Characterisation of Single Ion Tracks for use in Ion Beam Lithography

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Abstract

To investigate the ultimate resolution in ion beam lithography (IBL) the resist material poly(methyl methacrylate) PMMA has been modified by single ion impacts. The latent damage tracks have been etched prior to imaging and characterisation. The interest in IBL comes from a unique advantage over more traditional electron beam or optical lithography. An ion with energy of the order of 1 MeV per nucleon evenly deposits its energy over a long range in a straight latent damage path. This gives IBL the ability to create high aspect ratio structures with a resolution in the order of 10 nm.

Precise ion counting into a spin coated PMMA film on top of an active substrate enabled control over the exact fluence delivered to the PMMA from homogenously irradiated areas down to separated single ion tracks. Using the homogenous areas it was possible to macroscopically measure the sensitivity of the PMMA as a function of the developing parameters.

Separated single ion tracks were created in the PMMA using 8 MeV F, 71 MeV Cu and 88 MeV I ions. These ion tracks were etched to create voids in the PMMA film. For characterisation the tracks were imaged primarily with atomic force microscopy (AFM) and also with scanning electron microscopy (SEM).

The series of studies presented here show that the sensitivity of the resist-developer combination can be tailored to allow the etching of specific single ion tracks. With the ability to etch only the damage track, and not the bulk material, one may experimentally characterise the damage track of any chosen ion. This offers the scientific community a useful tool in the study and fabrication of etched ion tracks.

Finally work has been conducted to allow the precise locating of an ion beam using a nanoscale mask and piezoelectrically driven scanning stage. This method of beam locating has been trailed in conjunction with single ion detection in an effort to test the practical limits of ion beam lithography in the single ion realm.
Declaration

I hereby declare that this thesis a presentation of my original research work. Wherever contributions of others are involved every effort has been made to indicate this clearly and provide acknowledgement. This work has not been submitted previously, in whole or in part, to qualify for any other academic award. The content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program.

Andrew Alves
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Chapter 1  Introduction

1.1  Project Overview

1.1.1  Nanotechnology

Nanotechnology is the science of analysis, fabrication and ultimately the use of structures with dimensions less than 1000 nm and more than 1 nm. With the desire to learn more about the structures inhabiting the nano-realm, the scientific community has begun by analysing structures that already exist and can be found in the natural environment. An example is the biological structures where nanoscale periodicity leads to optical effects and iridescent colours [1-2]. These structures which ‘mold the flow of light’ [3] are discussed in sub-section 1.3.2. Although nature has mastered the fabrication of structures with nanoscale periodicity in three dimensions it is something the scientific community is only now beginning to investigate and exploit.

1.1.2  Ion Beam Lithography

Ion beam lithography (IBL) in the energy regime above 1 MeV per nucleon has established itself as a technique capable of producing 3D nanoscale structures through its ability to create high aspect ratio voids in a resist material. A recent shift towards applying an ion beam to modification as well as the analysis of materials has seen IBL beamlines present in accelerator laboratories. An early attempt was on the Oxford microprobe in 1993 [4], and subsequently a dedicated beamline has been developed in Singapore with emphasis on the ability to focus the beamspot to between 100 to 10 nm for use in direct write lithography [5]. Other attempts at IBL have also been made [6-9]. This interest in IBL is driven by the many possible applications for precise 3D nanoscale structures—comprehensively reviewed in the “National nanotechnology initiative” review prepared for the US government [10] and will be discussed in more detail in section 1.3.

1.1.3  Poly methyl methacrylate (PMMA)

To study IBL a resist material is first selected. A suitable choice is the common positive tone resist poly(methyl methacrylate) (PMMA) which is extensively used in electron beam lithography (EBL)—a well established technique of the microelectronic industry [11-12]. The procedures for spin coating, baking and developing a PMMA film on a substrate are well known and PMMA has already been widely used by the IBL community [4-9, 13].
1.1.4 Scope

To extend the field of IBL this thesis explores the fundamental resolution limit of a single ion impact in PMMA resist. The RMIT University, Department of Applied Physics, together with the Microanalytical Research Centre (MARC) at the University of Melbourne has the necessary expertise in ion beam technology to conduct such a foundation study into IBL. In collaboration with associates at the Australian Nuclear Science and Technology Organisation (ANSTO) the necessary ion beam infrastructure is available. This exploration will also serve as a precursor to the design of an IBL facility for the 5 MV Pelletron at the University of Melbourne.

In IBL the ultimate resolution structure is created by applying the fundamental resolution limit of a single ion impact. There must be precise control over the detection and placement of individual ions in the resist material. This concept has been crystallised into four research questions (expanded in the next section) that aim to quantify the resolution and aspect ratio limit of IBL using PMMA as a resist.

1) Can a single ion be detected after passage through a PMMA film?
2) Does a single ion produce a latent damage track in PMMA that can be etched?
3) Can the etched track be imaged to determine its radius?
4) To what accuracy can a single ion strike be located?

1.2 Research Questions

1.2.1 Can a single ion be detected after passage through a PMMA film?

Many methods have been used to normalise the number of ions traversing the resist in IBL. A removable Faraday cup [7] measures beam current before and after the ion beam exposure, but does not take into account variation in the beam current during exposure and does not resolve individual ions. A charge integrator connected to the target can account for variations in the beam current during exposure, however the minimum detection limit is well above single ion resolution and charging in the resist material can lead to inaccurate measurement. Other techniques that rely on secondary particles or photons being detected after interaction of the incident beam have been successful in normalising during exposure [14], however, they do not usually provide single ion detection capability. They also require the installation of charged particle or photon detectors close to the exposure site to be calibrated upon each different experimental configuration.
In this thesis ion beam normalisation was achieved by use of an ‘active substrate’. The PMMA film was spin coated onto a Si PIN photodiode. During the exposure the photodiode acted as a charged particle detector sensitive to individual ions. This enabled precise counting of the number of ions striking the PMMA in the area defined by the beamspot.

1.2.2 Does a single ion produce a latent damage track in PMMA that can be etched?

Answering this question through experiments confirms that a single ion track can be used as a structuring tool. At present, as shown in Figure 1.1, an IBL exposure has a resolution defined by the size of a focused beamspot of overlapping ion impacts. IBL is currently being performed by predominately using the lightest ion, H, which is easily accelerated to the 1 MeV.u⁻¹ energy regime using a terminal voltage of 1 MV. A resolution of less than 100 nm using a focused and scanned microprobe of 2 MeV protons in PMMA has been demonstrated [13]. Ultimately with improvements to the technology used to define the beam, a fundamental limiting factor will be reached—the latent damage radius of a single ion track—and further confinement of the beam will be pointless.

This thesis aims to find whether individual H and He ions produce etchable tracks in PMMA or if heavier ions with a higher linear energy transfer (LET) are required. PMMA films were exposed to a focused beam of high energy ions over a range of LET values. As illustrated in Figure 1.2 (a-c) single ion detection was used to precisely count the number of ions randomly placed within the area of a single 5 × 5 µm² focused beam spot. To prevent overlapping and allow the study of single ion tracks the beamspot fluence was less than 10 ions.µm⁻².
1.2.3 Can the etched track be imaged to determine its radius?

The size of the structuring tool is revealed by determining the radius of the void etched along the track of a single ion.

Atomic force microscopy (AFM) is a technique used previously for imaging single ion tracks in PMMA and other materials [15-17]. AFM imaging was performed to confirm that etching of single ion tracks had occurred. A high aspect ratio ‘nanowhisker’ type tip was used and quantitative analysis of the AFM images was performed to find the radii of etched tracks. The results of the track etching and imaging revealed radii ranging from 15 to 30 nm (Figure 1.2 (d)).
To what accuracy can a single ion strike be located?

To fully realise the lithographic process each ion impact must be located in the resist and the location accuracy reveals the precision of the structuring tool.

In this thesis development of an alternate technique to using a focused beam was initiated. The technique introduces a nanoscale aperture to define the size of the beamspot. The sample was mounted on a piezoelectrically driven scanning stage to position the beamspot on target (Figure 1.3). With accurate placement of the ion impacts and irradiation at different tilt angles a three dimensional nano-structuring technique can be developed. This thesis investigates whether such a system can be developed with a finer resolution than the more traditional ion beam focusing method. The motivation for using this method comes from recent developments in the construction of nanoscale apertures used as movable masks, referred to at this point as nano-stencils, for metallic evaporation [18] and in implantation of single keV ions [19-20].
Table 1.1: List of fields where IBL shows potential.

<table>
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<tr>
<th>General Reference</th>
<th>Reference where IBL has been applied</th>
</tr>
</thead>
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<td>[26]</td>
</tr>
<tr>
<td>Stamp making for nanoimprint lithography</td>
<td>[22] [26] [27]</td>
</tr>
<tr>
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<td>[23] [28]</td>
</tr>
<tr>
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<td>[24]</td>
</tr>
<tr>
<td>Monolithic microwave integrated circuits</td>
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</tr>
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1.3 Key Applications

1.3.1 Introduction to applications

Understanding the physics of materials and precise material modification are primary research goals of the two departments (RMIT University and the University of Melbourne) in which this PhD thesis was conducted. While this thesis is sensitive to the many applications its aim is to concentrate on the underpinning physics and technology of nanoscale materials modification. We do not aim to construct operational devices at this stage, nor are we investigating the methods with specific applications in mind. However, we do have in mind general applications as discussed below.

The promising applications of IBL do not wait for the new technology to mature and therefore, in the meantime, structures are fabricated by other means. A review of other techniques used to fabricate nanoscale structures is given in section 2.2. The future will only see IBL applied where it provides definite advantage over more established techniques. While at present IBL has been applied in many different cases (mainly as demonstrations) it is not always the best technique.

The potential for creating a high aspect ratio structure using IBL has been recognised and therefore technological development is underway in a research capacity. A standard text in the lithography field by S.M. Sze [21] published in 1985, points out the significant advantages of the technique. This thesis serves to determine the fundamental limits of the technology as a critical step to determine whether it will be, and, where it will be successfully applied.

As a direct write technique IBL must be viewed as a serial process not capable of high throughput. At present the high resolution/direct write technique of EBL is central in fulfilling
the roles of rapid prototyping, mask making for optical, UV and X-ray lithography and fabrication of stamps for nanoimprint lithography. It is comprehensible that IBL will fulfil the similar rolls of prototyping, mask and stamp making, but in cases where a high aspect ratio structure is required.

Table 1.1 presents a list of fields where IBL shows potential and in some cases has already been applied. For further information on each of these applications the reader is referred to the generic references and to the references for specific IBL applications. The area of particular interest in which the results of this thesis may have a direct impact is nano-photonics, particularly photonic band gap materials. This is expanded in the next sub-section, 1.3.2.

1.3.2 Photonic band gap materials

Classical photonic structures, such as waveguides, with a minimum feature size of 100 nm have been demonstrated using IBL [29]. With theoretical advances in photonics new structures have become possible. These structures are known as photonic band gap materials, or photonic crystals. A photonic crystal is a material in which periodic changes in refractive index lead to a photonic band gap (1D, 2D and 3D examples are shown in Figure 1.4) preventing light of certain wavelengths from propagating inside the medium. This phenomenon is analogous to a band gap for the propagation of electrons in a semiconductor material. Many of the properties of an electron in a semiconductor can apply to a photon in a photonic crystal.

The positioning of voids in a material with dimensions less than the desired band gap wavelength leads to the ability to fabricate an operational photonic crystal and is an ideal application for the high aspect ratio structuring of IBL.

Photonic crystals promise a revolution in computing and communication with uses such as optical waveguides that can perform a right angle turn, optical switches, filters or couplers to be made utilising the photonic band gap. These structures are presently being developed theoretically, an example is the three dimensional structure Yablonovite, named after its inventor, E. Yablonovitch [30] (see Figure 1.4). The book by Joannopoulos et. al. gives a good overview and theoretical analysis of photonic crystals [3]. These materials draw their inspiration from photonic structures in biology that produce iridescent colours and have already been studied extensively [1-2]. Many applications and previous work were reviewed in the August 2001 MRS Bulletin [31].
Figure 1.4: Examples of the geometry used to produce photonic structures (extracted from Joannopoulos et. al. [3]). (a) A 1D structure is periodic in one direction and therefore the band gap only exists for a plane wave travelling in the direction of periodicity. (b) A 2D structure has periodicity in two dimensions. (c) A 3D structure, Yablonovite, named after its discoverer E. Yablonovitch [30] is constructed by ‘drilling’ an array of holes along three separate axes.
<table>
<thead>
<tr>
<th>Air</th>
<th>PMMA</th>
<th>lattice constant</th>
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<td>(d_1) (nm)</td>
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Table 1.2: Calculated lattice constant and band gap wavelength for a 1D photonic band gap material, using air and PMMA. The calculation was made using the equations in Wehrspohn et. al. [32].

- **Photonic crystal size and band gap wavelength**

The wavelength of the photonic band gap is dependent on the size of the periodic structure. A calculation for a simple 1D photonic crystal (shown in Figure 1.4 (a)) can be made using the equations given in the reference by Wehrspohn et. al. [32]:

\[
a = d_1(n_1) + d_2(n_2)
\]

\[
\lambda = 2n_1d_1 + 2n_2d_2
\]

Where \(a\) is the lattice constant, \(d_i\) is the thickness of the layer with refractive index \(n_i\), and \(\lambda\) is the centre wavelength of the photonic band gap. Using the resist material PMMA (refractive index ~1.5) and air (~1) typical band gap wavelengths can be calculated (the results are shown in Table 1.2). It follows that if a similar size scale was used in 2D and 3D photonic crystals the result would be a similar band gap wavelength to the 1D case.

Ion beam lithography using the common resist, PMMA, can realistically be used to fabricate structures similar to the 2D and 3D photonic crystal examples shown in Figure 1.4. With an IBL resolution in the range from 10-1000 nm the photonic crystals fabricated would operate at near infrared and optical wavelengths, such as the 1550 nm used in telecommunications applications.
1.4 Thesis Overview

1.4.1 Summary

This thesis is based on experimental work in the fields of IBL and ion tracks. The distribution of chapters is representative of this. In the literature review an explanation of other experimental lithographic methods is presented along with experimental results and theories of single ion tracks. This is followed by generic, specific then applied experimental chapters. Finally conclusions are drawn from the experimental work that relate to the applications and general theory raised in chapters 1 and 2:

1.4.2 Chapter Overview

Chapter 2 (Literature Review and Physical Model) begins with a review of nanoscale structuring techniques currently being used followed by an explanation of IBL and the energy regime of ions used in IBL. The physical models used to describe the passage of single ions in matter are reviewed over an array of ion track studies with varying target materials and LETs. Finally a discussion on the properties of PMMA is presented. The outcome of this chapter is a qualitative determination of the radial latent damage profile for single ion tracks with LETs ranging over five orders of magnitude, from 1 eV.nm\(^{-1}\) to 5\(\times\)10\(^5\) eV.nm\(^{-1}\).

Chapter 3 (Experimental—Equipment and Procedures) describes the generic experimental infrastructure for conducting IBL experiments. It covers the procedures used for sample preparation, registration markers, ion beam exposures, developing and imaging. Several key technical achievements have been demonstrated. The detection of individual ions through a PMMA film was achieved by coating a PIN photodiode which was sensitive to single ion impacts. The spatial location of individual ions was defined using a beamspot located relative to a registration grid—this grid was as a necessary aid in nanoscale imaging of etched single ion tracks. Imaging of etched single ion tracks was demonstrated with AFM which was the primary tool for quantitative analysis.

Chapter 4 (Experimental—Studies) details four specific ion track formation studies that were conducted with the aim of finding holes etched along latent damage tracks. (1) In the first study the material CR-39 was investigated for its well known ability to produce visible etched single ion tracks. (2) Following this experiments were conducted using PMMA. A macroscopic experimental method was established to measure the sensitivity of PMMA as a function of the developing conditions. (3) The etch rate and surface roughening of PMMA was measured as a function of developing conditions. (4) Single ion tracks were etched to create voids using different ion energies and masses under varied development conditions.
Etching only latent damage and not bulk material was a key achievement. The width of etched single ion tracks was measured with AFM, offering the ability to attach experimental data to the study of single ion track formation in PMMA.

Chapter 5 (Development of a nano-positioning system) addresses the problem of ion placement in IBL. To achieve lithography at single ion resolution one must be able to define the ion’s location with accuracy smaller than the diameter of a single ion strike. The technical issues associated with positioning ion strikes using a focused beam in conjunction with a nano-aperture and piezoelectrically driven scanning stage are examined. This method is compared against conventional beam focusing and electromagnetic scanning.

Chapter 6 (Project and Research Conclusions) contains the conclusions drawn from the experimental work that relate to the applications and general theory raised in chapters 1 and 2.

The peer reviewed publications resulting from this work are listed here and printed in entirety at the end of the thesis.


1.5 Bibliography


Chapter 2  Literature Review and Physical Model

2.1  Introduction to the Chapter

2.1.1  Project Overview

The goal of this project is to develop the field of ion beam lithography (IBL) by experimentally demonstrating the smallest feature size attainable. Single latent damage tracks have been etched in the resist material poly methyl methacrylate (PMMA). Atomic force microscopy (AFM) has been used to image individual holes and quantify the radii under different conditions (results are shown in section 4.5).

2.1.2  Chapter Overview

To put the experimental results of this thesis in context this chapter investigates the concept—the smallest structural element—using a review of the literature. Experimental results, simulations and analytical formulae are reviewed for determining the radial energy deposition of a single ion. From this review the latent radial damage profile and eventual track radius has been estimated. Section 2.2 gives a literature review of alternate structuring techniques for comparison to IBL. Section 2.3 gives a description of the IBL process and considers its resolution limit. To explore the IBL process in greater detail Section 2.4 presents the physical models used to describe the passage of a single ion, first in a generic medium and then more specifically in PMMA. Section 2.5 is a summary of important previous knowledge from published work that can be applied in this study.

2.2  Other structuring techniques for comparison to IBL

2.2.1  Overview of structuring in nanotechnology

In determining the fundamental limit for a new technology one must also understand the limits of other technologies. This section presents a review of alternate nanoscale structuring techniques so that it is clear where IBL might be applied with greatest success. In the fabrication of structures with nanoscale dimensions one may consider two groupings of methods; stochastic and lithographic fabrication.
• **Stochastic**

Structures formed by self assembly have been demonstrated. Fabrication is based on chemical potentials forming structures considerably larger than atomic scale. Structures such as carbon nanotubes have been produced and offer many applications [1]. These fabrication methods should be mentioned in a discussion on nanoscale fabrication. However, building of such nanoscale structures or groups of structures is a stochastic process without precise control over each element. This is characterised by fast, large volume fabrication, and the application of these structures are also governed by stochastic processes. The distinction between stochastic and non stochastic fabrication is required because some applications (e.g. quantum computing or wave guiding photonic crystals) require exactness and stochastic fabrication does not provide enough control.

