of the overlap points in the structure. This effect has been seen before in Figure 67 (e) and (f) in Section 5.5.1 for bar structures with fluences of $9.38 \times 10^{16}$ ions/cm$^2$ and $1.25 \times 10^{17}$ ions/cm$^2$. A possible explanation for this is could be that these structures are overdosed at these overlapping regions. If a structure is given too high a fluence, hopping conduction occurs because the band structure becomes heavily populated with levels, some of which are reasonably shallow so electrons can actually jump between the states.

One reason why the edges of the structure do not appear to be affected is because they may have a lower fluence than that of the centre of the structure, alternatively a current could just flow though the centre of the structure due to the hopping conduction mechanism.

**Figure 89** - SEM image of Olympic rings produced by 2 MeV protons in GaAs using the Ionscan scanning software.
5.10 Photoluminescence Measurements

To observe the photoluminescence properties of the structures produced by PBW, photoluminescence (PL) measurements were conducted on two GaAs samples that were irradiated with the following patterns:

- Olympic rings structure seen in Figure 89
- Concentric rings structure seen in Figure 88

![Graph showing photoluminescence measurements](image)

**Figure 90** – Photoluminescence measurements of Olympic rings GaAs sample seen in Figure 89. Blue line indicates the PL intensity on virgin GaAs, purple line indicates the PL intensity on the GaAs etched to 12.8μm and the turquoise line indicates the PL intensity on the Olympic rings structure which was etched to a depth of 12.8μm (structure height 12.7μm).
PL measurements were performed on parts of the samples that had not been irradiated or etched (virgin GaAs) and PL measurements (seen in Figure 90 and Figure 91) for both samples were the same with an intensity of 694 a.u. (arbitrary units). The peaks occurred at a wavelength of 885 nm, the band gap of the GaAs sample. The next set of PL measurements were performed on part of the samples that had been etched. The Olympic rings sample (SEM image seen in Figure 89) had been etched to a depth of 12.8 μm and the concentric rings sample (SEM image seen in Figure 88) had been etched to a deeper depth of 17.8 μm. Looking at the PL measurements in the Olympic rings sample which was etched to a depth of 12.8 μm, the PL results (seen in Figure 90) show a considerable reduction in the PL intensity in these etched regions which was measured to be 66.75 a.u. compared to that from the virgin regions of the GaAs sample which had PL intensities of
694 a.u.. Once again the peak occurs at a wavelength of 885 nm which represents the band gap of the sample.

Now looking at the concentric rings sample which was etched to a deeper depth of 17.8 µm, the PL measurements (seen in Figure 91) indicates that a PL intensity of 53.71 a.u. was observed in this deeper etched region. This PL reading is 13.04 a.u. less than that of the sample that was etched to 12.8 µm. This implies that the deeper the sample is etched, the lower the PL intensity is in these regions.

PL measurements were then conducted on the irradiated regions (on the structures after etching) and it was observed that for the Olympic rings structure etched to 12.8 µm (structure height 12.7 µm) an intensity of 7.27 a.u. occurred (Figure 90). When performing the PL measurements on the concentric rings structure which was etched to a deeper depth of 17.8 µm (structure height 17.7µm) an intensity of 7.21 a.u. was observed (Figure 91). It is interesting to see that even though one structure was etched to a deeper depth the PL measurements are very similar. This would imply that irradiated regions with the same fluence have similar PL measurements even when etched to different depths.

5.11 OMDAQ

The first structure to be produced by PBW in GaAs was the logo for the University of Surrey seen in Figure 92. This structure was selected because of the practical design and the symbolic reference to the University. The OMDAQ software was used to scan this pattern.