• **Lithographic fabrication (not stochastic)**

In the electronic age lithography has been used as a construction tool used for the fabrication of microscale structures—mostly structures built for the microelectronics industry—where a resist material is altered as a result of selective exposure to some radiation (e.g. photons in photolithography). However, in general the word ‘lithography’ in the technological domain has come to represent any fabrication method that gives control over the size, shape and position of each structural element. Over time lithography has had to evolve to improve its precision to below the 1000 nm barrier and well established lithographic techniques do not allow the structuring of features to a depth very much greater than their width. This has resulted in a split of lithographic methods, based on different forms of radiation and different resist materials, where payoffs between speed, cost, resolution and aspect ratio separate the methods. Sub-section 2.2.2 gives a description of lithographic techniques that are being used to produce nanoscale structures but do not have the capacity to produce high aspect ratio structures.

• **High aspect ratio**

As the scientific community contemplates the potential uses of different nanoscale structures it begins to theorise structures that have no current fabrication method. The main lag is in development of a lithographic technique with the ability to fabricate structures with dimensions less than 1000 nm and also with a high aspect ratio. An overview of the applications of such structures is given in section 1.3 in chapter 1. The key to a nanoscale/high aspect ratio lithographic process is radiation that can deeply penetrate the resist material without scattering. The foremost two candidates are *energetic ions* and *X-rays*, though some other approaches exist and are mentioned here. Sub-section 2.2.3 gives an overview of the techniques currently being investigated to produce structures with a high aspect ratio and nanoscale dimensions.
2.2.2 Nanoscale Lithographic methods

In a generic lithographic process a resist layer is spin coated onto a flat substrate and exposed to a radiation source either through a patterned mask or by direct write, resulting in a chemical modification of the resist in the exposed region. For positive resist processing the modified region of resist becomes more soluble and is etched during developing. For negative resist processing the modified region of resist becomes less soluble and remains intact during developing while the un-exposed region is removed. The result is a patterned resist layer which can be used in a variety of ways, for example, as a mask for electroplating, etching a surface layer, etching the substrate, for depositing a metal or dielectric onto the substrate, implanting into the substrate or simply as a structure itself.

- **Optical/UV lithography**

The most predominant lithographic method in terms of world-wide use is optical lithography. Since its inception optical lithography has been the standard fabrication method used in microelectronics manufacturing. A photo-mask is used to define the regions of optical exposure. A large area (for example, a 12 inch wafer) can be patterned in one exposure resulting in a large throughput. The ultimate resolution, which is limited by the diffraction of light, for optical lithography has already been foreseen. However, the desire to miniaturise transistors and fit more onto one chip has driven resolution into the nano-realm. This has been achieved by a considerable amount of technological development, most importantly the use of shorter wavelengths into the Ultra-Violet (UV).

At present structures with dimension smaller than 100 nm are being fabricated using photons with wavelength of 193 nm [2] (shown in Figure 2.1 (a)). Development of extreme UV lithography (EUV) with a wavelength less than 100 nm will push the resolution finer still. But with shorter wavelengths the absorption of photons in the lens, mask and resist materials increases. Figure 2.1 (b) shows transmission as a function of wavelength for the common UV optics material, CaF$_2$. This necessitates significant redesign of all aspects of the process and, therefore, other lithographic techniques become more competitive in comparison to EUV lithography.

- **Electron Beam Lithography (EBL)**

As EBL is a direct write technique it does not compete with optical/UV lithography in terms of throughput. However, structures with dimensions smaller than 10 nm have been demonstrated with EBL in 40 nm thick PMMA using an 80 keV electron beam [3] (Figure 2.1 (c)). EBL is an established lithographic technique, commercially developed for rapid prototyping, making masks for photolithography and stamps for imprint lithography. It makes use of a compact and easy to operate piece of equipment—the electron microscope.
Figure 2.1: Lithographic techniques used for nanoscale structuring. (a) Structures created using 193 nm photolithography (extracted from [2]). (b) Transmission through the optics material CaF$_2$ (extracted from [33]). (c) 80 keV electron beam lithography (extracted from [3]). (d) CASINO simulation of 80 keV electrons. (e) A dot pattern imprinted into PMMA (extracted from [5]). (f) A pit in a 2.4 nm thick oxide generated by applying a voltage pulse from a SPM tip (extracted from [9]).
However, EBL is incapable of producing high aspect ratio structures. In Figure 2.1 (d) the electron Monte Carlo package CASINO [4] is used to simulate 80 keV electrons in the resist material PMMA. This demonstrates that a well defined electron beam is broadened as a function of depth due to electron scattering in the resist material making production of high aspect ratio structures unattainable.

- **Nanoimprint Lithography**

Imprint technology using a metallic stamp to compression mold thermoplastic polymers is a low cost and high-throughput technology that has been around for several decades with imprints at the nanoscale recently achieved [5] (shown in Figure 2.1 (e)). Stamp negatives are traditionally created in PMMA using direct write EBL and stamps are then cast in a metallic form by electroplating. The aspect ratio of the imprint depends on the aspect ratio of the EBL defined stamp negative. Electroplating of high aspect ratio IBL written structures has recently been demonstrated [6], therefore when IBL is used to write the stamp negative a higher aspect ratio imprint can be achieved compared with the EBL method, as show by Ansari et.al. [7].

- **Scanning Probe Microscope (SPM) lithography**

To push the dimensions of structures even smaller a scanning probe tip can be used to manipulate the placement of only a few atoms and produce structures with dimension below 10 nm [8,9] (Figure 2.1 (f)). However, this technique is immature and does not offer the ability to produce structures beyond very small surface features, and is extremely slow.

### 2.2.3 Nanoscale high aspect ratio methods

A nanoscale high aspect ratio method is defined by the ability to produce aspect ratios well beyond the EBL limit of ~10:1 while remaining inside the 1000 nm resolution limit. The techniques described in this section have demonstrated structures with nanoscale dimensions, below 1000 nm and with aspect ratio far greater than 10:1. To push the boundaries of nanoscale fabrication the 100 nm resolution limit must be broken and not all methods described here have reached this milestone. Explained are four methods which have been chosen for their ability to produce nanoscale high aspect ratio structures. IBL is given its own, more detailed, explanation in section 2.3.
Figure 2.2: (a) Structures created using two photon polymerisation (2PP) (SEM image extracted from [10]). (b) Pillars etched out of bulk Si using reactive ion etching (RIE) (SEM image extracted from [11]). (c) Pillars (8 µm diameter) created in SU-8 using X-ray lithography (SEM image extracted from [12]). (d) Three dimensional structures in diamond machined using a focused beam of keV ions (SEM image extracted from [13]).
• **Two Photon Polymerisation (2PP)**

This technique has produced intricate 3D structures by a photo-induced chemical polymerisation localised in a small volume of resin. This technology has not yet produced structures with sub-100 nm dimensions due to the limit imposed by the diffraction of photons [10] (Figure 2.2 (a)).

• **Reactive Ion Etching (RIE)**

In this technique EBL is used to create an etch mask, and then a Si substrate is subjected to a highly anisotropic etching process, thus creating high aspect ratio voids in the bulk Si. The minimum feature size that has been demonstrated is greater than 200 nm [11] (Figure 2.2 (b)).

• **X-ray lithography**

X-ray lithography is a photolithographic method characterised by the use of photons with wavelength below 1 nm. X-ray photons can be used to replicate a patterned mask with high accuracy and as a masked based process there is potential for high throughput when using an adequate X-ray source such as synchrotron radiation. For X-rays with wavelengths below 1 nm the penetration is in the order of millimetres in resist materials. Therefore X-rays can be used to make high aspect ratio structures [12] (Figure 2.2 (c)).

The mask material must be thick enough to stop the incoming photons and self-supporting or created on a thin membrane. This is a particular problem for X-ray lithography because for nanoscale lithography the mask itself must be a high aspect ratio structure and making the mask itself is a significant challenge. A possible application for IBL is the production of masks for X-ray lithography so that the advantage of high throughput due to mask based lithography can be achieved. X-ray lithography provides the first stage of the process referred by the acronym LIGA Lithografie, Galvanoformung, Abformung (German: Lithography, Electroplating, and Molding) and has seen significant development at synchrotron facilities.

• **Low energy ions in the nuclear LET regime**

Similar to the electron microscope the keV ion beam is a compact, easy to operate piece of commercial equipment. The ion beam can typically be focused to less than 100 nm. It is a direct resistless machining technique using energetic ions in the nuclear linear energy transfer (LET) regime (~1 keV / u) to directly sputter ions from the substrate. As depth increases resolution is compromised as surface atoms are sputtered and incident ions implanted. A disadvantage of this technique is that the atom removal rate is very slow, slower than direct write lithography, so large throughput can not be achieved. An example of structures created using FIB machining is shown in Figure 2.2 (d) [13].
Figure 2.3: The modelling package SRIM [14] has been used. (a) To produce linear energy transfer curves for different ions in PMMA as a function of the ion energy. For ions with an energy above 1 MeV/u⁻¹ the electronic LET is at least two orders of magnitude greater than the nuclear LET. (b) The spatial distribution of 1 MeV H ions in PMMA. (c) The energy loss as a function of depth.
2.3 Description and resolution limit of IBL

2.3.1 Introduction and energy regime

This Section gives a description of IBL and highlights why it has been chosen as a technique to produce nanoscale high aspect ratio structures. The deep penetration into a resist of a highly energetic ion has inspired the field of IBL. It is first necessary to specify energy regime of the ion and the energy it deposits in the sample. An ion with energy above 1 MeV per nucleon passing through a material will have a LET due to electronic interactions at least two orders of magnitude greater than the nuclear LET. The Monte Carlo code SRIM [14] has been used to calculate the electronic and nuclear LET in PMMA and is plotted against the ion’s energy for masses ranging from H to Au in Figure 2.3 (a).

The interactions with both the target electrons and nuclei determine the trajectory of the incident ion and the rate of energy deposition. The large mass difference between even the lightest element, H, and an electron means that the transfer of momentum between the two bodies will be small. Therefore, as the energetic ion passes through the resist material there is little change in its direction with each electronic interaction. This results in a straight damage track with nearly uniform energy deposition over the majority of the ion’s range as demonstrated by the SRIM simulations of 1 MeV H in PMMA shown in Figure 2.3 (b and c). It is crucial that the incident ion is in the electronic LET regime for high aspect ratio lithography.

2.3.2 Ultimate resolution—single ion lithography

Notable structures in PMMA with a resolution of less than 100 nm have been created at the Centre for Ion Beam Applications (CIBA) at the University of Singapore using a focused...
beam of 2 MeV protons [15] (Figure 2.4). With improvements to the technology used to define the beam the fundamental limiting factor of the latent damage radius of a single ion track will be reached. As stated in the research questions (section 1.2) this thesis aims to find which single ions can be etched to create a hole in PMMA. By imaging the holes that result from etching along the tracks of individual ions this thesis aims to experimentally determine the hole radius and therefore the ultimate resolution of the IBL process. The choice of ion mass and energy is critical to ensure that single ion tracks are etched during the developing process so that a measurement of the radius can be made. A specific ion was chosen based on the criterion that the deposited energy density in the small cylindrical volume of track was above the sensitivity threshold for the PMMA–developer combination. This threshold has been determined experimentally in section 4.3 using a macroscopic method.

To calculate the energy density in a single ion track requires two pieces of information; (1) the linear energy transfer, $LET$, and (2) the track radius, $r$.

$$\text{Energy Density}_{\text{ion, track}} \approx \frac{LET}{\pi r^2}$$

(This calculation is used in section 4.5 for specific ions). One can see that a problem arises. To choose an appropriate ion requires knowledge of the track radius, however the aim of the experiment is to determine this unknown radius. A theoretical treatment is required to initiate the experimental study. One must first acknowledge that the above relationship is only an approximation because it assumes that the track has a well defined boundary at the distance, $r$, from the track’s centre when in fact the energy deposition decreases with $r$. The aim of the following sections is to estimate the shape of the profile for the following reasons:

1) So that an approximate single value for the radius can be used to estimate the mean energy density for a specific ion track. The value chosen is the radius at which 90% of the ion’s energy is deposited.

2) When attempting to optimise the lithographic process for a minimum hole radius it will no longer be acceptable to regard the energy density profile as uniform out to, $r$. The resultant hole radius is dependent on the damage profile shape in combination with the developing solution and time. Before developing conditions have been optimised the measurement of hole radius will not reveal the possible minimum. Therefore an estimate of the shape of the profile will be useful for optimisation of the developing parameters.
2.4 Physical models of an energetic single ion

2.4.1 Introduction physical models

This section considers the mechanisms for the transfer of energy from an energetic ion to a generic solid target material and more specifically, PMMA. The aim is to qualitatively understand the form of the radial energy distribution function and therefore the radial damage profile. The large varieties of materials in which tracks are studied make the field vast and there is not a simple formula that will easily yield the radial damage profile for any specific incident ion in any specific target material. To an ion beam physicist, there are a large range of ions and energies to choose from. If one considers ions ranging in mass from H to U with energies above 1 MeV.u\(^{-1}\), then the range of possible LETs is large (10-50 000 eV.nm\(^{-1}\)).

A successful theoretical model is only achieved when all the relevant physical interactions have been included. It is a large task to include all interactions over a large LET range so most models for determining the radial energy deposition and damage are developed for a specific application where the ion energy and target materials lie within a well defined range. It is not the intention in this thesis to develop a quantitative model and/or simulation as there is already enough information in the literature to develop a qualitative picture.

2.4.2 Physical processes

The journal papers by Schiwietz et. al. [16] for high LET ions, and Lee [17] for low LET ions, give good overviews of all the physical processes that can occur for ions above 1 MeV.u\(^{-1}\) where electronic LET dominates. The primary mechanism for the delocalisation of energy from the track path to the surrounding material is via delta electrons that radiate out from the track core.

- Delta electron range

The energetic delta electrons scattered from the track core have a maximum energy which can be calculated using the non relativistic kinematic formula:

\[
\Delta T = T \left( \frac{4m}{M} \right)
\]

[18] page 193

For all ions with energy of 1 MeV.u\(^{-1}\) the maximum electron energy is 2.2 keV. To give an indication of the order of magnitude of the lateral electron range a simulation using CASINO [4], a well established electron Monte Carlo code, can be performed. The lateral range of only the maximum energy delta electrons is simulated using a beam of 2.2 keV electrons incident on a PMMA target. Modelling gives electrons travelling a maximum range of 80 nm perpendicular to the track with fifty percent of the energy deposited within a radius of 4 nm shown in Figure 2.5.
• Energy deposition models

This thesis proposes three different models for energy deposition and subsequent latent damage—one model considers only the motion of electrons and two models consider electronic and atomic motion:

1) Delta electrons deposit their energy via ionisation or plasmon generation in a crystal.

2) Displaced delta electrons create a region of electronic potential in the core leading to atomic motion, referred to as coulomb explosion [19].

3) Electron-phonon coupling leads to an increased thermal atomic motion (thermal spike) proposed by Desauer [20] and used by Toulemonde et. al. and Wang et. al. [21-22].

The LET range required for each model to take effect is considered through a literature survey.
• **High LET Survey**

It is possible to record a latent track via a significant amount of atomic displacements. In the electronic LET regime there are negligible atomic displacements due to direct collisions with the incident ion. However, atomic motion may occur when multiple delta electrons are displaced from the central core. Studies have been conducted for highly energetic ions with LETs ranging from $10^3$-$5\times10^4$ eV.nm$^{-1}$ striking thin, free standing, targets. The ion LETs are plotted against energy per nucleon in Figure 2.6. Direct measurement of radius has been made using high resolution electron microscopy on a thin cross section of the damage track. The work by Meftah et. al., Wiesner et. al. and Vetter et. al. [23-25] in crystals presents TEM images showing a well defined latent columnar tracks consisting of totally amorphous material divided by a sharp transition to the surrounding crystalline material. For non-crystalline polymer materials Adla et. al. have imaged damage tracks treated with a staining agent using ions with LETs of 9-18 keV.nm$^{-1}$ [26]. For poststained samples the staining agent preferentially accumulates in the lower density track region leading to higher mass density image of the track. For pre stained samples imaging reveals a reduced mass density in the track. Both examples show evidence of atomic motion inside the track due to the passage of the energetic ion. Due to the difficulty of track imaging in the order of 10 nm the method described in Apel et. al. [27] uses a conductometric technique to quantify the hole’s radius as
a function of etching time for the polymer PET after irradiation to high LET ions. This gives some insight on the original radial energy deposition profile by plotting etch rate verse radius, finding two regions, a track core with a range of diameters from 7 to 26 nm and a track halo with a diameter exceeding 100 nm. A relationship between the track core diameter and the LET was found given by $d \propto (\text{LET})^{0.55}$.

These measurements of track radius rely on atomic motion to occur and it is evident that atomic motion is present in these targets and can be attributed to either the coulomb explosion or thermal spike models. With most evidence suggesting that the coulomb explosion model is only valid in insulating materials, where the charge neutralisation time is sufficiently long [16], the thermal spike model is preferred. Using the thermal spike model, based on heat diffusion, calculations of the track core radii have been made which agree with experimental results [28].

- **Low LET Survey**

For ions with an LET below $10^3$ eV.nm$^{-1}$, the literature yields no examples of directly imaging the latent damage tracks of single ions in any materials. The material will appear unchanged in an electron microscopy image because there have been insignificant atomic displacements. It is proposed (based on the high LET survey) that the density of displaced delta electrons in a single ion strike is below the critical limit for atomic motion to occur. Latent damage can only be recorded via a change in chemistry of the target. While chemical modification may lead to atomic displacement, it is on such a small scale that there is negligible change in density or crystallinity. In this regime only appropriate materials will record a damage track. In the case of polymers electronic displacement, leads directly to breakage of chemical bonds, therefore, phenomena such as scission or cross-linking may occur and latent damage is recorded without the necessity of a large number of atomic displacements.

Etching is required to reveal the track. Imaging an etched track in a nuclear track detector, such as CR-39 on the micrometre scale [29], will not directly reveal the initial radial latent damage profile because etching occurs well beyond the radius of latent damage. The result is a radius that is dependent on the developing time. This fact presents a problem for the study in PMMA. What if, as in CR-39, the undamaged PMMA is also etched? The etch rate of the undamaged PMMA must be found and if possible minimised. This is the subject of sections 4.2 and 4.4. Subsequently finding the latent damage profile requires an imaging technique that can probe into the initial stages of track etching where the radius is of the order of 10 nm. This work has been attempted in the paper by Miller et. al. [30] with He and Ga ions. The results give compelling evidence that a single ion track in PMMA in the electronic LET regime may be etched and imaged. However, the evidence is not conclusive and gives motivation for the further examination presented in this thesis.
In the literature several analytical formulae or Monte Carlo simulations exist that aim to determine the radial energy deposition surrounding a single ion track. These simulations consider only the energy deposition of the delta electrons and are therefore valid when the LET is below $10^3 \text{ eV.nm}^{-1}$. In the paper by Udalagama et. al. [31] protons have been modelled at 2 MeV in PMMA and in the paper by Waligorski et. al. [32] protons over the range of 1-100 MeV were modelled in water. These models tell us that approximately 90% of the energy deposition is within a radius of 2 nm. These simulations take into account the contributions to energy deposition from delta electrons of all energies, therefore are more accurate than the simple CASINO model of only maximum energy delta electrons presented at the beginning of this section. In the low LET regime it is the velocity of the incident ion that defines the range of delta electrons, and therefore the shape of the radial energy deposition profile. The LET of the ion defines the scale of the energy deposition and does not contribute to its shape. Therefore the relationship given by Apel ($d \propto (\text{LET})^{0.55}$) will no longer hold in the low LET regime.

2.4.3 Chemical structure of PMMA

The resist material poly methyl methacrylate (PMMA) has been investigated because of the advantage of a long history in lithography and well established processing techniques. Defining the chemical structure of PMMA allows consideration of how the energy deposition is converted into latent damage.

- **Structure of PMMA**

PMMA is the synthetic polymer of the methyl methacrylate monomer ($\text{C}_5\text{O}_2\text{H}_8$) with each monomer having the molecular weight of 100 g.mol$^{-1}$. In solutions prepared for spin coating PMMA is defined by the weight of the total polymer chain. Therefore in 950 K PMMA there are 9500 monomers per polymer chain. A high molecular weight is desirable in lithography because it means that a large contrast can be achieved between the damaged (low molecular weight) region and the surrounding (high molecular weight) bulk material. The density of polymerised PMMA is $\sim 1 \text{ g.cm}^{-3}$ therefore PMMA has a molecular density of approximately 6 monomers per cubic nm. This information is used to build up a picture at a molecular level as shown in Figure 2.7. The size scale for recording a single damage event cannot be smaller than the space occupied by one monomer and therefore the lowest limit on a void constructed in PMMA must be 1/6 of a cubic nm. For the polymer to be successfully removed during developing the molecular weight in the damaged region must be significantly reduced, compared with the surrounding bulk PMMA. The two types of damage centre in the polymer matrix are (1) chain scission or (2) cross-linking.
Methyl methacrylate

PMMA contains atomic mass number of atoms mass of monomer
H 1 8 8
C 12 5 60
O 16 2 32

Avogadro's number
6.02×10^{23} (g.mol^{-1})

Density
1 (g.cm^{-3})

Mass of monomer
1.66×10^{-22} (g.nm^{-3})

Figure 2.7: Illustration of PMMA at the molecular level. From the density of PMMA and the molecular weight of one monomer of PMMA a calculation reveals the density of monomers to be ~6 per cubic nanometre.

Figure 2.8: G value vs LET in PMMA extracted from the paper by Lee[17]. This work has extracted the G value from a series of experimental results and found that at approximately 15 eV.nm^{-1} the G value begins to decrease. This is attributed to scission site, or spur, overlap as the LET increases.
area = $3.14 \times 2^2 = 12.6$
monomers = $12.6 \times 10 \times 6 = 754$

LET = 10 eV.nm$^{-1}$
scission events = 1

LET = 100 eV.nm$^{-1}$
scission events = 7

Figure 2.9: Illustration of the spatial distribution of scission events in a section of ion track. G values are taken from the graph presented in [17]. The number of scission events has been calculated in a 10 nm × 2 nm radius cylinder, equal to the G value / 100 × 0.9 × LET × track section length. The number of cross-linked events will also increase as the scission density increases. This picture demonstrates that because the track diameter is not very much greater than the distance between monomers damage should be considered as discrete sites rather than a smooth profile when the number of scission events is not statistically very large.

- **G Value**

The distribution of latent damage in PMMA can be determined using the *G value*. This value has been defined in the paper by Lee [17] as the number of scission events per 100 eV of deposited energy. If the energy per unit volume along a single ion track is known then it is possible, using the *G value*, to determine the number of scission events per unit volume along the track. The G value is given as approximately 1.3 events per 100 eV for LET values below 15 eV.nm$^{-1}$ and decreasing for values above 15 eV.nm$^{-1}$. The graph of G value vs LET has been extracted from the Lee paper and shown in Figure 2.8. If there are 1.3 scissions per 100 eV then there is 77 eV of ion energy loss per scission event.
• Damage from energy deposition

As discussed earlier a typical radius for a 1 MeV.u\(^{-1}\) ion with LET below 10\(^3\) eV.nm\(^{-1}\) is 2 nm. This is taken as the radius in which 90% of the energy is deposited from the results of Udalagama and Waligorski [30-31].

Further to the G value Lee gives the average scission site energy, or spur energy, as 35 eV. Therefore 77 eV of ion energy loss goes into making a 35 eV site and a portion of the ion’s energy is not captured in a scission site. As the LET increases above 15 eV.nm\(^{-1}\) this portion increases with higher LET as the scission sites become closer together and, according to Lee’s model, converted to a pair of cross-linked radicals. This has been demonstrated in the illustration in Figure 2.9 showing the increase in damage sites out to the nominal radius of 2 nm over a 10 nm length of ion damage track. Lee has concluded that the separation of scission sites, or spurs, is 2 nm when the LET is equal to the threshold value of 15 eV.nm\(^{-1}\).

If the distance between scission sites is too large the molecular weight reduction will not be significant and the polymer will remain insoluble. To create a damage profile in the polymer matrix which is proportional to the energy deposition profile there must be a statistically large enough group of discrete damage events for the damage profile to be smooth and if the ion LET is below 15 eV.nm\(^{-1}\) this is not the case.

2.4.4 Conclusions to the physical model section

The aim here was to develop a qualitative picture of the passage of a 1 MeV.u\(^{-1}\) ion in a medium, specifically PMMA. The key variable is the LET of the ion and three regions have been identified.

• High LET (greater than 10\(^3\) eV.nm\(^{-1}\))

1) The motion of delta electrons is converted into atomic motion therefore the initial radial energy deposition profile cannot be determined by simply modelling delta electrons.

2) There is no direct relationship between the energy deposition profile and the level of latent damage because once the damage has reached saturation further deposition of energy does not make the track ‘more damaged’ and cannot increase the etch rate.

3) The result is a damaged region with a well defined boundary and therefore a radius proportional to LET relationship.

• Low LET (less than 10\(^3\) eV.nm\(^{-1}\))

1) In a polymer the LET is high enough for a continuous track of scission or cross-linking events.
2) The radial energy deposition can be considered smooth and determined by the transport of only delta electrons and a relationship exists between the profiles of energy deposition and latent damage.

3) The damage has not reached saturation so damage scales with LET but the effective radius (90% of the total damage) is limited to a value of approximately 2 nm.

4) The damage is a mix of scission and cross-linking. In PMMA a cross-linked network has not formed so the polymer remains soluble.

- Extremely low LET (less than 15 eV.nm$^{-1}$)

1) In a polymer scission events are isolated from each other and the latent track will only etch if the bulk etch rate of un-damaged material is high.

2) It is difficult to analyse the early stages of track etching because there is only a small contrast between the track etch rate and the bulk etch rate.

3) To use extremely low LET ion for lithography it is necessary to use the overlap of multiple ions to achieve a suitable damage density and therefore good contrast in the lithographic process.

2.5 Conclusion to the chapter

IBL is uniquely placed to offer a route to 3D nanostructures that cannot be fabricated by any other means. While the physics of ion interactions through matter provides a well defined nanoscale damage profile the technology and processing techniques are not as mature as those of the well established optical/UV photolithography and EBL.

Lithography with ions has always been in the realm of a focused beam of multiple ions. In this thesis the stated aim is to find the smallest structural element and therefore conduct lithography at its ultimate resolution. To make such a structural element I have chosen the passage of a single ion in the resist material PMMA. To decide which single ion is appropriate a review of single ion tracks has been conducted. The results of the review show that if the ion LET is above 15 eV.nm$^{-1}$ then the track should be continuous. To further increase the contrast between the damage track and the bulk a higher LET would be desired, however, when the LET reaches a value above $10^3$ eV.nm$^{-1}$ the damage would begin to delocalise and the etched hole increases in size.

The next chapters are dedicated to the creation and characterisation of holes etched along the tracks of single ions in PMMA, and the precise placement of ions in the PMMA.
2.6 Bibliography


Chapter 3  Experimental—Equipment and Procedures

3.1 Introduction to the chapter

3.1.1 Project overview
It is the aim of this project to investigate the ultimate resolution in ion beam lithography (IBL). While the exposure conditions for ions are vastly different to those employed by the more established optical or electron beam lithography the basic sequence still holds:

\[ \text{Prepare film} \rightarrow \text{Exposes} \rightarrow \text{Develop} \rightarrow \text{Assess} . \]

The nature of lithography as a multi parameter process means any study into IBL must be based around a set of well defined generic procedures which can be applied to any specific experiment.

3.1.2 Chapter overview
This chapter describes the experimental infrastructure; the equipment, fabrication steps and imaging techniques used (Figure 3.1). In the majority of this work studies were performed by exposing Micro Chem 950 K poly methyl methacrylate (PMMA) films to a focused beam of high energy ions over a range of linear energy transfer (LET) values. In any lithographic process film preparation, exposure conditions and developing conditions are finely tuned and maintained to give a robust process with repeatable results. During fabrication a sample lithographic structure is often removed from production and quantitatively assessed. The monitoring process must also be robust so that reliable data can be used as feedback for the fabrication process. At semiconductor device fabrication plants a huge amount of effort is put into installing and maintaining quality control over the fabrication and monitoring processes so that any problem can be quickly and easily traced to its source. It is the aim of this chapter to develop these generic procedures for the purpose of conducting this investigation. These procedures have been developed using similar lithographic methods used elsewhere as a starting point and appropriate references are given section by section.
<table>
<thead>
<tr>
<th>Variable</th>
<th>Generic Procedure</th>
<th>Equipment</th>
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<tbody>
<tr>
<td></td>
<td>Sample Preparation</td>
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<td></td>
<td>De-capping</td>
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<td></td>
<td>Cleaning</td>
<td>Wet chemistry area</td>
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<td></td>
<td>Film Thickness</td>
<td>Spin coater</td>
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<td>Spin coating</td>
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<td>Baking</td>
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<td>Storage and transport</td>
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<td></td>
<td>Registration Markers</td>
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<td>UV source</td>
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<td>E SEM</td>
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<tr>
<td></td>
<td>Ion Beam Exposure</td>
<td></td>
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<tr>
<td></td>
<td>Ion energy</td>
<td>5 MV Pelletron Van de Graff accelerator</td>
</tr>
<tr>
<td></td>
<td>Ion mass</td>
<td>10 MV Tandem accelerator</td>
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<td></td>
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<td>Micro probe beam line</td>
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<td></td>
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<td>Data acquisition electronics</td>
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<td></td>
<td>Developing</td>
<td>Wet chemistry area</td>
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<td></td>
<td>Development time</td>
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<td></td>
<td>Development formula</td>
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<td></td>
<td>Imaging</td>
<td></td>
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<tr>
<td></td>
<td>Optical microscope</td>
<td></td>
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<td></td>
<td>AFM</td>
<td></td>
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<td></td>
<td>FEG SEM</td>
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</tbody>
</table>

Figure 3.1: Diagrammatic representation of the generic procedures and their relationship with experimental variables and the equipment used.

Figure 3.2: Photo and Schematic of Hamamatsu s1223 series photodiode, extracted from Hamamatsu data sheet on website [1].
In general a PMMA film was prepared on the front surface of a Hamamatsu S1223-01 Si PIN photodiode (Figure 3.2). The photodiode acted as a detector sensitive to single ion impacts. This enabled a very accurate measurement of the number ions hitting the PMMA film in an area which could be defined by focusing and scanning the ion beam. The PMMA was then developed and the resulting structures imaged. Imaging was predominately performed using an Atomic Force Microscope (AFM) in non-contact mode. Samples went through at most five generic procedures and these procedures are the titles for the following five section headings of this chapter.

1) Sample preparation
2) Registration markers
3) Ion beam exposure
4) Developing
5) Imaging

The variables associated with each procedure and the equipment used are summarised in Figure 3.1. Studies involved adjusting one parameter at a time in the generic procedure and investigating the outcome. The specific scientific studies are presented in chapter 4.

### 3.2 Sample preparation

#### 3.2.1 Introduction to sample preparation

This section details the procedures used to prepare a PMMA film on the surface of the photodiode, covering de-capping, cleaning, spin coating, baking and storage. The routine procedure of spinning PMMA onto a Si wafer is complicated when attempting to deposit the film on the surface of a photodiode. First the protective cap of the photodiode had to be removed and the Si surface cleaned. A method to couple the photodiode with the vacuum chuck of the spin coater was devised. Processing guidelines for film preparation are given by the manufacturer [2] and a useful reference [3] explains the spin coating process in detail.

#### 3.2.2 De-capping the photodiodes

Photodiodes purchased from the manufacturer are intended for optical measurements and so are designed with a glass cap to protect the Si photodiode surface (photodiodes purchased without a cap are highly priced).
Figure 3.3: Graph of spin speed versus thickness curves, extracted from MicroChem datasheet [2]. It was not possible to use a spin speed below 4000 RPM due to the small surface area of the photodiodes; therefore, different concentrations were required to achieve different film thicknesses.

Figure 3.4: Applying drop to surface—section view: Photodiode legs are folded under, the o-ring is used to make a seal with the vacuum chuck, the PMMA drop covers the whole top surface of the photodiode. After spinning, the PMMA edge bead is approximately 0.5 mm wide and the remaining Si surface is covered with uniform thickness.
A MeV ion will not travel through the glass layers so therefore to detect the ions the glass cap must be removed locally. To remove the cap the glass surface was glued to a stainless steel bolt and allowed to set. The bolt was held in a vice and a fine jeweller’s saw used to create a groove around the body of the cap. A fine screwdriver was inserted into the groove and twisted to remove the cap.

### 3.2.3 Cleaning

During the de-capping process a small amount of dust may get onto the surface of the photodiode. The surface was blown dry with compressed air. The electrical contact legs were shortened and folded under the photodiode body. The photodiode was placed in a beaker, covered with acetone and agitated ultrasonically for 10 minutes. After the acetone bath the photodiode was rinsed in isopropanol and immediately dried with compressed N\textsubscript{2} gas.

### 3.2.4 Spin Coating

A solution consisting of PMMA dissolved in anisole is purchased from the manufacturer with concentrations to allow a predetermined film thickness to be achieved for a given spin speed. Data from MicroChem shows the film thickness as a function of spin speed for various solutions of PMMA mixed in anisole (Figure 3.3).

A spin coater\(^1\) was used to spin coat PMMA films on the surface of the photodiodes. The PMMA solution was decanted into a clean glass beaker. A neoprene o-ring was used to create a seal between the photodiode body and the vacuum chuck of the spin coater. A plastic disposable pipette was used to place a drop of PMMA onto the entire Si face and body of the photodiode (Figure 3.4). The drop was placed while at an initial speed of 100 RPM then the spinning ramped up to the desired speed and held for 60 s. To maximise the region of uniform thickness the PMMA edge bead needed to be minimised (the edge bead is shown in the image of a prepared photodiode in Figure 3.5). The surface area of the Si face of the photodiode is small (4 × 4 mm\(^2\)) so a large spin speed was required to prevent the edge bead covering the whole surface. Therefore a value of 5000 RPM was used consistently. The spin curves tend to flatten out at above 4000 RPM so to achieve different film thicknesses the ratio of PMMA to anisole was altered. Two solutions were used, A2 (2% in anisole) and A8 (8% in anisole), to make thin films (~55 nm) and thick films (~700 nm).

\(^1\) Specialty Coating Systems, INC. SPINCOATER®, model P6700 series
Figure 3.5: Photo of a finished PMMA coated photodiode. MicroChem 950 K PMMA A8 (8% in Anisole) spun at 5000 RPM for 60 s, hotplate baked at 180° for 10 min.
3.2.5 Baking

Following spinning the film is soft baked to further drive off the anisole via evaporation. The photodiode was transferred to a programmable hotplate\(^1\). The photodiode was placed on a sheet of Al foil to allow easy removal after baking. PMMA films were hotplate baked at 180 degrees for 10 min.

3.2.6 Storage

Plastic Petri dishes with lids were used for storage and during transport. A piece of double-sided carbon tape was used to hold photodiode samples down. To minimise the exposure of the PMMA films to UV light the Petri dish was wrapped in Al foil and stored in a light tight box. However during handling and experimentation the samples were exposed to the ambient UV of the lab.

3.2.7 Summary

The photodiode was found to be very robust and its performance was not degraded by any of the sample preparation processes. Table 3.1 summarises the sample preparation.

### Cleaning

<table>
<thead>
<tr>
<th>Cleaning agent</th>
<th>Method</th>
<th>Rinsing agent</th>
<th>Drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>ultrasonic 10 min</td>
<td>IPA</td>
<td>compressed N(_2)</td>
</tr>
</tbody>
</table>

### Spin coating

<table>
<thead>
<tr>
<th>PMMA Manufacturer</th>
<th>Molecular weight</th>
<th>Solution</th>
<th>Spin speed</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>MicroChem(^TM)</td>
<td>950K</td>
<td>A2</td>
<td>5000 RPM</td>
<td>55 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A8</td>
<td>5000 RPM</td>
<td>800 nm</td>
</tr>
</tbody>
</table>

### Baking

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 degrees</td>
<td>10 min</td>
</tr>
</tbody>
</table>

Table 3.1: Summary table of PMMA film production.

---

\(^1\) PMC DATAPLATE® Digital Hot Plate 732 Series
3.3 Registration markers

3.3.1 Motivation for creating registration markers

It is very difficult to find small, sub 100 nm, single ion tracks on the $4 \times 4$ mm$^2$ surface with an optical microscope and even more so with an AFM, especially when there is uncertainty whether single ion tracks have actually been etched. Registration markers assured that ion beam exposures were placed with micrometer precision in a particular area of the sample. Multiple ion beam exposure sites were created all on one sample, indexed with different ion species and fluences at each site. Each site could then be easily imaged with reference to the registration markers, with AFM or SEM with precise knowledge of the exposure conditions.