The irradiation parameters are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Energy</td>
<td>2 MeV</td>
</tr>
<tr>
<td>Beam Current</td>
<td>10 nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>8 µm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>9 µm</td>
</tr>
<tr>
<td>Time</td>
<td>30 min</td>
</tr>
<tr>
<td>Fluence</td>
<td>$1.75 \times 10^{17}$ ions/cm²</td>
</tr>
</tbody>
</table>

Table 22 – Irradiation parameters for University of Surrey logo structure.
This structure was produced using a proton beam with an energy of 2 MeV and a fluence of \( \sim 1.75 \times 10^{17} \) ions/cm\(^2\). This high fluence was chosen because this structure was produced prior to the optimum fluence studies and it was determined that a high fluence was required for the initial experiments in order to increase the chance of successfully producing a structure in GaAs using PBW. The etch rate for this particular sample was 0.11\( \mu \)m/min. The critical depth for this structure was measured to be 0 \( \mu \)m. This supports the results from the previous sections of Section 5.5.1 and 5.5.4 which indicate that structures with a fluence of \( 1.25 \times 10^{17} \) ions/cm\(^2\) and above have zero critical depth. The structure height is \( \sim 19 \mu \)m.

It can be seen that the holes in the “S” shape are not etched to the same depth as rest of the structure. This effect is thought to occur due to the effects of the beam scanning and beam overlap due to the large beam spot size. The rest of the structure appears to have been revealed well.

![Figure 92](image)

**Figure 92** – *SEM image of the University of Surrey logo produced by protons with an energy of 2MeV in GaAs using the OMDAQ scanning software.*

From the studies investigating PBW in p-type GaAs in the previous sections it has been determined that the optimum fluence for producing structures in this material is \( 6.25 \times 10^{16} \) ions/cm\(^2\) and for consistent etching, spacings between structures that are 20\( \mu \)m in width should not be smaller than 12 \( \mu \)m. Using this information complex structures were attempted.
5.12 OMDAQ++

A new version of the OMDAQ scanning software was released in 2007 which had a scanning resolution of up to 1024 x 1024. This coincided with the release of the new Surrey University logo which resembled a stag. As this new logo is a complex image, it was initially thought that the Ionscan software would be the best system to scan this image. However, due to the turtle scan, scanning method of the Ionscan software, the beam blanking system is essential for the scan of this pattern. Unfortunately, the beam blanking system was not operational over this period. This opened up an opportunity to use the new OMDAQ++ scanning system as this system scans its patterns in a raster scan. This implies that the pattern will be scanned but at the spacings in the pattern, the beam will jump to the next position and as the beam is irradiating the sample during these ‘jumps’, sufficient damage may occur to the sample to produce structures at these points. For the first attempt it was decided that a scan of 1000 μm x 1000 μm would be beneficial to test if the complex details of the could be etched successfully. The irradiation parameters are as follows:

<table>
<thead>
<tr>
<th>Proton Energy</th>
<th>2 MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam Current</td>
<td>1 nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>3 μm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>4 μm</td>
</tr>
<tr>
<td>Fluence</td>
<td>$6.25 \times 10^{16}$ ions/cm²</td>
</tr>
</tbody>
</table>

Table 23 - Irradiation parameters for the new University of Surrey logo structure.

A 2 MeV proton beam was scanned to produce this structure seen in Figure 93, that has a fluence of $6.25 \times 10^{16}$ ions/cm². The etch rate for this sample was 0.11 μm/min which agrees with the previous results. Looking at the patterned stag, it can be seen that the pattern has etched well. There seems to be some reduced etching in the enclosed spacings of the antlers however the actual pattern is clearly distinguishable. It can be seen that there are vertical line structures from the antlers to the main body and also around the legs of the stag. This is the result of the beam jumping from one position to the next which has resulted in these residual structures.
Since the new OMDAQ++ was successful at producing a 1000 μm x 1000 μm pattern of the university logo, a smaller scan of 250 μm x 250 μm was performed. During this scan it was decided to see the effects of reducing the scanning speed so that the beam remains on each pixel for 10 counts of the PIXE detector. Theoretically, this would give the structure a more uniform fluence and as the beam would spend less time across the ‘jump’ positions. The scan parameters are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Energy</td>
<td>2 MeV</td>
</tr>
<tr>
<td>Beam Current</td>
<td>1 nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>3 μm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>4 μm</td>
</tr>
<tr>
<td>Fluence</td>
<td>$6.25 \times 10^{16}$ ions/cm$^2$</td>
</tr>
</tbody>
</table>

Table 24 - Irradiation parameters for the new University of Surrey logo structure 250 μm x 250 μm.