3.3.2 Registration specifications

The requirement for a registration marker is that it should be visible under a low magnification optical microscope. At first the ion beam itself was used to generate the markers, however, it was found that an area of approximately 500 µm$^2$ was required to be seen easily in an optical microscope or the optical viewing system of the AFM. The maximum count rate limit of the data acquisition electronics is of the order of $10^4$ counts per second. Table 3.2 calculates the time required to form a registration marker. Multiple registration markers are required and take approximately 1 hour per marker to prepare. This is an inefficient use of accelerator beam time because the time consumed by creating registration markers is up to an order of magnitude greater than the time required for the actual experimental exposures.

<table>
<thead>
<tr>
<th>$10^{13}$ He ions / cm$^2$</th>
<th>PMMA sensitivity (result from Section 4.3, Figure 4.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^6$ cm$^2$</td>
<td>Area of a registration marker</td>
</tr>
<tr>
<td>$5 \times 10^7$</td>
<td>Ions required per registration marker</td>
</tr>
<tr>
<td>$\approx 5 \times 10^7$ s ~ 1 hr</td>
<td>per registration marker</td>
</tr>
</tbody>
</table>

Table 3.2: Calculation of the time required to perform the registration mark exposure in the PMMA film.

3.3.3 Methods

Two alternative methods for creating registration markers are presented here, (1) UV lithography and (2) electron beam lithography. It was not the aim of the project to develop the processes of UV or electron beam lithography, but it was necessary to quickly produce some visible marks in the PMMA films without overstretching the capabilities of the equipment at hand, a UV lamp and an environmental SEM.
3.3.4 UV lithography

To create a registration grid using UV lithography the PMMA film was exposed to a UV lamp with a 200 mesh (127 µm pitch, 34 µm thick) Cu grid acting as a mask. With the Cu grid gently placed on its surface the film was exposed for 1 hr to the UV light with the area under the grid remaining in shadow (Figure 3.6). The PMMA was developed in MIBK:IPA 1:3 for 20 s to leave behind a positive image of the grid in the PMMA (Figure 3.7). Subsequent ion beam exposures were then performed at different locations on the patterned PMMA. The optical viewing system in the ion microprobe target chamber was used to align exposure sites to the registration grid. Using UV lithography to make registration markers only worked for 55 nm films and did not work for the thick 700 nm PMMA layer. The UV source wavelength was not short enough to penetrate through the 700 nm PMMA thickness and after developing the PMMA was not completely removed in the exposed regions. Although this technique was developed and used to produce well located ion beam exposures the technique was ultimately superseded in favour of the electron beam lithography method of making registration markers.
Figure 3.7: Optical micrographs of the PMMA coated photodiode surface after UV and ion beam lithography had been performed. The UV lithography process generated the large grid pattern so that the ion beam exposures could be located at indexed sites on the registration grid.
3.3.5 Electron beam lithography

To create a registration grid using electron beam lithography the PMMA coated photodiodes were loaded into the chamber of a FEI Quanta 200 Environmental SEM in the centre of the sample stage. The PMMA film could not be imaged by the SEM because the PMMA would be exposed by the electron beam. With the beam off the magnification was set to 500 times (an area of 0.2 × 0.2 mm$^2$). To give a viewing area some distance away from the PMMA surface an absolute offset of 3.0 mm was set to the y-axis of the mechanical positioning stage. When the beam was turned on it was possible to image the small viewing area. Using small increments in the positioning stage (x, y and angle) the photodiode was orientated with its edge parallel with the scanning direction of the SEM beam and the Si corner in the centre of the image, thus calibrating the position of the sample with respect to the electron beam. With the SEM in line scan mode 10 lines were written in the centre of the photodiode, 100 µm apart, each with a 10 s exposure. The sample was rotated 90° and the process repeated, creating a grid pattern (Figure 3.8). The sample was developed in MIBK:IPA 1:3 for 30 seconds which effectively etched the PMMA completely to the substrate.
Figure 3.9: Following exposure the PMMA film was developed and imaged using non-contact AFM (a) The ANSTO heavy ion microprobe beam spot formed by exposing a PMMA film to a single focused beam of 88 MeV I ions. (b) The Melbourne microprobe beam spot formed by exposing a PMMA film to a single focused beam of 3 MeV H ions. The scale bar is the same for both images.
3.4 Ion Beam Exposure

3.4.1 Requirements of ion beam exposures

This thesis aims to find which single ion tracks in PMMA can be etched to create nanoscale holes. Stated in the physical model section of chapter 2 is the key variable to be studied, linear energy transfer (LET). Therefore this project must have access to different ion beams over a large range of LET values. Exposures were carried out on nuclear microprobe beam lines on accelerators in two laboratories. The two accelerators have different sets of accessible ions and energies that can be produced and are detailed in the following sections. The beam spot size for the two microprobes is shown in Figure 3.9.

3.4.2 5 MV Pelletron Van de Graaff Accelerator

The single-ended 5 MV Pelletron Van de Graaff accelerator facility at the University of Melbourne was used to produce proton beams of energy up to 3 MeV H and He beams of up to 2 MeV. The maximum LET of He in PMMA is 216 eV.nm\(^{-1}\) at 0.6 MeV, however for He ions, beam energies of 1.5 and 2 MeV were preferred because of optimal focus through the microprobe. Experiments conducted on this accelerator were in the low and extremely low LET regimes (regimes described in sub-section 2.4.4).

The accelerator is equipped with a microprobe beam line (MP2) consisting of an object box assembly, inverted V shaped µ-slits used for continuous beam cutting, and an aperture box assembly used for limiting beam divergence entering the probe forming lens system. The lens system is made up of quadruplet lenses and different ratio scanning coils (2× 8× 16×) with a beam resolution of 1 to 2 µm and scan range of up to a few mm [4].

3.4.3 10 MV Tandem Accelerator

The tandem 10 MV ANTARES facility at Australian Nuclear Science and Technology Organisation (ANSTO) is capable of accelerating heavy ions, with a beam resolution of approximately 5 µm. The halogens are favoured ions because of the ease with which negative ions are formed in the ion source. This accelerator was used to achieve LETs in the range 1-10 keV.nm\(^{-1}\).

The ANTARES accelerator is equipped with a microprobe beam line consisting of object and image aperture slits controlled by micrometer in the x and y directions resulting in a square aperture, an Oxford Microprobe triplet lens system and OM scanning coils with a beam resolution of 5 µm for heavy ions and scan range of up to a few mm. The development of the beam spot in the PMMA film gives a good measurement of the beam spot size for the three different focused beams.
Figure 3.10: (a) Scanning voltages used to create a 2D pixel array on the surface of the sample. (b) Diagram of the data acquisition circuit.

Figure 3.11: Photograph of the custom built multiple sample holder designed and built to hold up to eight photodiodes. This allowed the ion beam exposure of many samples without the need to reload the target chamber.
3.4.4 Data acquisition

Both laboratories are equipped with the MPSYS data acquisition software and the MICRODAS data acquisition and control hardware. An ion striking the photodiode detector produced a signal which was processed using a pre-amp\(^1\), amplifier\(^2\) and analogue to digital converter (ADC)\(^3\) with the range set to 1024 channels. The digital signal was sent to the computer where the pulse height spectrum was recorded. The gain of the amplifier was set such that the full energy peak from the ion impact occurred at approximately channel 800. The scanning coil signals, generated by the MICRODAS hardware, were amplified by the scan amplifier\(^4\). The scanning coil voltage steps corresponded to the x-y coordinates of the beam on the target (Figure 3.10). The beam could be set to dwell at each pixel in the scan either by time, data, charge or some external trigger. An event file is created whereby the pulse height spectrum is stored for each pixel in the exposure array.

3.4.5 Exposure procedure

- Sample loading

The PMMA coated photodiodes were mounted in the target chamber of the nuclear microprobe system on a custom built mounting jig (Figure 3.11). It was equipped with a glass slide and Caesium Iodide fluorescent screen for beam focusing. In-line mounting sockets were used to hold up to eight photodiodes. This gave provision for one test photodiode and seven PMMA coated sample photodiodes. For quick and easy manipulation of the signal path from each photodiode wires were wrapped around the socket pins as required. Each photodiode was independently connected to a BNC electrical feed-through to allow access to the photodiode signal from outside the vacuum chamber. The ability to hold many samples was valuable because it enabled parallel sample processing, without the need to reload the chamber.

In these series of experiments all samples were subject to the same exposure regime, with multiple ion species, therefore a range of LETs, located on each sample. After exposure each sample was then subject to different developing conditions.

---

\(^1\) Pre-amp at Melbourne was the Ortec 142B and at ANSTO was the Ortec 142A

\(^2\) Amplifier used in both cases was the Ortec 572

\(^3\) ADC at Melbourne was the Ortec 500 and at ANSTO was the Canberra 8701

\(^4\) Scan amplifier at Melbourne was the MARC scan amplifier and at ANSTO was the OM scan amplifier.
Figure 3.12: Scanning transmission ion microscopy images of a 2000 mesh Cu grid made using the focused I ion beam.

Figure 3.13: (a) The method used to calibrate the optical viewing system. A calibration scan is made in the area of the photodiode wire-bond. (b) Optical micrograph of the wire-band pad of the PMMA coated photodiode. (c) An IBIC image of the corner of the wire-band pad imaged using a focused 8 MeV F beam.
• **Beam preparation**

A beam current of ~ 1 nA was measured on an ammeter\(^1\) connected to a Faraday cup in the beam line. The lenses were focused by viewing the ion beam on a glass slide or caesium iodide fluorescent screen. The incident beam current was then adjusted down to beyond the measurable limit (~10 pA) of the ammeter by closing the object, micro-slits and image apertures. The beam was brought onto a Cu calibration grid mounted in front of a blank photodiode detector. The detector was used to measure the beam current. It was adjusted to few thousand ions per second by slightly opening the micro-slits as the focused beam was scanned the over the grid (time base 1 ms, resolution 256 × 256). This generated a scanning transmission ion microscopy (STIM) image (Figure 3.12) of the grid which was then used to calibrate the microprobe scan size from the known grid period. The STIM image of the calibration grid was also used to indicate of the quality of the beam focusing. Upon viewing the image of the grid adjustments were made to the focusing lenses and micro-slits in order to sharpen the grid image.

• **Position calibration**

To calibrate the position of the beam on target with the optical viewing system an ion beam induced charge (IBIC) image of the photodiode’s wire-bond was captured. The beam was scanned (time base 1 ms, resolution 256 × 256), first at large scan size (~1 mm), over the approximate area of the wire-bond at a safe distance away from the experimental exposure area (Figure 3.13 (a)). The scan size was then decreased to the size desired for the experiment. The corner of the wire-bond pad was placed in the middle of this image (Figure 3.13 (b and c)) using the translation motion of the sample mounting stage. A mark was placed on the TV monitor to signify the position of the beam on the target. The beam could then be set relative to the registration markers in the PMMA by adjusting the translation stage.

• **Ion beam normalisation**

The data acquisition system was set to dwell on counts in the pulse height spectrum of the photodiode detector, each count representing a single ion impact. This allowed exposure to a preset number of ion impacts in an array created by positioning the beam with x-y scanning coils at a precise location relative to the registration grid.

---

\(^{1}\) Keithley 610B Electrometer
Figure 3.14: A comparison between optical imaging and AFM for an area of PMMA film. (a) An optical image with a 40× objective lens. The maximum achievable magnification is 100× giving a minimum field of view 50 µm across. (b) An AFM image taken using the Jeol JSTM-4200A and with the scan size set to 60 µm. The maximum field of view of this instrument is 95 µm.
3.5 Developing

The developing procedure has been developed from the process used commonly in electron beam lithography and can be found in the references [2, 5-9]. A range of different developing solutions were used made up of various mixtures of the three components methyl isobutyl ketone (MIBK), Isopropyl alcohol (IPA) and water. These solutions were either purchased pre-mixed or mixed in the laboratory. Mixing was performed by volume in a graduated cylinder with an uncertainty of 1 mL (%2).

Samples were immersed in the developer solution and agitated ultrasonically to etch latent damage from the ion beam exposure. Next the samples were placed into IPA to halt the etching process. The IPA rinse was performed in two beakers to maintain a final rinse of pure IPA over rinsing multiple samples. Samples were then dried with compressed N₂ gas.

3.6 Imaging techniques

3.6.1 Introduction

Just as important as the fabrication steps are the procedures used to perform analysis, specifically to generate images, of regions of PMMA following exposure to ions and development of the latent damage. Three uniquely different types of microscope were used.

1) Optical microscope
2) Atomic Force Microscope AFM
3) Scanning Electron microscope SEM

These three imaging techniques will be explained in detail in the following sub-sections along with descriptions of the instruments and procedures used.

3.6.2 Optical Microscopy

Optical microscopy was primarily used to create low magnification images quickly. These were used for qualitative analysis of the lithographically defined structures. They were also a useful reference when performing AFM imaging. An optical microscope with 5×-100× objective lenses was used in conjunction with a digital camera to capture optical micrographs of the PMMA samples. The camera was connected to a standard PC running Lab-view with image grab capabilities and 1024 × 768 pixels resolution. Using optical microscopy it was possible to image areas of the sample between 1 × 1 mm² and 50 × 50 μm². A 150 μm wide optical image is compared to an AFM image in Figure 3.14.
Figure 3.15: Comparison (a) measuring a large area feature using a standard AFM cantilever tip and (b) measuring a small etched single ion track using a Si nanowhisker AFM cantilever tip.

Figure 3.16: SEM images of cantilevers and tips from the NT-MDT website [15] (a) Standard cantilever is used to image large area structures (b) Nanowhisker type cantilever is used to image high resolution and high aspect ratio features.
3.6.3 Atomic Force Microscopy

Non-contact AFM\textsuperscript{1} imaging was the primary tool for performing quantitative topographical analysis of the structures that had been lithographically defined in the PMMA film. AFM has been previously used to image single ion features in polymers [10]. The AFM was equipped with two scanning stages; a $95 \times 95 \, \mu m^2$ stage and a $30 \times 30 \, \mu m^2$ stage with up to $512 \times 512$ pixels image resolution and 16 bit image depth.

For micrometre scale exposures in the PMMA (see section 4.3 Macroscopic study of PMMA sensitivity) an AFM cantilever with a standard tip was adequate. For etched single ion impacts it was necessary to use a high aspect ratio Si nanowhisker tip (see diagram in Figure 3.15). The nanowhisker tip produced images with higher resolution and increased scanned depth for narrow features. This choice of tip was critical in imaging etched single ion tracks to differentiate the etched hole from the background surface roughness of the PMMA film. The tips were supplied by NT-MTD either as a standard\textsuperscript{2} or Si nanowhisker\textsuperscript{3} (images shown in Figure 3.16). The Si nanowhisker tip with an inclination of $15^\circ$ was specially supplied to match the mounting angle in the AFM. The resolution of images created with the AFM was dependent on the tip used and was found to worsen as the tip was worn. Resolution was sub 1 nm and the depth into high aspect ratio features depended of the aspect ratio of the tip, tip diameter and hole diameter. The time taken to perform AFM scans varied based on the size of the area to be imaged and the type of tip used. Because of the fragility of the nanowhisker tips an upper limit of 20 $\mu m$ per second was imposed on scanning speed and therefore imaging was much faster with the more robust standard tips.

3.6.4 SEM

In the literature it is common to see SEM images of structures created in PMMA [11-14]. SEM was attempted but it was difficult to create high resolution (sub 1 nm) images due to the damage and charging of the insulating PMMA during the imaging process. Eventually SEM was performed at University of Western Australia Centre for Microscopy on a field emission gun (FEG) SEM\textsuperscript{4} with a low beam voltage of 100 eV and a 2 nm platinum coating to prevent charging.

\textsuperscript{1} JEOL JSTM-4200A scanning probe microscope
\textsuperscript{2} NT-MDT NSG 01/Pt
\textsuperscript{3} NT-MTD, NSC05, 15$^\circ$ inclination
\textsuperscript{4} ZEISS 1555 VP FESEM
<table>
<thead>
<tr>
<th>Pros</th>
<th>Cons</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>higher resolution</td>
<td>very slow</td>
<td>quantitative</td>
<td>sample must be coated</td>
</tr>
<tr>
<td>easy access</td>
<td>difficult to find areas of interest</td>
<td>fast</td>
<td>limited access</td>
</tr>
<tr>
<td>no sample preparation</td>
<td>aspect ratio limited by tip</td>
<td>easy to image large areas</td>
<td>resolution not as fine as AFM</td>
</tr>
<tr>
<td>Quantitative for surface features</td>
<td></td>
<td></td>
<td>Extremely low voltage required</td>
</tr>
<tr>
<td>non-destructive</td>
<td></td>
<td></td>
<td>Electron beam exposure damages PMMA</td>
</tr>
</tbody>
</table>

Table 3.3: Table of pros and cons for imaging single ion features in PMMA using Atomic force microscopy or Scanning electron microscopy.

Figure 3.17: A comparison between (a) an AFM image and (b) a FEG SEM image of etched single 71 MeV Cu ion tracks in PMMA.
The field emission gun provided the emittance required to achieve a measurable signal from the secondary electrons. The UWA machine was also equipped with a high sensitivity secondary electron detector. Although it was possible to image the etched single ion tracks using the FEG SEM no quantitative analysis was performed using these images. It was concluded that SEM was not suitable for routine characterisation of ion tracks in PMMA.

### 3.6.5 AFM verses SEM

In Table 3.3 presented is a list of PROS and CONS for the two analysis techniques. As the goal here was to image single ion tracks the resolution of the instrument was of primary importance. Two images (Figure 3.17) qualitatively demonstrate that etched single ion tracks from 71 MeV Cu ions could be imaged using both AFM and SEM. The figure shows that the resolution of the AFM imaging was superior, and with the capacity to access the AFM at the University of Melbourne regularly all quantitative studies were performed using AFM imaging.

### 3.7 Chapter summary

A five stage experimental infrastructure has been put into place and has allowed a series of studies to be conducted (see chapter 4). This infrastructure can be implemented to allow ongoing study in the field of ion beam lithography.

The key features of this infrastructure are the abilities:

1) To detect single ions after passage through the PMMA layer.

2) To precisely position microscopic exposure sites in the PMMA film using a focused beam, therefore allowing multiple exposure sites on one photodiode sample.

3) To use a registration grid to index each site to the conditions of the exposure.

4) To process parallel samples thus investigating multiple variables in a single course of experiments.

5) To perform quantitative analysis of the PMMA thickness for micrometre scale area exposures using AFM.

6) To perform quantitative analysis of the width of single ion impacts sites using AFM.
3.8 Bibliography


Chapter 4 Experimental—Studies

4.1 Introduction to the chapter

4.1.1 Project Overview

To investigate the ultimate resolution in ion beam lithography (IBL) this project aims to create and characterise etched tracks of single ions in poly(methyl methacrylate) (PMMA). Using the experimental infrastructure described in Chapter 3 a number of experimental studies have been performed which aim to show PMMA’s suitability for use as a resist in IBL. The experimental conditions found here produce high resolution structures in PMMA and can be further optimised by exploration of the multi parameter space for the lithographic process. The initial three parameters chosen for exploration were the linear energy transfer (LET) of the incident ion, the developing time and developing formula. The experiments conducted form a data set which is shown in the three dimensional parameter space diagram shown in Figure 4.1.

4.1.2 Chapter Overview

This chapter consists of four experimental studies summarised here. Each study is presented in a standard format using the headings; Introduction, Experiment, Results and Conclusions.

- Holes in CR-39 (Section 4.2)

In this study the material CR-39 was exposed to energetic alpha particles from an Am$^{241}$ source. This study tested the ability of an atomic force microscope (AFM) to image well formed etched single ion tracks. Also a measurement was made of the radial etch rate of the CR-39 polymer. This section considers how the bulk etch rate will affect a resist material’s performance in high aspect ratio lithography at the nano-scale, and the study of CR-39 offers a counterpoint to the study of PMMA.

- Macroscopic study of PMMA sensitivity (Section 4.3)

In this study PMMA films were exposed to 3 MeV H ions in homogeneously irradiated macroscopic areas. Upon developing and analysis this study was able to determine the sensitivity of PMMA for three separate developing formulas over different developing times (shown as $X$s in Figure 4.1). Sensitivity is defined as the deposited energy per unit volume required for the PMMA to fully etch. This sensitivity value was used as a guide to determine the likelihood of etching any specific single ion track in PMMA.
Figure 4.1: Diagram exploring the parameter space for lithography using single ions. Four ion species have been investigated, H, F, Cu and I, over a range of Linear Energy Transfer (LET) values. Three developing solutions have been investigated over different developing times.

- Single ion tracks imaged using AFM
- Single ion tracks, if any, not resolved by AFM
- Macroscopic sensitivity measurement
• **PMMA thickness and roughness versus developer (Section 4.4)**

In this study the bulk etch rate and surface roughening of PMMA were measured after development in different solutions. The measurement of bulk etch rate was made to determine if PMMA would be suited to nanoscale high aspect ratio lithography. The bulk etch rate was found to be not constant indicating that there is a period of time when the bulk material is not etched and during this period high contrast processing can be achieved. Experiment has also shown that there is an upper limit on the developing time of PMMA in water:IPA 1:4 because the film mechanically fails and delaminates from the substrate after extended time in the developing solution.

• **Study of single ion holes in PMMA at the nanoscale (Section 4.5)**

This study examined the formation of single ion tracks over a range of LET values, developing times and developing formulas. The results show that it is possible to etch and image single ion tracks but only in a region of the parameter space defined by high LET (greater than 4000 eV.nm\(^{-1}\)) or long developing time (greater than 8 min) for the most aggressive developing formula used (water:IPA 1:4). In doing these experiments some valuable experimental results have emerged that can be compared with theoretical models for ion track formation.

### 4.2 Holes in CR-39

#### 4.2.1 Introduction

A material used for single ion detection is poly(allyl diglycol carbonate) (PADC), more commonly known by its commercial brand name CR-39 (Columbia Resin number 39). This material was chosen for its well known ability to produce visible etched single ion tracks under optical microscopy. On the other hand imaging of single ion tracks in PMMA has not been widely reported therefore the conditions required to create and image a single ion track have not been firmly established. Papaleo et. al. [1] imaged single ion features in the surface of PMMA films following bombardment with heavy ions, without subsequent etching. Miller [2] indicated the presence of pits from 2 MeV He bombardment in etched PMMA films, but whether these were due to single ions is unclear.

This preliminary study imaged CR-39 during the early stages of track etching to investigate the capabilities of AFM imaging in the sub 1 µm realm, confident that holes actually existed.
Figure 4.2: (a) Diagram of the alpha source exposure setup. (b) Optical micrograph of the resulting exposure site (development time: 20 min).

Figure 4.3: Optical micrographs of holes in CR-39 made by etching the tracks of alpha particles showing increasing hole radius with etch time. When the hole diameter is less than 500 nm it can no longer be easily imaged with an optical microscope.
4.2.2 Experiment

To simplify the experiment, so there would be no need for an accelerator, the CR-39 was exposed to an Am$^{241}$ 1.5 µCi α-source, emitting alpha particles of up to 5.6 MeV (Figure 4.2). The exposure time was 30 min at a distance of ~ 5 mm. Samples were etched in 3.125 M NaOH solution, referring to the procedure of Balcazar et. al. [3], for times ranging from 1 min to 20 min.

4.2.3 Results

The optical images of CR-39 in Figure 4.3 clearly show the dependence of the hole diameter on etching time. As expected, for short etching times, the holes were too small to be seen with an optical microscope. Therefore, small diameter holes were imaged with AFM using a standard cantilever and are shown in Figure 4.4. A measurement of the radius was plotted as a function of the developing time in Figure 4.5. The linear radial etch rate is measured from the graph to be 42 nm.min$^{-1}$. For comparison Fromm [4] gives values for the bulk etch rate of variants of CR-39, Tastrak and Baryotrac, etched also in a NaOH solution of between 27 and 32 nm.min$^{-1}$.

4.2.4 Conclusions

To determine the hole characteristics a two rate etch model can be applied where the etching velocity along the particle trajectory is larger than the etching velocity of bulk material [5-6]. For a material to be useful for high aspect ratio nanolithography the radial etch rate must be small. The undamaged material must be resistant to the developing solution. If this is not the case then the feature size will be heavily dependent on the developing time and features will tend more towards a conical shape in the case of single ions.
CR-39 has been developed for use as a single ion track detector, not as a resist for lithography. As a track detector it is desirable for the holes to increase in size so that the track can easily be imaged by an optical method. However for making high aspect ratio features in the sub 100 nm realm CR-39 is not suitable.

From the lithographic point of view the CR-39–NaOH resist-developer combination can be thought of as a high sensitivity and low contrast. The high sensitivity is required so that the low damage density of a single ion track (such as those from an alpha source) will etch. This sensitivity is gained at the detriment to the contrast of the resist-developer combination.

To quantify the contrast of the CR-39–NaOH combination one would need to produce a response curve by experimentally characterising a thin film (~1 µm) of CR-39 on a substrate. Spin coating of CR-39 is not a well established practice therefore our study of CR-39 ends here, in favour of a resist material that has a well established history in lithography—PMMA. However the ion tracks in CR-39 were very useful in the evaluation of the AFM imaging ultimately applied to PMMA.
4.3 Macroscopic study of PMMA sensitivity

4.3.1 Introduction

The first study has shown that the CR-39–NaOH combination achieves the required sensitivity to allow the etching of single alpha particles of approximately 1 MeV.u\(^{-1}\). The question is; what is the sensitivity of PMMA? If a PMMA film is developed without knowing the sensitivity there is no guarantee that etching of single ion tracks will occur. An attempt at characterisation of the nanoscale holes would rely on blind searching.

- **Sensitivity**

  The sensitivity of a resist material is usually defined as the particle fluence required for etching to occur [7]. This can be determined experimentally by exposing the resist to a series regions containing varying fluence followed by development and measurement of the quantity of material etched. A preliminary experiment investigated PMMA by exposure to 2 MeV He ions over fluence ranging 6 orders of magnitude using the ion microprobe. The fluence in each exposed region was measured using a standard current integration technique. Following the developing of PMMA in MIBK:IPA 1:3 for 5min optical micrographs of the exposure sites were used to estimate the normalised thickness (shown in Figure 4.6).

- **Response function**

  A response function was generated by plotting the estimated PMMA thickness against the ion fluence in Figure 4.7. This function demonstrates that the PMMA becomes more susceptible to etching as a result of chain scission. The film is completely removed at a fluence of approximately \(10^{13}\) ions per square cm. As the ion fluence is increased even further the polymer begins to cross link and becomes insoluble to the developing solution. From the experiment we see that cross linking begins to affect solubility at approximately \(10^{14}\) ions per square cm.

- **Quantifying sensitivity**

  Using a response function the positive tone resist sensitivity is defined as the fluence where the film is completely removed. This is found by linearly extrapolating the negative gradient section of the function to the full thickness of the film. The preliminary experimental results cannot give us an accurate measurement of the sensitivity because we cannot apply a linear fit to the single data point that lies on this section of the response function. One must first experimentally determine more than one data point.
Figure 4.6: Optical micrographs, regions of PMMA exposed to varying fluences of 2 MeV He. The normalised PMMA thickness was estimated from these images.

Figure 4.7: The response function from the initial experiment using 2 MeV He ions. It shows the phenomena of chain scission and cross linking as a function of fluence. We are interested in examining the negative gradient slope of the response curve to determine the positive resist sensitivity of PMMA under different developing conditions.
The sensitivity of a resist is not a single universal value and is very much dependent on all of the variables in the lithographic process; film production, exposure and development. A study of sensitivity should involve experimentally generating the response function many times over with incremental adjustments to the variable under investigation. A good example of this type of study is given for electron beam lithography in the paper by Yasin et al. [8].

• **Relevance to single ion tracks**

This is referred to as a ‘macroscopic’ study of PMMA sensitivity because the irradiated areas are large and easy to view compared with the damaged area of a single ion strike. To put sensitivity in a useful form we redefine it from particle fluence to energy density. Converting from particle fluence to energy density is achieved by multiplying by the LET of the incident ions.

\[
\text{Energy Density}_{\text{macroscopic area}} = \text{LET} \times \text{Fluence}
\]

The macroscopic determination of PMMA sensitivity offers us a route to determine whether single ion tracks are likely to be etched prior to actually searching for the small etched tracks which may or may not actually exist. The energy density of a single ion strike can be estimated using the relationship given in sub-section 2.3.2 (shown again here). If the energy density of a specific ion strike exceeds the sensitivity value then the latent damage should etch.

\[
\text{Energy Density}_{\text{ion track}} \approx \text{LET} / \pi r^2
\]

• **Contrast**

An additional piece of information that can be attained from the response function is the contrast of the resist-developer combination. The contrast represents the difference in deposited energy density between the undeveloped resist and the fully developed resist. The formula for calculating contrast is given in the paper by Bernstein et al. [7]. In this definition the \( D \) represents the initial and final dose in units of Coulomb.cm\(^{-2}\), of the negative gradient section of the response function but can easily be applied to whatever value has been used on the x-axis of the response function.

\[
\text{contrast} = [\log(D_i / D_f)]^{-1}
\]

4.3.2 **Experiment**

A refined version of the preliminary experiment tested the sensitivity of 55 nm thick PMMA films. A key advantage over the preliminary experiment was using the single ion detection capability of an active substrate, as opposed to a standard current integration technique. The precise measurement of number of incident ions in a well defined area allowed fluence to be accurately calculated. The two variables under investigation were developing formula and developing time.
Figure 4.8: An optical micrograph of the $25 \times 2.5 \mu m^2$ areas of PMMA that were exposed to 3 MeV H ions with varying fluence. The number below each region represents the number of individually counted ions in each exposure region.

Figure 4.9: Diagram of the possible fluence profiles along the line of uniform fluence for the rectangular array.

Figure 4.10: (a) AFM image of the exposure area. The image is sheared to make the exposure perpendicular to the horizontal line scan. Line scans from rows 50 to 200 of the 256 row image are averaged together. (b) The average line scan is plotted to measure the depth of the exposed region.
PMMA films were exposed to 3 MeV H ions of varying fluence in areas large enough to be easily found and imaged using an optical microscope and analysed with the AFM. 3 MeV H ions were used to achieve uniform deposited energy density across the irradiated area as H ions deliver the smallest possible LET (in the electronic regime) per ion (11.2 eV.nm\(^{-1}\)), thus distributing the damage to the PMMA over many overlapping ions. The exposures were 250 × 25 beam spot arrays generated by the ion microprobe forming rectangular areas 25 × 2.5 µm\(^2\). An optical micrograph of these exposures is shown in Figure 4.8. The beam spot was approximately 2 µm in diameter (see chapter 3, Figure 3.9) ensuring multiple overlap of beam spots and an area of effectively uniform irradiation.

• **Uncertainty**

The main source of uncertainty in generating the response function comes from the measurement of fluence in the macroscopic area. The fluence can be considered uniform in the long axis of the rectangular exposed region but probably has some non-uniform profile along the short axis. The fluence profile has been calculated by convoluting the beam spot array with a single beamspot function. Two types of beamspot function have been used, square and Gaussian, representing the two likely limits of the actual function. When using a square function the maximum fluence is equal to the total number of ions in each beam spot, \(N_{\text{ions}}\), multiplied by the number of beam spots, \(N_{BS}\), divided by the total area of the exposed region. When using the Gaussian beam spot profile the resulting maximum fluence is equal to 86% of the result in the square case. Uncertainty in the experimental fluence takes into account the limits defined by the two possible beamspot functions (see Figure 4.9).

\[
\text{For overlapping square functions} \quad \text{max. fluence} = \frac{N_{\text{ions}} \times N_{BS}}{\text{Area}}
\]

\[
\text{For overlapping Gaussian functions} \quad \text{max. fluence} = 0.86 \times \left(\frac{N_{\text{ions}} \times N_{BS}}{\text{Area}}\right)
\]

During the exposure fluctuations in the count rate meant that the dead time varied between 15% and 25% with an uncertainty in the dead time measurement of 50%. The uncertainties are displayed as error bars on the response function plot in Figure 4.11.

### 4.3.3 Results and analysis

AFM imaging was used to generate a 256 × 256 pixel topographic image for each of the exposed regions. Matlab [9] was used to load and analyse the topographic images. ASCII format image files were imported into Matlab for analysis and the unwanted offset gradient of the AFM scan was removed. The PMMA depth in the exposed region was measured by creating a depth profile averaged together from rows 50 to 200 in the image (Figure 4.10). Each image was first slightly distorted using a shearing data transformation to align the depth profiles prior to averaging.
Figure 4.11: (a) Graph of the data points for PMMA height as a function of deposited energy density under different developing conditions. (b) Data points outside the linear section of each data set were removed and a linear fit applied and extrapolated to -55nm to find the sensitivity.
The PMMA height was taken as the deepest point of the average depth profile. For each exposure the measured PMMA height was plotted against the deposited energy density. Three developer combinations have been investigated, MIBK:IPA 1:3, MIBK:IPA 1:1 and water:IPA 1:4 and response functions generated are shown in Figure 4.11 (a).

- Curve fit to data

Data points outside the linear section of each data set, less than -50 nm and greater than -1 nm, were removed so that a linear fit could be applied. The linear fit was extrapolated to the 55 nm thickness of the PMMA films to give the sensitivity of each developing combination. The exclusion of data points outside the linear section and the linear fit are shown on the plot in Figure 4.11 (b). The results of sensitivity and contrast are displayed in Table 4.1.

- Comparison

Yasin et al. [8] gives a comparison between developer combinations for electron beam lithography. Response functions were generated using $10 \times 100 \mu m^2$ exposures in 1 µm thick PMMA using 50 keV electrons. The results show that maximum sensitivity was achieved using the developing solution water:IPA 1:4 for 5 minutes.

In the IBL study presented here of the three developing solutions tested the highest sensitivity is for the water:IPA 1:4 mixture. The sensitivity of any developing formula can be increased by increasing the developing time. There is however an upper limit on the time because PMMA films have been shown to fail mechanically over time (see Figure 4.12).
<table>
<thead>
<tr>
<th>Components</th>
<th>Ratio</th>
<th>Time (s)</th>
<th>Sensitivity (55 nm) (eV.nm(^{-3}))</th>
<th>Sensitivity (1 µm) (eV.nm(^{-3}))</th>
<th>Contrast</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIBK:IPA</td>
<td>1:3</td>
<td>600</td>
<td>1.4</td>
<td>17.6</td>
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<td></td>
</tr>
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<td></td>
<td></td>
<td>30</td>
<td></td>
<td>32.5</td>
<td>5.4</td>
<td>Yasin[8]</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>60</td>
<td>3.5</td>
<td>51.5</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>Water:IPA</td>
<td>1:4</td>
<td>60</td>
<td>1.7</td>
<td>25.2</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>300</td>
<td>1.0</td>
<td>18.5</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3:7</td>
<td>30</td>
<td></td>
<td>23.7</td>
<td>6.4</td>
<td>Yasin[8]</td>
</tr>
</tbody>
</table>

Table 4.1: Sensitivity and contrast of the developing solutions.

For comparison between the EBL and IBL results the charge fluence of the EBL paper (units µC.cm\(^{-2}\)) had to be converted to deposited energy by multiplying by the energy loss of 50 keV electrons in PMMA. This energy loss was calculated to be \(\sim 1\) eV.nm\(^{-1}\) using the electron modelling program CASINO [10]. The linear fit was extrapolated to a thickness of 1 µm to match the film thickness used in the EBL experiment. However, the extrapolation to 1 µm is far away from the original data set so the errors are large. A key difference in the parameters used in the Yasin paper was that the PMMA film was baked at 180 °C for 24 hours as opposed to 10 minutes for this study. The sensitivity and contrast values from the EBL experiment are also shown in Table 4.1 for comparison with the results from the IBL study.

The EBL sensitivity values (with a developing time of 30 s) are close to the values measured here (with double the developing time – 60 s). There is a difference in contrast between the two sets of results and there are three possible reasons for this:

1) The shorter developing time of 30 s improves contrast.
2) The extra baking time has increased the resistance of the undamaged PMMA to the developing solution thus improving contrast.
3) The measurements of contrast in IBL are not accurate due to greater noise on the fluence coming from fluctuations in ion beam current, thus impeding the ability to measure contrast accurately.
4.3.4 Conclusion

The maximum sensitivity found was 0.1 eV nm\(^{-3}\) for a 55 nm thick PMMA film using the developer water:IPA 1:4 for 5 minutes. It is reasonable to assume that this sensitivity value gives the greatest likelihood of being able to etch low LET, light ion tracks (a calculation of energy density for different ion tracks is given in section 4.5). For initial studies contrast is not considered to be of primary importance. If a single ion track can be etched and imaged then the initial aims (stated in section 1.2) of the project have been met. One would logically choose a resist–developer combination with high sensitivity.

However, while a high sensitivity might provide the ability to etch single ion tracks the contrast of the resist–developer combination is worsened. As shown in the next section 4.4, the thickness and surface roughness of the undamaged PMMA is changed when using a high sensitivity process. These changes represent characteristics of a low contrast process and have important consequences. The change in thickness represents bulk etching of PMMA and therefore makes it difficult to examine the radial damage profile of the native ion track. All information is washed away as the bulk undamaged material is etched. Also, the increase in surface roughness is a critical factor when attempting to image the etched holes of single ions. The roughness is exhibited as the noise in the topographic AFM image. The useful information about the radial profile of a hole may be lost within this noise. To continue the development of the IBL process contrast does become an important factor. It is generally accepted that the resolution of a resist–developer system depends on contrast [8] [11].