The structure can be seen in Figure 94. The SEM image shows that the structure has etched better than the previous scan and the definition around the antlers is very clear. Another observation is that there are no vertical lines visible where the beam jumps from one position to another. As the scanning speed has been reduced the number of scan cycles too have been reduced. Therefore the ‘jump’ regions have not had as much exposure as with the previous scan resulting in a lower fluence in these regions. As insufficient damage has occurred at these ‘jump’ positions to stop the carriers, no structures have been produced in these regions.
5.13 Annealed Samples

Previous studies in the literature described in Section 3.6.1.1.1 [81, 91-93], indicate that increased levels of sheet resistance can be achieved in GaAs samples through the use of annealing techniques after implantation. Based on this literature, preliminary annealing studies were conducted in this investigation to observe the effects of these annealing techniques to aid PBW in GaAs.

A bar structure with decreasing spacings was scanned using the Ionscan system onto three separate GaAs samples. The pattern was scanned using 2 MeV protons with a fluence of $6.25 \times 10^{16} \text{ ions/cm}^2$.

The irradiation parameters are as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton Energy</td>
<td>2 MeV</td>
</tr>
<tr>
<td>Beam Current</td>
<td>1.65 nA</td>
</tr>
<tr>
<td>Horizontal Beam Spot Size</td>
<td>5.4 µm</td>
</tr>
<tr>
<td>Vertical Beam Spot Size</td>
<td>5.4 µm</td>
</tr>
<tr>
<td>Time</td>
<td>243 min</td>
</tr>
<tr>
<td>Fluence</td>
<td>$6.25 \times 10^{16} \text{ ions/cm}^2$</td>
</tr>
</tbody>
</table>

Table 25 – Irradiation parameters for decreasing spaced bar structure.
The samples were then annealed, each at a different temperature, 300°C, 350°C and 400°C for 30 seconds. The results of these anneals on the structures are shown in Figure 95 and Table 26 where the samples have been etched to a depth of 0.5μm.

<table>
<thead>
<tr>
<th>Anneal Temperature (°C)</th>
<th>Etch Depth (μm)</th>
<th>Structure Height (μm)</th>
<th>Critical Depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 °C</td>
<td>0.5 μm</td>
<td>0.40 μm</td>
<td>0.10 μm</td>
</tr>
<tr>
<td>350 °C</td>
<td>0.5 μm</td>
<td>0.46 μm</td>
<td>0.04 μm</td>
</tr>
<tr>
<td>400 °C</td>
<td>0.5 μm</td>
<td>0.40μm</td>
<td>0.10 μm</td>
</tr>
</tbody>
</table>

Table 26 – Anneal temperatures and effects on decreasing spaced bar structure.

The results shown in Figure 95 and Table 26 indicate that after annealing at 300 °C and 400 °C the structure has a critical depth of 0.1μm. This is the same critical depth seen for non-annealed samples in the previous sections so it appears that annealing at these temperatures have no effect. Looking at the results for the 350 °C anneal, the critical depth can be seen to be reduced to 0.04 μm. This would suggest that the surface damage induced by the proton irradiation is increased when the sample is annealed at 350 °C. From the literature, S. Ahmed et al. [91, 92] have also found that annealing implanted GaAs at 350 °C leads to maximum sheet resistance values being achieved for room temperature and elevated temperature implants. This is a classical feature observed in
previous implant-isolation studies [81], where the annealing treatment causes extensive hydrogen diffusion and accumulation at particular interfaces. It is well established that hydrogen is attached to any deformation in a semiconductor lattice and actually may force its way to weakened bonds [93]. As with the previous results in the prior sections, a small dip (~1% of the etch depth) around the structure was also observed using the talystep.