Yasin [8] reports that the water:IPA combination gives improved contrast over the MIBK:IPA combination and that the developer strength can be adjusted by changing the ratio of components, with the 1:4 ratio the most aggressive (highest sensitivity but lowest contrast). To achieve the best resolution in high aspect ratio lithography it is necessary to maintain high contrast, therefore one would use a low strength developer to avoid etching the unirradiated PMMA. The required sensitivity can then be achieved by tailoring the developing time to match the time required for complete etching of the long narrow tube of a single ion track.

It is clear that to create an etched hole along the track of a single ion—but without over-etching the bulk material—a high sensitivity and high contrast process is needed. The best way to achieve a good balance between sensitivity and contrast is to relax the necessity for high sensitivity. This is done by creating a damage track with the largest possible damage density; achieved by either using a single high LET ion or multiple overlapping low LET ions.
Figure 4.13: (a) An optical micrograph of the PMMA film and registration markers. (b) An AFM image of the registration marker, the dashed line indicates the position of the depth profile. (c) The depth profile across the registration marker indicates the height of the unexposed PMMA. A flat bottom on the profile shows that the PMMA has been fully exposed in the region of the marker.

Figure 4.14: (a) Depth profiles of line features made in five separate PMMA films. The height of the unexposed PMMA can be measured because the line has been fully developed down to the Si substrate in each case. The depth profiles are measured using non contact AFM with a standard tip. (b) The unexposed PMMA height is plotted against the developing time. For the sample developed for 16 minutes the film was completely removed.


4.4 PMMA thickness and roughness versus developer

4.4.1 Introduction

The importance of creating a developing process with high contrast was raised in the previous section. This section aims to characterise the etch rate and surface roughening of unirradiated/undamaged PMMA with a view to minimising these two effects. By increased resistance of undamaged PMMA to the developing solution the contrast of the process will be improved. Two studies have been conducted, (1) the etch rate of unexposed PMMA and (2) surface roughness as a function of developing time.

4.4.2 Experiment – Etch rate of unexposed PMMA

To measure the etch rate of unexposed PMMA a film was exposed using electron beam lithography to create a line feature. Samples were then developed over a range of developing times and the PMMA height measured with non-contact AFM (Figure 4.13). This experiment was performed on the registration markers of PMMA samples. Because the EBL defined line was previously developed (see sub-section 3.3.5) the measurement of the PMMA height was always relative to the substrate surface. The developer water:IPA (1:4) was used and developing times ranged from 30 s to 16 min.

4.4.3 Results – Etch rate of unexposed PMMA

There was no change in bulk unexposed film thickness, shown in Figure 4.14, for the first 4 data points over a time period of 4 minutes. Then there was a reduction in film thickness of approximately 80 nm over the following 4 minutes. Finally, over the following 8 minutes, the solution penetrates the polymer matrix and the PMMA film fails mechanically and delaminates from the surface. Evidence of delamination is given in an optical micrograph of an auxiliary sample that was developed for 7 min (Figure 4.12). In this case cracking and removal of large plates of the PMMA is observed.
Figure 4.15: (a) An example of a 4 µm² AFM image used to quantify the PMMA surface roughness. (b) A Gaussian function is fitted to a pixel height histogram of the image. The Gaussian width is used to quantify the surface roughness.

Figure 4.16: (a) Plot of surface roughness versus developing time for the solution water:IPA 1:4. (b) Shown are AFM topographic images for developing times 1, 2, 4 and 8 minutes. For each image a height profile (in nm) of the PMMA surface is shown.
4.4.4 Experiment – PMMA surface roughness

When using AFM a major limitation in finding etched single ion tracks is the surface roughness of the material being imaged. This surface roughness is exhibited as the “noise” in the topographic AFM image, in the sense that the fine structure of the PMMA surface may mask the presence of single ion tracks. If the amplitude of the surface roughness is greater than the scanned depth of the holes under study it is impossible to perform analysis. The quantified surface roughness as a function of developing conditions was extracted from the AFM images collected during the single ion impacts study of Section 4.5.

4.4.5 Results – PMMA surface roughness

A pixel height histogram was generated for each AFM image and is shown in Figure 4.15. The distribution of pixels at the PMMA surface formed a peak in the histogram. A Gaussian curve was fitted to this peak using the function:

\[ \text{Number of pixels} = A_i \exp \left\{ -\frac{(z-\mu_i)^2}{2\sigma_i^2} \right\} \]

The Gaussian width, \( \sigma_i \), was used to quantify the surface roughness (the subscript, \( i \), indicates a curve fit to the image histogram). During the acquisition of the many PMMA surface images it was found that the quality of the Si nanowhisker tip degraded due to incidental contact with the surface. For this reason a new tip was selected after there was an observed loss in image quality. Therefore it was not possible to maintain the tip as a constant. The roughness value, \( \sigma_i \), for each image is plotted as a function of the developing time in Figure 4.16.

4.4.6 Conclusions

In the early stages of developing the films are roughening though the thickness remains unchanged. In later stages the PMMA film gradually decreases in thickness and the surface becomes less rough. The latter effect is not necessarily intuitive, and so two possible explanations are given:

1) The lower surface roughness value for the 8 min development could be attributed to the AFM tip selection. Different tips were used because it was found that tip quality deteriorated over multiple images therefore it was not possible to use a single tip for all images.

2) During early stages of development lower molecular weight polymer chains at the surface of the PMMA are preferentially removed thus roughening the surface. These shorter polymer chains could be the result of chain scission at the surface of the film from incidental exposure to ambient UV light, not penetrating more than a few nanometres. After a longer period of time the developer has a chance to further penetrate the polymer matrix and begin to remove the bulk undamaged PMMA, thus having a smoothing effect.
<table>
<thead>
<tr>
<th>Ion (MeV)</th>
<th>$e$ LET (eV/nm)</th>
<th>Radius (nm)</th>
<th>Energy density (eV/nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 H</td>
<td>$1.1 \times 10^4$</td>
<td>2</td>
<td>0.9</td>
</tr>
<tr>
<td>2 He</td>
<td>$1.5 \times 10^4$</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>8 F</td>
<td>$1.4 \times 10^3$</td>
<td>10</td>
<td>4.4</td>
</tr>
<tr>
<td>71 Cu</td>
<td>$4.8 \times 10^3$</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>88 I</td>
<td>$7.2 \times 10^3$</td>
<td>10</td>
<td>23</td>
</tr>
</tbody>
</table>

Table 4.2: Table of calculated damage densities. For low LET ions, H and He, 2 nm is used for the track radius. For high LET ions, F, Cu and I, 10 nm is used as an estimate of the track radius.

Figure 4.17. AFM images of 20000 and 10000 2 MeV ions in developed PMMA.

The time frame in which the bulk/undamaged PMMA is not etched for water:IPA 1:4 is 4 minutes. This is an interesting result because it means that the etch rate of the PMMA is not constant. An interpretation of this effect is that the contrast of the process is stable over this time period, even as the sensitivity increases with increasing developing time. It follows that this time frame is scaleable based on the strength of the developer used. For example, if a less aggressive developer is used, the time in which no PMMA etching occurs may be longer. This may prove to be a useful feature of the lithographic process, offering a way to achieve the sensitivity required to etch the tracks of low LET single ions without a loss in the contrast of the process.
4.5 Study of single ion holes in PMMA at the nanoscale

4.5.1 Introduction

A sensitivity threshold of 0.1 eV nm\(^{-3}\) has been measured from the response function generated in section 4.3 for the most sensitive resist–developer combination. A relationship, introduced in section 2.3 is used to calculate the approximate damage density deposited along a single track (see Table 4.2).

\[ \text{Energy Density}_{\text{ion track}} \approx \frac{\text{LET}}{\pi r^2} \]

From the review in chapter 2 the effective radius of an ion track is approximately equal to 2 nm for a 1 MeV u\(^{-1}\) ion with a low LET. The effective radius is expected to increase when the LET increases above some threshold value and into the high LET regime and an estimate of 10 nm has been used.

If the energy density inside a single ion track is above the sensitivity threshold then the track should etch. All of the calculated values for energy density, including H and He ions, are above the threshold therefore should etch. However, the high aspect ratio geometry of the latent damage track may also have an additional effect slowing the etch rate due to the reduced mobility of the finitely viscous developer inside the track compared with a macroscopic area. Therefore a direct comparison between sensitivity of a macroscopic area with the sensitivity of a single ion track may not be applicable.

4.5.2 Preliminary Experiment (low LET)

Initially a 2 MeV He ion beam was used to produce holes etched along single ion tracks. This experiment was performed before the sensitivity data had been compiled. Therefore, the PMMA film was developed in MIBK:IPA 1:3 for only 60 seconds (based on the results of the Miller et. al. paper [2]). The images shown in Figure 4.17 of 20000 and 10000 ion impacts do not clearly show individual ion impacts. It was also not possible to easily identify any features in the PMMA when the number of ions inside the beamspot was reduced to below 10000.

4.5.3 Experiment (high LET)

The aim in this experiment is to create single ion tracks that can confidently be predicted to etch so it is therefore sensible to choose ions where the expected energy density is well above the required threshold. This was ensured by employing heavy ions: 8 MeV F, 71 MeV Cu, 88 MeV I. PMMA films were exposed to the ion beams with a low enough particle fluence so that single ion strikes would not overlap. This allowed the study of hole formation for the three separate incident ions under different developing conditions.
Figure 4.18: Optical micrographs of the exposed regions of the five samples. This shows that the ion beam exposures have been well located on the registration grid. The number of ions per beam spot is displayed against each row of the registration grid.
A PMMA covered photodiode (700 nm thick) was prepared with an electron beam lithography registration grid. At selected points on the grid the PMMA film was exposed to 4 × 4 arrays of focused beam spots. The number of ions for each exposure ranged from 10 to 3×10^4 ions per beam spot, ensuring that a region existed with low enough fluence to prevent overlap of single ions. All three ion species were exposed on one sample. Samples were developed for 1, 2, 4, 8 and 16 mins and there was a different sample for each development parameter set. For the sample developed for 16 minutes the film was completely removed. Figure 4.18 shows how the 4 × 4 arrays have been located relative to the registration grid.

4.5.4 Results

Non-contact AFM was used to image the ion irradiated areas. A high aspect ratio Si nanowhisker tip allowed higher resolution and image depth than a standard tip. Areas containing less than 300 ions in the 5 µm beam spot showed very little overlap between the single ion impacts.

This result demonstrates the precise counting achieved by the photodiode detector. In the bottom-centre image of Figure 4.19 it is possible to count exactly 30 holes, the same number of ions that were detected during the exposure. However this accuracy was not readily achieved. In most cases the number of holes counted was not equal to the number of ions detected, variations of up to ±30 % were observed with fewer and extra ions observed over the data set. There were two reasons for the discrepancy between the number of holes and the number of ions detected.

1. Beam current variation and scanning coil latency. The accelerator does not deliver one ion at a time in even intervals. It is possible that multiple ions could be detected in quick succession in a short time frame, or as a single pile-up event, before the signal has been passed to the scanning coils to move the beam spot to the next position resulting in more holes than ions detected.

2. Ion scattering. It is possible for an ion to be counted but actually hits the detector in some region outside the focused beam spot resulting less holes than ions detected. For large numbers of ion impacts this can be seen as a full energy peak that does not move to lower energy even as the detector is damaged in the region of the focused beam spot.

Figure 4.20 shows the evolution of single track etching over increasing developing time in a 2 × 2 µm^2 area containing 30 ions per beam spot. It can be seen that as the etching occurs the PMMA surface is roughened and the width and depth of the holes increases.
Figure 4.19: AFM images of the 5 µm beam spot made using 88 MeV I and developed in water:IPA 1:4 for 8 minutes. The number of ions in each beam spot is precisely controlled.
Figure 4.20: The evolution of single track etching for the three ions species 88 MeV I, 71 MeV Cu and 8 MeV F. Each image is a $2 \times 2 \mu m^2$ area located inside a single beam spot containing 30 ions. The developing solution was water:IPA 1:4.
Figure 4.21: Image processing flow: generating a pixel height histogram, subtracting the horizontal offset, finding the surface roughness discriminator level and generating a one-bit image with the surface at 0 nm.

Figure 4.22: (a) From the one bit image holes are selected at random and a depth profile generated from the 16 bit image. (b) For each depth profile a Gaussian function is fitted so that the hole depth, $A_h$, and width, $\sigma_h$, can be quantified.
**Image analysis**

An algorithm to identify ion impacts was adopted as follows. AFM imaging was performed at a resolution of 512 × 512 pixels. The 16 bit ASCII format topology data was loaded into Matlab, the image height was calibrated to scanned height, \( z \), and the image displayed. For each \( 2 \times 2 \mu m^2 \) image a pixel height histogram was generated, as was used in the surface roughness study of Section 4.4. A Gaussian curve was fitted to the histogram data using the equation, \( A_i \exp[-(z-\mu_i)^2/(2\sigma_i^2)] \), the subscript, \( i \), indicating a curve fit to the image. A tail on the height data, at lower \( z \) values, represented those pixels inside the holes. The horizontal offset of the Gaussian function, \( \mu_i \), was subtracted from the entire image to normalise the PMMA surface equal to a height of 0 nm. A surface roughness discriminator level was set at the pixel height where the Gaussian fit intersected the y-axis equal to 1 pixel. As each sample had a different surface roughness the discriminator level was dependent on the Gaussian fit. This level was used to create a one-bit image showing the location of holes. The process for creating the one-bit image is shown diagrammatically in Figure 4.21.

A depth profile was generated for a select number of holes in the one-bit image. An example one-bit image is shown in Figure 4.22 (a) with six holes selected and numbered at random. The depth profile of hole number 3 is shown in Figure 4.22 (b). A Gaussian curve was fitted to each depth profile, \( z = A_h \exp[-(x-\mu_h)^2/(2\sigma_h^2)] \), the subscript, \( h \), indicates a curve fit to the hole. The amplitude, \( A_h \), and sigma value, \( \sigma_h \), were used to quantify the measured hole depth and width.

**Tip quality**

For accurate imaging tip quality was an issue. Tip quality was monitored by re-imaging previously imaged areas. An observed loss in the measured depth of the holes meant that the tip was not penetrating as deeply and necessitated the selection of a new tip (as shown in Figure 4.23).

**Actual hole depth**

The actual hole depth is not necessarily known because the scanned depth depends on the shape of the AFM tip. If the holes are sufficiently deep, beyond the probed depth, it is anticipated that the measured depth and width are related solely to the shape of the AFM tip, with the consequence that when plotting width versus depth all of the data should lie on a unique curve. However, if the holes are not sufficiently deep then the measured depth will be equal to the actual hole depth and the depth and width will be uncorrelated. This concept is illustrated in Figure 4.24. Therefore a change in the damage density brought about by a different ion would lead to a difference in probed depth for each ion species.
Figure 4.23: To monitor tip quality three images are compared; the impacts of 88 MeV I, developed for 8min in water:IPA 1:4. The hole width versus depth for the three images shown. After performing multiple images of similar areas the hole depth is observed to reduce therefore indicating that the tip quality has decreased.

Figure 4.24: Illustration of the scanned depths of an AFM tip when scanning a hole. The scanned depth is governed by the shape of the tip or the actual hole depth, depending on the geometry of the situation.
Figure 4.25: (a) Hole depth versus hole width for single ion impacts from F, Cu and I ions. (b) For each data set the mean values have been plotted.

- **F ions**

  In Figure 4.25 the mean value for the width versus depth for every hole in the data set is shown and only F ion impacts developed for 8 min are shown. For a developing time of 4 min holes can be observed (see Figure 4.20) but a higher surface roughness value meant that the surface roughness discriminator level disallowed quantitative analysis of the holes.

- **Cu and I ions**

  For Cu and I ion impacts the data was collected for 1, 2, 4, and 8 minutes developing time. A hole width below $\sigma_h \approx 10$ nm was not measured and it is believed that this is due to the finite width of the cantilever tip.
The hole radius is approximately equal to one width parameter, \( \sigma_h \), of the Gaussian distribution fitted to the depth profiles. Can the radius of damage due to secondary electrons be extracted from this measurement of the hole’s radius? When developing the tracks of Cu and I ions longer than 4 minutes the hole radius does not significantly increase. Therefore all material that can be removed has been removed when using the water:IPA 1:4 solution. No excess, undamaged material has been removed because there is no change in hole radius for the 8 min developing time.

The damage density due to energy deposition beyond the measured radii is therefore zero. The damage threshold for the etching of PMMA is no greater than zero because a reduction in film thickness of 80 nm was observed in the unirradiated/undamaged PMMA over the time period from 4 minutes to 8 minutes. Therefore the hole’s diameter after 4 minutes developing is equal to the maximum damage radius of the track. This is an important result because the radius out to which all damage is occurring can be experimentally determined. Even though the result set for F has only one data point we can still deduce that the maximum radius has been reached based on the assumption that all possible damage has been etched.

4.5.5 Conclusion

It has been shown that it is possible to create holes in the PMMA film using the tracks of I, Cu and F ions. It has not yet been determined if the high aspect ratio of the tracks has been fully converted into a fully etched void along the length of the track Owing to the difficulty of measuring high aspect ratio tracks. The depth of holes etched along the Cu ion tracks are marginally shallower that those etched along the I ion tracks even though the widths are the similar. This indicates that the widths and depths are possibly uncorrelated for the two separate ion species, therefore the measured depth is due to the actual hole depth and not limited by the shape of the tip as demonstrated in Figure 4.24. This effect however is only slight and not beyond the tolerance imposed by the measurement uncertainties.

This result is surprising because the damage density inside the tracks, a result calculated by dividing the LET by the measured track radius, is above 1 eV.nm\(^{-3}\) for all three ion species developed for 8 min. This is well above the sensitivity value of 0.1 eV.nm\(^{-3}\) measured for the 5 min developing time in the macroscopic exposure experiment. It is however possible that because of the confined nature of the single ion track some delay in removing the etchable material is imposed. The mobility of the etchant is slowed in the long narrow capillary of the latent damage track.
4.6 Chapter summary

For holes etched along the tracks of single He ions in CR-39 (from an alpha source, energy up to 5 MeV) AFM was used to produce images of the holes. For He ions with an LET of 152 eV.nm\(^{-1}\) and energy density of approximately 12 eV.nm\(^{-3}\), inside a 2 nm cylinder, this experimental work has attempted to find holes etched along single tracks in PMMA. Using a low sensitivity developing process (MIBK:IPA 1:3 for 60 s) it was not possible to find the tracks of single ions.

The sensitivity of several PMMA resist-developer combinations was determined using a macroscopic exposure to 3 MeV H ions. The sensitivity was calculated in units of eV.nm\(^{-3}\) so that sensitivity values could be used to determine the likelihood of etching single ion tracks.