Building on these annealing results, a further set of identical bar structures were scanned with the Ionscan [37], software onto a single GaAs sample using 2 MeV protons. Each bar structure was irradiated with a different fluence ranging from $1.56 \times 10^{16}$ ions/cm$^2$, $3.13 \times 10^{16}$ ions/cm$^2$, $4.69 \times 10^{16}$ ions/cm$^2$, $6.25 \times 10^{16}$ ions/cm$^2$ and $1.88 \times 10^{17}$ ions/cm$^2$. This sample was then annealed at 350 °C for 30 seconds after irradiation to observe the annealing effects on variable fluence structures. The sample was then etched to a depth of 6 μm.

(i) SEM Images

![SEM Images](image)

(ii) Talystep

![Talystep](image)

Figure 96 – (i) SEM images of bar structures with varying fluences after annealing at 350 °C. (a) $1.56 \times 10^{16}$ ions/cm$^2$, (b) $3.13 \times 10^{16}$ ions/cm$^2$, (c) $4.69 \times 10^{16}$ ions/cm$^2$, (d) $6.25 \times 10^{16}$ ions/cm$^2$ and (e) $1.88 \times 10^{17}$ ions/cm$^2$. (ii) Replication of Talystep profiles for the respective structures.
Chapter 5 — Results and Discussion

<table>
<thead>
<tr>
<th>Anneal Temperature (°C)</th>
<th>Fluence (ions/cm²)</th>
<th>Etch Depth (μm)</th>
<th>Structure Height (μm)</th>
<th>Critical Depth (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350 °C</td>
<td>1.56 x 10¹⁵</td>
<td>6 μm</td>
<td>5.86 μm</td>
<td>0.14 μm</td>
</tr>
<tr>
<td>350 °C</td>
<td>3.13 x 10¹⁶</td>
<td>6 μm</td>
<td>5.89 μm</td>
<td>0.11 μm</td>
</tr>
<tr>
<td>350 °C</td>
<td>4.69 x 10¹⁵</td>
<td>6 μm</td>
<td>5.92 μm</td>
<td>0.08 μm</td>
</tr>
<tr>
<td>350 °C</td>
<td>6.25 x 10¹⁶</td>
<td>6 μm</td>
<td>5.96 μm</td>
<td>0.04 μm</td>
</tr>
<tr>
<td>350 °C</td>
<td>1.88 x 10¹⁷</td>
<td>6 μm</td>
<td>6.000 μm</td>
<td>0.00 μm</td>
</tr>
</tbody>
</table>

Table 27 - Anneal temperatures and effects on variable fluence bar structures.

The results shown in Figure 96 and Table 27 indicate, as expected, that as the fluence is increased, the critical depth decreases. When these results are compared to prior results on the fluence studies of the non-annealed samples in Figure 67 in Section 5.5.1, some interesting findings are observed. The comparison is shown in Figure 97 and the results indicate that the 350 °C annealed samples have a smaller critical depth for the respective fluences. A representation of the talystep profiles for the annealed structures can be seen in Figure 96 (ii) where the critical depth is shown. This implies that the structures form closer to the surface of the material when the sample is annealed at 350 °C as the hydrogen is attached to any deformation in a semiconductor lattice and actually may force its way to weakened bonds [93]. This increases the lattice damage near the surface, removing more carriers in this region, and thereby the structure forms closer to the surface of the sample.

Another interesting observation of the 350 °C annealed samples is that the structure formed with the highest fluence of 1.88 x 10¹⁷ ions/cm², does not exhibit the semicircular grooves at the centre of the structure, as seen for the high fluence bar structures with fluences of 9.38 x 10¹⁶ ions/cm² and 1.25 x 10¹⁷ ions/cm² for the non-annealed samples seen in Figure 67 in Section 5.5.1. A possible explanation for this is that when the damage concentration is high enough for fluences beyond the optimal fluence, the resistivity decreases due to the onset of hopping conduction. The samples annealed at
350 °C shows a decrease in the hopping conductivity by virtue of the damage annealing which increases the resistivity.