To improve the chances of finding holes etched along single ion tracks the highest sensitivity resist process was used and higher LET ions were used. The result was the ability to image single ion tracks of F, Cu and I ions and characterise the radii of these tracks. These measurements of radii are characteristic of the initial energy deposition profile and not simply dependent on the development time. While this experimental result gives us the maximum radius of damage for these three ion species it does not tell us the shape of the damage profile about the core of the ion track.

The results from the F ions suggest that for ions lighter than F, either holes are not produced or are too small to be seen. It is difficult to see how a single He ion, with an LET approximately one order of magnitude below F, could be developed into an etched hole in PMMA. The limitation imposed by surface roughening, poor contrast with increasing sensitivity and a limit of AFM tip diameters of ~10 nm means that to image and measure the actual damaged area resulting form a low LET ion impact, such as 2 MeV He will be challenging.

Provided the ion LET is sufficiently high to provide successful single ion track imaging, the technique demonstrated in this chapter may be used to produce experimental data for comparison to the results from theoretical models of track formation [12-13] (refer to discussion in section 2.4).

In some theoretical models the latent damage may extend beyond the delta electron range due to a Coulomb implosion or thermal spike that is the result of a large displacement of charge around the ion track for high LET ions. In future work this experimental method may be used to pin point the LET value at which the atomic motion phenomena begin to take effect and broaden the damage profile of a single ion strike beyond the initial range of delta electrons. However, in this experiment the data set is not large enough to clearly indicate whether or not atomic motion has yet to have an effect in the ion tracks studied.
4.7 Bibliography


Chapter 5  Development of a nano-positioning system

5.1  Introduction to the chapter

5.1.1  Project Overview

The proceeding chapters have demonstrated the creation of lithographic features using the latent damage track from a single ion track. From experiment it has been observed that the maximum damage radii for 71 MeV Cu and 88 MeV I ions is approximately 30 nm and 15 nm for 8 MeV F ions. This technique offers the unique ability to damage the resist over a very large depth while maintaining the resolution that was delivered to the surface. Upon development, in positive resist processing, the latent damage is etched to create an extremely high aspect ratio void in the resist material, a hole. This thesis has also demonstrated that a single ion can be detected once it has passed through the resist layer. This is achieved by spin coating the resist film onto a photodiode which acts as a detector sensitive to the ion’s impact. Therefore extremely accurate dose normalisation is achieved. The final ingredient in the development of a high resolution ion beam lithographic process is the ability to precisely position each ion impact on the target. This chapter presents work undertaken towards the development of such a system.

5.1.2  Proposal

In all forms of lithography there are two ways to define the location of the structure being patterned. (1) Using a mask, and (2) direct write. As ion beam lithography is relatively new compared to other lithographic techniques the field has seen the use of masks [1-2] and direct write using by electromagnetic scanning [3] or by moving the target sample on a positioning stage relative to the beam position [4].

The question posed is which method gives the best chance of achieving resolution in the same order of magnitude as the diameter of a single ion track? First the idea of using a broad beam exposure and a patterned mask can be excluded. The features on the mask would have to have the same small resolution that are intended to be pattern into resist, and also have a high aspect ratio so that ions would be stopped by the mask. The mask making process would have to completely produce the same high aspect ratio nano structure as the intended lithographic structure. Additionally the highly accurate dose normalisation achieved with single ion detection would be lost as the dose would be normalised over the entire pattern rather than point by point.
Figure 5.1: Set up proposed for using a nano scale aperture and scanning stage in ion beam lithography. (a) An AFM tip is used to register the position of the beam on the target. (b) The beam spot size is defined by a nano-scale aperture. The thickness of the aperture must be greater than the ion range. (c) Single ion impacts are detected by an active substrate. The beam spot position is defined by a piezoelectric scanning stage.
With recent developments in the construction of high aspect ratio nano-scale apertures (for example the work detailed in [5-8]) comes the prospect of using such apertures as a mask to define the beam of ions at a single point on the target. The method proposed here is a direct write method on a scanning stage (illustrated in Figure 5.1). Scanning is achieved by mounting the sample on a piezoelectric scanning stage with a minimum step size below 1 nm. In this scenario some beam focusing is required to achieve a sufficient fluence on the aperture, however the beam spot size is defined by the aperture not the focusing. The aperture is milled in a Si cantilever using focused ion beam (FIB) milling using low energy ions in the nuclear LET regime. The Si cantilever is sourced from those used in atomic force microscopy (AFM) and imaging of the target surface may be possible with appropriate feedback from the motion of the cantilever.

This technique offers us some advantages over the more traditional direct write focusing and magnetic scanning method as seen in the work by Watt et. al. [3].

(1) The system can be retrofitted to any ion accelerator. While state of the art ion beam focusing systems are currently creating beam spot sizes below 100 nm, the pay offs that result from improving the resolution of the focusing and scanning systems offer diminishing returns due to (1) difficulty in manufacturing sufficiently accurate ion optic lenses, (2) influences of vibrations and stray fields, (3) focusing difficulties and (4) brightness and chromaticity limitations. This technology may provide an improvement over many orders of magnitude for focusing systems operating at 1-10 µm straight to the sub 100 nm realm.

(2) A built in AFM provides imaging and registration. With the aperture drilled in an AFM cantilever the possibility exists to perform imaging on the target prior to ion beam irradiation and therefore register the ion beam lithography with some existing feature on the sample’s surface.

5.1.3 Chapter Overview

The section headings in this chapter refer to progress made towards the development of an aperture based ion beam lithography technique. In section 5.2 Creation of a nanoscale aperture, results are shown of experimentally created apertures. In section 5.3 Modelling an ion beam through an aperture, the angular spread of ions, starting as a parallel beam, after passage through a nanoscale aperture has been modelled with an ion Monte Carlo transport code. In section 5.4 Design of the hardware, the technical issues towards mounting the scanning and single ion detection components are addressed. In section 5.5 Lithography through an aperture, the first experimental results are presented.
Figure 5.2: TRIM simulations of H and He ions (1 MeV/u) give the range in Si. For an aperture to be effective the Si thickness must be greater than the ion range.

Figure 5.3: (a) SEM image of milled apertures through an 8 µm thick cantilever using the Orsay Physics Canion FIB. Registration of the location of the holes was difficult. (b) SEM image of milled slots and apertures through a 3 µm thick cantilever using the FEI Nova Nanolab FIB. Good calibration of the Ga beam on the sample with respect to the SEM imaging meant that the milling was well located.
5.2 Creation of a nanoscale aperture

5.2.1 Specifications

The layer of material in which the aperture is placed should be thick enough to stop ions of 1 MeV.u\(^{-1}\). A range of 17-18 µm in Si is determined by modelling 1 MeV H and 4 MeV He using SRIM (Figure 5.2). The FIB milling aims to form an aperture with a diameter of less than 100 nm. This first milestone will realise the fine resolution that can be achieved with a precision focusing system, demonstrated in the work of van Kan et. al. [9]. The aim is to improve the FIB milling procedure so that the hole size approaches a second milestone of 10 nm, thus entering the realm where the lithographic resolution is limited by the diameter of a single ion track.

5.2.2 Experiment

Work towards the creation of apertures milled in Si was carried out by Michael Taylor of RMIT University and Michael Beljaars, visiting from the Technial University of Eindhoven, under the supervision of Sergey Rubanov at the University of Melbourne. Two FIBs at the University of Melbourne can produce focused beams of Ga ions in the nuclear LET regime at a nominal energy of 30 keV. The FIBs can be routinely focused to 100 nm and are equipped with SEM columns to allow viewing of the structures created. AFM Si cantilevers were purchased from NT-MTD and experiments were carried out to mill the Si cantilevers. The Ga beam current was measured at 3.6 nA. As it was only possible to view the holes after milling and with the Ga beam turned off some experimentation was needed to determine the conditions required to produce a hole through the full thickness of the Si cantilever without overexposing and increasing the hole size.

5.2.3 Results

Two Si cantilevers have been machined to produce a series of apertures. The Orsay Physics Canion FIB milled a holes in an 8 µm thick Si cantilever. Upon investigation with SEM an completely milled hole had a diameter of 1.4 µm on the top surface and approximately 200 nm on the opposite side. An SEM image that was used for measurement is shown in Figure 5.3 (a). Positioning of the holes on the Si cantilever was difficult because the location of the Ga ion beam spot with respect to the SEM imaging was not well known.

The FEI Nova Nanolab FIB was used to mill two perpendicular slots and a series of holes in a 3 µm thick Si cantilever. Upon investigation with SEM a completely milled hole was observed with a diameter of 250 nm on the top surface and an irregularly shaped hole, 240 nm × 60 nm, on the opposite side and is shown in Figure 5.3 (b). Good alignment between the location of the Ga and SEM beams meant milling sites were accurately positioned.
5.2.4 Conclusions

Initial experiments show that it is possible to mill holes in Si cantilevers with an aspect ratio of approximately 10:1 and resolution approaching 100 nm. Holes are conical due to the nature of the FIB milling process. The paper Schenkel et al. [6] reports a 30 nm diameter hole in a 30 nm thick silicon nitride film. It is expected that further refinement to the milling process will improve the current results with at least some portion of the aperture’s diameter below the milestone of 100 nm. With the FIB it is not expected that it will be possible create a hole less than 10 nm in diameter through 10 µm thick Si. Work beyond this thesis will attempt to back fill a conical shaped hole by evaporating metal onto the Si after FIB machining as illustrated in Figure 5.4, a method proposed by Schenkel et al. [10].

In current investigations the maximum Si thickness for cantilevers purchased from NT-MDT is 8 µm therefore the ion range in Si must be less than this. By choosing an ion beam 1.5 MeV He with range 5.5 µm in Si experiments can be conducted to test the viability of using such a nano aperture as a mask in ion beam lithography.
5.3 Modelling an ion beam through an aperture

5.3.1 Motivation

If the ion range is less than the thickness of the mask there still exists the possibility of an incident ion colliding with atoms in the aperture material and a scattered ion emerging from the mask, at some reduced energy. This is illustrated in Figure 5.5 (a). For an aperture masking technique to be successful the number of ions scattering from the aperture must be negligible compared to the number of ions passing through the aperture.

5.3.2 Simulations

Ion scattering was investigated by a 3D Monte Carlo modelling program based on the TRIM code of Zeigler [11]. Modification to the code was needed to incorporate the geometry of the aperture. Simulation work was carried out by Michael Taylor and Rick Franich from the RMIT University Department of Applied Physics. Presented here is a summary of the work as the results are highly relevant to the application of the nano aperture to ion beam lithography. The work is also presented in the paper by Taylor et.al.[12].

Simulations of 2 MeV He, 8 MeV F and 71 MeV Cu ions through an aperture indicate that the masking is highly effective. The mask is defined as uniform Si slab with a cylindrical aperture either 100 or 40 nm radius and the thickness is equal to twice the range of the ion.
Figure 5.6: Plot of ion beam intensity and mean energy as a function of radial distance\cite{12} for 2 MeV He ions passing through an aperture (radius 100 nm). (a) zero degrees (b) half closure angle (c) full closure angle.

A percentage of the total number of ions transmitted through the aperture is given. $T$ (82-93\%) represents those not scattered therefore have no change in energy or direction, $S_{in}$ (4-14\%) represents those scattered inside the region of the aperture and $S_{out}$ (2-5\%) represents those scattered outside the region of the aperture (see). This indicates a large contrast between the density of ions in the beamspot defined by ions passing through the aperture, and the beam halo defined by the ions scattering from the aperture material. A plot of ion beam intensity and mean energy as a function of radial distance is given in Figure 5.6.

The paper by Taylor et. al \cite{12} also investigated the ratio of scattered ions to transmitted ions as the tilt of the aperture is changed with respect to the ion beam. The aperture closure angle is chosen as the angle at which the path length through edges of the aperture becomes equal to
the ion range. To calculate path length, $P$, of an ion in Si for an aperture with thickness, $L$, and diameter, $d$, for tilt angle, $\theta$, the following formula was used.

$$ P = \frac{(L - d \tan \theta)}{\cos \theta} $$

A diagrammatic representation of the closure angle is shown in Figure 5.5 (b). The simulations show an increase in the percentage of scattered ions for a misaligned beam, leading to a broadening of the beamspot size and decreased contrast between the aperture defined beamspot and the halo of scattered ions (Figure 5.6 (b and c)). Therefore if the tilt angle for any configuration of aperture thickness, radius and ion range is greater than the half closure angle one should expect the high contrast intensity profile to be lost, to the detriment of the lithographic process. It is therefore crucial that, experimentally, the aperture is aligned with an accuracy greater than half the closure angle.

5.3.3 Conclusions

The key element in the simulation results is the sharp side walls of the function ‘ion intensity versus radial distance’. In a lithographic process the deposited energy density in the resist can easily be scaled with multiple ion strikes and this sharp nature exploited by tailoring the sensitivity threshold of the resist to be above any damage due to the halo of scattered ions. From the experimental results in section 4.3 it is observed that the PMMA sensitivity can be easily adjusted using changes to the development time and formula.

The level of accuracy required for tilt alignment may be determined by performing a lithographic experiment using the aperture that has been fabricated in section 5.2. Where $L = 8 \ \mu$m, $d = 0.7 \ \mu$m and the ion range of 1.5 MeV He in Si is 5.5 $\mu$m. There is no simple analytical solution for $\theta$ in the equation describing the path length of an ion travelling through a tilted aperture. Therefore it has been solved numerically. The half closure angle for this specific case is approximately 7°. Beyond this initial experiment the aim is to produce an aperture with a radius of 10 nm. Again using 1.5 MeV He in 8 $\mu$m thick Si the half closure angle is approximately 0.1°.

Though an experimental apparatus may easily be constructed which allows fine adjustment (less than 0.1 of a degree) of the tilt angle the challenge will be to make an accurate measurement of this angle with respect to the ion beam. By placing a detector behind the aperture one will be able to generate an energy spectrum for each tilt angle and therefore determine the best possible alignment. A spectrum with the largest number of full energy ions compared to reduced energy ions will reveal the optimised tilt alignment.
Figure 5.7: Diagram demonstrating the position of the eucentric point.

Figure 5.8: Schematic of the assembly of the scanning stage.
5.4  Design of the hardware

5.4.1  Aim of hardware

The aim was to build the appropriate components for performing ion beam lithography using a single aperture as a mask with the sample mounted on a piezoelectrically driven scanning stage. The set up should also include the single ion detection capability demonstrated in chapter 3 and 4. The technical challenges that have been encountered and addressed are presented here.

5.4.2  Mounting the scanning stage

The piezoelectric scanning stage was a 70 x 70 µm Nanonics 3D Flatscanner™. It provided incremental movement in three dimensions with less than one nanometre positioning accuracy. A computer controller card was used to deliver a drive voltage of up to ±125 V DC. The position repeatability and drift of the Flatscanner has not been determined. The mounting assembly was designed and built in house. A mounting disk placed in the central opening of the Flatscanner allowed mounting of photodiodes. A base plate was made to attach the 3D Flatscanner to the mounting plate of the target stage. A goniometer with four degrees of freedom (lateral x and y and tilt \( \varphi \) and \( \theta \), see diagram in Figure 5.7) enabled movement of the target around an eucentric point. The base plate and centre disk were designed so that the front surface of the photodiode would sit in the target plane containing the eucentric point.

With the beam axis of accelerator aligned with the eucentric point there should be no translational movement of the beam spot on the front surface of the photodiode when adjusting the tilt angles \( \varphi \) and \( \theta \). The design of the mounting assembly is shown in Figure 5.8 and a photograph of the assembly mounted onto the goniometer shown in Figure 5.9.

5.4.3  Photodiode loading and signal connections

Three holes in the centre disk gave provision for two photodiodes to be mounted with the signal cables exiting through the third hole. The signal cables were in close proximity to the lines that applied the drive voltage to the piezoelectric scanner. It was therefore necessary to have shielding around these signal lines. A backing plate was attached to the centre disk to act as a Faraday cage, fully enclosing the socket connections between the photodiodes and the signal lines.
Figure 5.9: Photo of the goniometer allowing lateral, x and y, alignment of the target with the accelerator beam. Tilt angles, $\varphi$ and $\theta$, of the target could be adjusted about an eucentric point.
5.4.4 Cantilever loading and lowering

The aperture must be mounted above the surface of the PMMA coated photodiode with some control over the height. Initial experiments aimed to have the Si cantilever as close as possible to the PMMA film, without touching and ruining the surface. A simple mechanism was devised consisting of a height adjustment arm with a screw to allow some fine adjustment. The cantilever was glued to a mounting block and attached to the arm, and then with the arm fully retracted the arm attached to the face plate of the assembly. Extreme caution was necessary to prevent the fragile Si cantilever from touching the photodiode as the adjustment screw lowered the Si cantilever into place. A portable, low magnification microscope was used to view the lowering process and an estimate of 10 to 50 µm was made of the separation between the PMMA film and the Si cantilever. Photographs of the assembly for housing the photodiodes and lowering the cantilever are shown in Figure 5.10.

Figure 5.10: Photographs of the assembly.
Figure 5.11: (a) SEM image of the cantilever with apertures. (b) Diagram representing the possible paths of ions during STIM imaging. (c, d and e) STIM median energy maps of the cantilever with apertures.

Figure 5.12: Pulse height spectra for the three apertures and the background full-energy stray ions.
5.5 Lithography through an aperture

5.5.1 Introduction

Preliminary experiments have been conducted to create a lithographic structure using the nano aperture method described in section 5.1.2 and the apparatus described in 5.4. The aperture material used was the 8 µm thick Si cantilever detailed in 5.2 and shown in Figure 5.3 (a). A 700 nm thick PMMA film was prepared on a photodiode using the method described in chapter 3 and the ion beam exposure was performed on the 5 MV Pelletron accelerator at the University of Melbourne using 1.5 MeV He.

5.5.2 Experiment

The ion beam was first focused and the beam current cut down to approximately 1000 ions per second and used to image 2000 mesh Cu grid above a test photodiode. The detector electronics were then switched to the PMMA coated photodiode. The location of the Si cantilever above the photodiode was found by performing a large area scan of the photodiode and producing a scanning transmission ion microscopy (STIM) image. The Si cantilever was positioned in the centre of the image and the scan gain decreased to zoom in on the cantilever. Apertures in the Si cantilever were visible as bright spots in the STIM image and corresponded to the apertures seen in the SEM image of the cantilever (Figure 5.11 (a)). Further zooming in on these apertures revealed there was a background of full-energy counts in the region under the shadow of the cantilever (Figure 5.11 (c)). The background was due to the halo of stray ions around the focused beam spot. Illustrated in Figure 5.11 (b) these ions miss the cantilever completely and register as a full energy counts in the pixel corresponding to the scanning position of the beam.