**Figure 97** - Graph showing a comparison of critical depth (µm) versus fluence (ions/cm²) for structures of different fluences produced by PBW which have been annealed at 350 °C and non-annealed.
Chapter 6

6 Conclusions and Further Work

6.1 Conclusions

The main objective of this work was to perform an investigation into the feasibility of proton beam writing (PBW) in p-type GaAs and to present simulations which help explain this process. This chapter presents some of the successes of this work in relation to the objectives. Since this was the first study of PBW in GaAs, at the beginning of this investigation, there was no literature concerning PBW in GaAs. After successfully performing PBW in GaAs and presenting and publishing the results, several research groups such as the University of Leipzig, have reported that they are investigating PBW in GaAs and this is an indication of the growing interest in this research area and relevance of this project. It has been well established that bombardment of a doped semiconductor by electrons or ions leads to a reduction in free carriers. With this in mind an MeV proton beam was scanned in selected patterns across the surface of the p-type GaAs samples and due to the nuclear stopping as the protons interact with the material, the removal of holes occur creating highly resistive regions in the scanned irradiated areas. As these MeV protons induce changes in the GaAs, this phenomenon can be exploited in a lithographic way to create structures in the material. To reveal these structures two electrochemical etch setups were investigated in order to find the most suitable technique. The effects of etch current, etch area and current density were investigated in detail. It was observed for both setups that, as the etch current is increased for a unit area, the etch rate increases. However the surface roughness of the etched region also increases. It was also observed that etch setup 2 had a better etch uniformity than that of setup 1 so setup 2 was chosen to etch the irradiated samples. It is to be noted that both etch set ups reveal the structures produced by PBW.

Fluence studies were conducted to determine the optimum fluence for the structures. From these studies it was found that a “critical depth” (depth that needs to be etched until
structure is revealed) was observed and that structures with fluences as small as $\sim 3.13 \times 10^{15}$ ions/cm$^2$ ($\sim 5$ pC/$\mu$m$^2$), produced structures. However when using these lower fluences, the structures tended to exhibit rounded corners instead of straight and the critical depth was much larger than that for structures produced using larger fluences, which resulted in the formation of buried structures.

Structures produced using fluences of $1.25 \times 10^{17}$ ions/cm$^2$ and above had a critical depth of zero but suffered from grooves being formed at the structure surface thought to be due to hopping conduction. Therefore the optimum fluence chosen was $6.25 \times 10^{16}$ ions/cm$^2$ which consistently produced the best structure definition even though it had a critical depth of 0.1 µm.

Preliminary studies in post implantation annealing indicated that annealing the irradiated sample at 350 °C for 30 seconds, after irradiation, increases the resistivity of the irradiated regions, thereby forming structures closer to the surface of the material over a range of fluences when compared to non-annealed samples. Structures formed at high fluences of $1.88 \times 10^{17}$ ions/cm$^2$ using this post annealing technique, did not suffer from the grooves at the structure surface. This is thought to be due to the lack of hopping conduction due to the increased resistivity. However further work needs to be performed with this process.

A large part of this work involved simulating the electrochemical etch using the Atlas© semiconductor device package from SILVACO. These simulations were then compared to the experimental results to help understand the mechanisms involved. It was found that the simulations fit well to the experimental data for structures with fixed spacings between them and hollow circles. However as the spacings between the structures reduce the simulations indicate an increase in current density in these spacing which would result in an increase in etch rate. This was not the case, as the experimental results showed a constant etch rate for the structure. A possible explanation for this is that the combination of the increased etch rate and the effects of chemical crowding in these small spacings result in the same etch depth for all the structures. It was observed that in the spacings of 12 µm or less, the etch rate in the individual spacings is not constant. At the ends of the structure the etch rate is constant but towards the structure centre the etch rate reduces considerably. This effect is thought to be due to chemical crowding.
Chapter 6 — Conclusions and Further Work

The simulations also indicated an increase in hole current density at the edges of the structures. This would imply a faster etch rate at these areas. This increase in etch rate was observed through small dips around the structures from the experimental results. It was found that for each etch, the dip around the structure etches to 1% of the total etch depth and at the ends of the structures, this dip, is more pronounced where the corners are visible. This increase in etch rate around the structure edge is due to the field gradients being steeper where there is a geometrical change of shape and at sharp edges.

These results are novel and together with the simulations provide a way forward for the development of PBW in GaAs for future technologies and its applications in lithography.

6.2 Further Work

This work has presented several significant findings related to proton beam writing (PBW) in GaAs. However there are many aspects of the research that should still be investigated. The aim of this chapter is to highlight some of the possible research projects that would be beneficial for furthering the study of PBW in GaAs.

6.2.1 Multi-Level and Buried Structures

It has been shown in Section 5.5 that by reducing the fluence, the critical depth increases and buried structures are formed as well as the corners of the structure become rounded. It would be interesting to see further development of buried structures produced by reducing the fluence of the structure and the potential this technique has for the formation of tapered structures. These same structures could be produced by varying the energy of the beam as well and a comparison could be made.
6.2.2 Beam Blanking

The results in Section 5.5 indicate the effects that if no beam blanking is available, structures form as the beam jumps from one part of the pattern to another linking all the structures. To avoid this effect it is highly recommended that an operational beam blanking system is implemented and used. This would enable more complex structures to be produced without the effects of this joining structure.

6.2.3 Nano Beam

This study has used a micro-beam line which can focus the beam spot size to micron dimension. This limits the size of the structures to micron sizes. If a nano-beam was used which has beam spot sizes of nanometers, then smaller structures could be investigated. Currently, a nanobeam is under development at the Ion Beam Centre at the University of Surrey and when constructed, this beam line would be ideal for producing and investigating nano structures.

6.2.4 Structure Spacings

The effects of the proximity of the structures have been seen in Section 5.5 which indicate that a reduction in the etch rate in the spacings of 12 μm or smaller between the structures occur. Further investigation to determine the effects of varying the structure size and spacings would be beneficial to determine the parameters required to achieve the smallest spacings between structures and also the smallest feature sizes.

6.2.5 Annealing

It has been shown in this work as well as previous work related to ion implantation in GaAs, that annealing samples after irradiation to 350 °C for 30 seconds causes a large increase in the resistivity of the irradiated regions. If the samples are annealed at higher temperatures the resistivity of the samples reduce due to the lattice repairing. It would be interesting to see the effect of annealing and its result on the structures produced over a range of annealing temperatures and times.
From this work, it is apparent that further investigation is required before proton beam writing (PBW) can be used to produce devices in p-type GaAs. However, these results have proved that PBW in p-type GaAs is possible and has shown the effects of fluence, energy, annealing and spacings on the formation of the structures. This work has also contributed to a better understanding of the processes involved in this technique.
References


19. M. Desmulliez, LIGA, 2008, Heriot-Watt University presentation, 


22. C.R. Friedrich, P.J. Coane, and M.J. Vasile, Micromilling development and applications for microfabrication. Microelectronic Engineering


58. A.L. Bogdanov, S.S.Peredkov.


Appendix A

Example Code for SILVACO Atlas Simulations:

go devedit
#-V simflags="-V 2.6.17.R"


work.area xl=-2 yl=-2 x2=305 y2=505
# devedit 2.6.17.R (Sat Jul 16 03:14:47 PDT 2005)
# libSflm 7.2.4 (Sat Jul 16 03:14:18 PDT 2005)
# libSDB 1.4.28 (Fri Jul 15 19:51:44 PDT 2005)
# libSvcline 1.8.27 (Tue Jul 5 15:52:43 PDT 2005)
# libDW_Version 2.4.0 (Mon May 16 20:06:10 PDT 2005)
region reg=1 mat=GaAs color=0x7f00 pattern=0x9 "polygon="0,0 300,0 300,500 0,500"

# constr.mesh region=1 default

region reg=2 name=cathode mat=Aluminum elec.id=1 work.func=0 color=0xffc8c8 pattern=0x7 "polygon="0,-0.1 300,-0.1 300,0 0,0"

# constr.mesh region=2 default max.height=0.05

region reg=3 name=anode mat=Aluminum elec.id=2 work.func=0 color=0xffc8c8 pattern=0x7 "polygon="0,500 300,500 300,500.1 0,500.1"

# constr.mesh region=3 default max.height=0.05

region reg=4 mat=GaAs color=0x7f00 pattern=0x9 "polygon="14.6,0 29.2,0 29.2,32 14.6,32"

# impurity id=1 region.id=4 imp=Donors "peak.value=1e+23 ref.value=1000000000000 comb.func=Multiply"

# constr.mesh region=4 default

region reg=5 mat=GaAs color=0x7f00 pattern=0x9 "polygon="73.1,0 87.7,0 87.7,32 73.1,32"

# impurity id=1 region.id=5 imp=Donors "peak.value=1e+23 ref.value=1000000000000 comb.func=Multiply"

# constr.mesh region=5 default

region reg=6 mat=GaAs color=0x7f00 pattern=0x9 \

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Appendix A

polygon="131.6,0 146.2,0 146.2,32 131.6,32"
#
impurity id=1 region.id=6 imp=Donors 
   peak.value=1e+23 ref.value=1000000000000 comb.func=Multiply
#
constr.mesh region=6 default

region reg=7 mat=GaAs color=0x7f00 pattern=0x9 
   polygon="190.1,0 204.7,0 204.7,32 190.1,32"
#
impurity id=1 region.id=7 imp=Donors 
   peak.value=1e+23 ref.value=1000000000000 comb.func=Multiply
#
constr.mesh region=7 default

region reg=8 mat=GaAs color=0x7f00 pattern=0x9 
   polygon="248.6,0 263.2,0 263.2,32 248.6,32"
#
impurity id=1 region.id=8 imp=Donors 
   peak.value=1e+23 ref.value=1000000000000 comb.func=Multiply
#
constr.mesh region=8 default

# Set Meshing Parameters
#
base.mesh height=10 width=10
#
bound.cond !apply max.slope=28 max.ratio=300 rnd.unit=0.001
line.straightening=1 align.points when=manual
#
imp.refine imp="Total Doping" scale=log transition=1e+10
imp.refine min.spacing=0.02
#
constr.mesh max.angle=90 max.ratio=300 max.height=10 
   max.width=10 min.height=0.0001 min.width=0.0001
#
constr.mesh type=Semiconductor default
#
constr.mesh type=Insulator default
#
constr.mesh type=Metal default
#
constr.mesh type=Other default
#
constr.mesh region=1 default
#
constr.mesh region=2 default max.height=0.05
#
constr.mesh region=3 default max.height=0.05
#
constr.mesh region=4 default
#
constr.mesh region=5 default
#
constr.mesh region=6 default
#
constr.mesh region=7 default
#
constr.mesh region=8 default
Mesh Mode=MeshBuild
refine mode=both x1=-0.8 y1=-0.1 x2=303.9 y2=47.2
base.mesh height=10 width=10
bound.cond !apply max.slope=28 max.ratio=300 rnd.unit=0.001
line.straightening=1 align.Points when=manual

structure outfile=prash99.str

go atlas

mesh inf=prash99.str

models conshr conmob fldmob b.electrons=2 b.holes=1 evsatmod=0
hsatmod=0 \ tfeldmb2 acc.sf=0.87 inv.sf=0.75 fnord bbt.std fermi bgn print \ temperature=300 trap.tunnel hei e.bending carrier=1 electron
impact selber an1=703000 an2=703000 bn1=1.231e+06 bn2=1.231e+06 \ ap1=671000 ap2=1.582e+06 bp1=1.693e+06 bp2=2.036e+06 betan=1 \ egran=400000
impact selber an1=703000 an2=703000 bn1=1.231e+06 bn2=1.231e+06 \ ap1=671000 ap2=1.582e+06 bp1=1.693e+06 bp2=2.036e+06 betan=1 \ egran=400000

method newton itlimit=25 trap atrap=0.5 maxtrap=10 autonr
ncriterion=0.1 \ tol.time=0.005 dt.min=1e-25
output e.field j.electron j.hole j.conduc j.total e.velocity
h.velocity \ ex.field ey.field flowlines e.mobility h.mobility qss e.temp
h.temp \ charge recomb val.band con.band qfn qfp j.disp photogen impact \ tot.doping band.param

solve init
save outf=prash1.dat

log outf=prash.log

solve name=anode vanode=0 vfinal=1500 vstep=50 master onefileonly
outf=prash1.dat
quit