5.5.3 Results

- Spectra

Four pulse height spectra from the STIM image are shown in Figure 5.12. The four regions of interest in the STIM image are the three apertures and the remaining area of the image in which stray full energy ions are counted. The number of counts in the spectra has been normalised to the area of each region of interest. The contribution of full energy ions passing through each aperture is in the same order of magnitude as the full energy counts across the whole image. Some full energy ions have been counted passing through the aperture but the stray ions must be subtracted to find the actual value. The spectra also show the contribution from lower energy counts due to scattering inside the aperture. The number of counts in each region of the STIM map (d) is low and therefore does not allow reasonable analysis of the data.
Figure 5.13: AFM images of the line of points created in the PMMA from the nano aperture exposures.

Figure 5.14: Depth profile of one of the point exposures containing ~ 10,000 ions.
To increase the number of counts the count rate was increased by slightly opening the Fischer V-slits (refer to Figure 3.10 (b)), however, this resulted in a large increase in the number of stray ions in the STIM image (shown in Figure 5.11 (e)).

A preference for high energy ions at one side of the aperture and low energy at the other has been observed indicating that the ion beam is tilted with respect to the aperture. However, it is not possible from these spectra to easily deduce the tilt offset. For further analysis of these spectra the number of stray ions must be reduced, and the spectra statistics must be improved.

- **Lithography**

PMMA exposures were performed during the creation of the STIM images. Two apertures were imaged leading to a double exposure in the PMMA film. A line of points was created in the PMMA by making a series of 800 nm translations to the sample stage. After 60K, 30K and 15K ions had been measured (on a counter timer) the sample shift was made with the image still acquiring. Following developing of the PMMA in MIBK:IPA 1:3 for 20 seconds a series of AFM images of the exposed region was created and is shown in Figure 5.13. Single lithographic features are 200 nm wide and separated by 800 nm. A depth profile through one of the holes is displayed in Figure 5.14 and shows that an aspect ratio of approximately 10:1 has been achieved. This experiment demonstrates that it is possible to confine the ion beam using a nanoscale aperture and scan the target with respect to the aperture to create a lithographic structure.

5.5.4 **Conclusion**

The inability to generate clean and high yield spectra from ions passing through the apertures means that it was not possible to achieve accurate dose normalisation on the target. It was also not possible to determine the optimum alignment of the aperture to the ion beam. The issue of ions passing around the outside of the cantilever edge must be addressed before further optimisation of the lithographic process can occur. This may be achieved by improved focusing of the beam on the cantilever to reduce the size of the beam penumbra. Another option may be to place a pre-collimator in front of the cantilever to block unwanted ions.

However the ability to collimate a beam of ions from a nominal diameter of 2 µm down to 200 nm has been demonstrated by the results of the lithographic exposure.
5.6 Chapter Summary

The creation of nanoscale apertures has been achieved through FIB milling of 8 µm and 3 µm thick Si cantilevers. The apertures created are not cylindrical but conical in shape with diameters ranging from less than 100 nm (at the exit of the 3 µm cantilever) to greater than 1 µm (at the entrance to the 8 µm cantilever). With further development of the FIB milling process and the inclusion of Pt deposition the size of the apertures is expected to decrease.

Modelling of the passage of ions through nanoscale apertures has been demonstrated. The model only considered cylindrical shaped apertures. Further development of the code is needed to model a conical aperture. The results of the model show that only a small fraction of ions (less than 5%) are scattered outside the open area of the aperture, indicating that this masking technique should be highly effective when applied to lithography.

The mounting assembly used to create the lithography apparatus has been constructed, based around two key components. (1) A Si photodiode onto which a PMMA film is spun. The photodiode acts as an active substrate, counting single ion impacts after passage through the PMMA layer. (2) A Nanonics 3D Flatscanner™ which provided incremental movement of the substrate relative to the aperture. The resolution of the scanner is in principle below 1 nm, however the issues of position repeatability, and drift have not yet been addressed.

The creation of this apparatus demonstrates the simplicity of the aperture and scanning stage IBL technique. With only the need to place a small amount of key components in the target chamber of an already existing ion microprobe the resolution of IBL is improved from greater than 1 µm to 200 nm.
5.7 Bibliography


Chapter 6  Project and Research Conclusions

This thesis serves to determine the fundamental limits of the technology of ion beam lithography (IBL). This determination is viewed here as a critical step to determine whether IBL will be, and, where IBL will be successfully applied.

Chapter one began by placing this fundamental limit in an experimentally realisable form, the etched track of a single ion. The conditions upon reaching this experimental result were placed in the form of four research questions:

1) Can a single ion be detected after passage through a PMMA film?
2) Does a single ion produce a latent damage track in PMMA that can be etched?
3) Can the etched track be imaged to determine its radius?
4) To what accuracy can a single ion strike be located?

This set of questions have been a useful guide for the direction of this thesis, and have all, in one way or another, been answered.

“Can a single ion be detected….?”, yes, provided the detector is sensitive to the specific ion. It has been shown that a commercial Si PIN photodiode can be used as a detector for ions in the 1 MeV.u\(^{-1}\) energy regime. This detector was utilised by spin coating PMMA directly onto the Si photodiode surface.

“Does a single ion produce a latent damage track in PMMA that can be etched?” The simple answer to this question is yes. However this answer on its own does not automatically mean that the smallest structural element of the lithographic process has been found. Nor is it an exceptional result, as there has been solid state nuclear track detectors for a long time.

In concluding this thesis I think it is important to rephrase the question before attempting an answer. “Can a single ion produce a high contrast latent damage track such that track etching is possible without any etching of bulk/undamaged material, thereby retaining the native high aspect ratio of the track during etching?” Production of a latent track with high contrast between the damaged material and the undamaged material is possible when using ions with sufficiently high linear energy transfer (LET).

The results of experimental work of this thesis show that the LET threshold for producing high contrast and continuous single ion tracks is approximately 1000 eV.nm\(^{-1}\), with 8 MeV F (LET = 1400 eV.nm\(^{-1}\)) being the lowest LET single ion tracks imaged.
An attempt was made to characterise, at a macroscopic scale, the energy density required to sufficiently damage the PMMA resist. Response curves for PMMA resist processing were generated and it was found that the energy density required for adequate resist processing was 0.1 eV.nm$^{-3}$ (experiment presented in section 4.3). When using the 2 nm estimated radius of a single ion track (from chapter 2) even the lightest ion, H, has sufficient LET to reach this energy density. However it was not possible to find single etched H tracks. These two results are not in agreement. Etching dynamics between large macroscopic areas and single ion tracks are clearly different.

“Can the etched track be imaged to determine its radius?” This thesis has shown that AFM is a suitable technique for imaging the openings to etched tracks, without determining the etched depth.

Without an imaging technique that has the ability to resolve features in PMMA below 10 nm one can only speculate as to whether the LET threshold of 1000 eV.nm$^{-1}$ is reasonable or not. The work of Lee (mentioned in chapter two) gives a value of 15 eV.nm$^{-1}$ for the LET threshold where scission sites become close enough to begin to cross-link, however, this condition does not necessarily constitute a high contrast and continuous single ion track. Therefore we may think of the two values (Lee’s and this thesis’) as lower and upper limits of the LET threshold. Further narrowing of these two bounds by experiment will be a challenge to the experimentalist requiring improvement to the lithographic process and the imaging technique.

The future for IBL as a technology is not in the form of one-off experiments that prove a concept but rather as repeatable manufacturing procedure. When IBL is viewed from this point of view the procurement of an accurate determination of the LET threshold for single ions becomes not so critical. One may simply increase the contrast in the track using multiple ions. With the ability to scale the ion track contrast light ions become preferable as they are more accessible on small accelerators. Answering the last of the four research questions becomes the critical factor “To what accuracy can a single ion strike be located?” This thesis has attempted to confine a beam of light 1.5 MeV He ions using a nanoscale aperture. The resulting beam spot on a PMMA target was approximately 200 nm in diameter.

This thesis provides me with two options for my obligatory ‘future work’ section. Does one continue down the path of the single ion track investigation, delving deeper into the physics of ion interactions with matter and finely honing the single track lithography and imaging techniques, with the aim to understand what is going on as each ion strikes the resist. Or does one simply set about the more technical task of beam confinement so that nanoscale structures may begin to be fabricated and studied, without requiring in-depth knowledge of individual track formation. The enquiring mind will go one way, the practical the other.
Publications
Macrochannelling: Characterisation of nano-structures by ion beam analysis

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Abstract

High aspect ratio microstructures produced by novel fabrication methods have important applications in micro-electro mechanical machines (MEMS) and photonics. Investigation of the internal structure of sub-micron scale devices is challenging although scanning electron microscopy (SEM) and scanning tunnelling microscopy (STM) are two commonly used techniques for this purpose. These techniques have the disadvantage that important information about sub-surface structure can be difficult to obtain. Especially difficult to analyse are high aspect ratio structures because of the limited reach of the scanning probe into deep wells, or the shallow penetration of the electron beam. Ion beam channelling, with Rutherford backscattering spectrometry (RBS) is already well-established as a technique for providing information about sub-microscopic structure at the atomic level. Based on this method, we are investigating the use of macroscopic ion beam channelling into micro and nano-scale high aspect ratio textured surfaces. We have developed a numerical simulation program that can calculate the RBS spectrum of textured surfaces, as a function of ion beam tilt angle, which can be used to interpret the experimental spectra from a real specimen. In this paper we compare our simulations with control samples.

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Keywords: RBS; MEMS; Ion beam channelling; Macroscopic channelling; High aspect ratio structures; Sub-surface structure; Nanophotonics

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1. Introduction

Artificial nano-scale high aspect ratio structures for photonics [1] and the natural analogues such as butterfly wings [2,3] contain sub-wavelength scale structures to control the scattering of light. Apart from the optical properties of the structures, direct imaging of the structures is challenging because of the lateral scale and the important function often played by the deep sub-surface structure. In this paper we investigate the use of Rutherford backscattering spectrometry (RBS), together with a new analytical model, to probe deep periodic nano-structures. We build on the well-established technique of ion channelling which can provide information about lattice structure at the sub-nanometre scale and use a similar concept to investigate macroscopic channelling into artificial periodic structures at the scale of 100 nm.

2. Macrochannelling

For the characterisation of samples containing periodic nano-structures with a scale of the order of 100 nm, we employ RBS with MeV ions. This is because the stopping power (2.3 eV/nm for 2 MeV He in Si) and hence the ion energy loss in one period of the nano-structure proposed for investigation is of the same order as the energy resolution of the particle detectors (15 keV). The energy loss of the ions due to their passage through the structure is determined by the sequence of voids along the ion path. This sequence will depend on the incident angle and also the angle of the detector used to collect the scattered ions. As with conventional ion channelling into periodic crystals, the angular dependence of the detector signal as a function of energy is related to the periodic structure of the sample. Although the inversion of the ion scattering signals to recover the three dimensional periodic structure of the sample is generally not unique, reasonable assumptions about the structure of the sample can allow detailed characterisation of the sample to be deduced from the ion scattering signal. By analogy to conventional ion channelling we term analysis of the signal of scattered ions from periodic nano-structures macroscopic channelling or macrochannelling.

It has been established in previous studies [4–7] that samples exhibiting porosity or surface roughness have diminished RBS yield. In the case of periodic nano-scale high aspect ratio structures, not only is the yield reduced but the RBS spectrum as a function of both tilt angle and energy forms a pattern that is characteristic of the structure, as will be shown in Section 3. The analysis of the structure allows parameters including the period length, surface fraction of the channels and the channel depth to be estimated.

A numerical simulation program has been developed that can calculate RBS macrochannelling spectra of textured surfaces as a function of ion beam tilt angle based on the multilayer 'slab' analysis method [8]. Textured surfaces that have been modelled include periodic arrays of columnar structures and periodic arrays of holes. In 'slab' analysis, the target is divided into a large number of layers of equal thickness. Particles travelling through the target can scatter in each layer. Firstly the program calculates the energy loss of the ions on their inward path to that layer taking into account voids due to periodic structure. Secondly, the yield of particles is calculated that will exit in the direction of the detector. Finally the program calculates the energy after the collision due to the kinematic factor and the energy loss along the outward path.

The numerical simulation program has been used to investigate the effects of macrochannelling in idealised structures and to interpret the experimental RBS spectra from an Ag/Cu-nano-structure obtained using 2 MeV He ions.

3. Investigation of idealised periodic high aspect ratio structures in Si

The RBS signal from a periodic array of square section Si columns (Fig. 1) has been modelled as a function of tilt angle (Fig. 2). Using a column height of 20 μm produces macrochannelling spectra with effectively no substrate as no ions scattering from the substrate reach the detector. The energy spectrum at tilt angle of 4° and the yield...
as a function of tilt for energies between 1100 keV and 1150 keV are shown in Fig. 3.

The angular scan curve exhibits features in a manner somewhat similar to channelling however no atomic steering occurs; there is a yield minimum when the ion beam is aligned with the walls of the grating. This is an effect due to macrochannelling and already discussed in previous studies [4,5]. However, the yield for a negative tilt angle is lower than for a positive tilt angle. This is not an effect due to macrochannelling. Comparing ions penetrating the material with different tilt angles but with an equal total energy loss. These ions will scatter from different depths, the ion penetrating with a more positive tilt angle scattering from a larger depth. Consequently the energy loss on the inward path is larger and for that the yield of ions is higher for more positive tilt angles.

The most striking effect are the periodic modulations in the yield. The yield has both high frequency and low frequency modulations. The high frequency modulations are due to periodic variations in the pathlength of the exiting ions. The low frequency modulations are due to periodic variations in the pathlength of the incident ions which is strongly dependent on the tilt angle. These statements are supported by the fact that the high frequency modulations are present at each angle, low frequency modulations only emerge when the ion beam is tilted. When the ion beam is perpendicular to the surface there are only high

Fig. 1. Side view of 3D microstructure for the RBS simulations of a textured surface; \( f = 25 \text{ nm}, \ p = 50 \text{ nm}, \ d = 20 \mu \text{m} \) and \( \theta \) the ion beam tilt angle.

Fig. 2. Calculated RBS spectra as a function of ion beam tilt angle (\( \theta \) in Fig. 1) displayed as a yield map as a function of angle and energy for the structure shown in Fig. 1.
frequency modulations because then there are no periodic variations in the pathlength of the incident ions.

To investigate the influence of a substrate, the spectra are also calculated for a 2 \( \mu \text{m} \) high grating. The calculated macrochannelling spectra are shown in Fig. 4, again represented in an intensity plot. It shows that the presence of a substrate cancels out the low frequency modulations; the periodic variations in the pathlength of the incident ions stop at 2 \( \mu \text{m} \) depth in the sample.

4. Experiment: analysis of nano-photonic resonator structure

The Ag/Cu-nano-structure is a nano-photonic resonator, an array of silver-coated parallel channels of which the parameters were originally estimated as shown in Fig. 5 from the fabrication methodology. To fabricate the specimen, channels were written into ZEP 7000 resist with electron beam lithography. After development a 100 nm thick silver layer film was sputtered over the patterned resist followed by an electroplated copper backing layer. The structure is then separated from the resist leaving an array of deep, narrow silver channels. Proximity effects associated with scattering of the electron beam in the resist can result in unintended exposure at the tops of the channels. On development, the tops dissolve slowly leading to uncertainties in the depth of the channel below the surface of the resist.

Fig. 6 shows both the experimental RBS spectrum and the calculated macrochannelling spectrum, both spectra are taken with the ion beam perpendicular to the sample surface and a detector angle of 145°. Initial modelling began with the structure parameters of Fig. 5; it was assumed that the silver layer is nominally 100 nm thick. However, this assumption did not lead to a good agreement between the experimental RBS spectrum and the calculated macrochannelling spectrum.

The experimental RBS spectrum shows a drop in the yield near the surface from which we can estimate that the thickness of the silver layers perpendicular to the surface should be 60 nm. Changing this in the model while not changing the other structure parameters leads to a calculated macrochannelling spectrum that has reasonable agreement with the experimental spectrum near the surface.

However, for the lower energies the peak around 1400 keV did not appear properly in the simulated spectrum using the structure depth of \( d = 250 \text{ nm} \) as determined by optical reflectance and by change in perspective using SEM. With \( d > 300 \text{ nm} \) this peak in the macrochannelling spectra develops. For \( d = 350 \text{ nm} \) we obtain the best fit to the experimental spectrum. Therefore, using this depth and the reduced thickness of the silver layer results in a macrochannelling spectrum.
that has the best agreement with the experimental spectrum (Fig. 6). The optical measurement relies on an assumed phase change for bottom reflection and the SEM tilting method has a large uncertainty. For that, the depth of the channels could indeed be about 350 nm.

Residual discrepancies between experimental results and the model are due to variations in the width and the depth of the channels. Also, the simulation program does not account for a finite solid angle of the detector, the detector resolution and statistical fluctuations in the energy loss (straggling) all of which will smear out variations in the yield.

Fig. 4. Calculated RBS spectra as a function of ion beam tilt angle $\theta$ (see Fig. 1) displayed as a yield map as a function of angle and energy for the structure shown in Fig. 1 but now with a depth of 2 $\mu$m.

Fig. 5. Side view of 3D microstructure of the nano-photonic resonator with the parameters which were initially assumed; the silver layer is nominally 100 nm thick.

Fig. 6. Comparison between experimental and calculated RBS spectra from the test sample. A 2 MeV He beam was used for the RBS measurement with a detector of 1.5 mrad solid angle at a scattering angle of 145°. The focused beam with a diameter of about 1 $\mu$m was scanned over an area of 100 $\times$ 100 $\mu$m$^2$, but the surface texture was not resolved.
5. Conclusions

Our numerical model was able to explain most of the main features of a RBS spectrum obtained from a sample with strong periodic surface texture that was much smaller than the resolution of the ion beam. The model was successfully able to determine the thickness of the silver layer on the vertical side walls and the best fit also allowed a reliable value for the structure depth to be estimated. Both are difficult to measure by other non-destructive methods without large uncertainties.

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References

Ion beam lithography using single ions

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Abstract

Presented here is a study to determine the conditions whereby holes etched along single ion tracks can be produced. Using standard tools of ion beam analysis a strategy has been developed to count single ions incident on a PMMA film spun onto a Si photodiode that functions as a detector. We investigate the sensitivity of PMMA to single ions as a function of the incident ion energy, mass and the PMMA development parameters. Non-contact atomic force microscopy (AFM) has been used to image the openings of holes etched along single ion tracks confirming the PMMA is sensitive to the passage of specific single ions. A high aspect ratio Si nanowhisker cantilever has been utilised to perform a quantitative analysis of the holes which are up to 45 nm in diameter for 71 MeV Cu ions.

Keywords: Ion beam lithography; PMMA; High aspect ratio structures; Nuclear microprobe; Single ion counting; Photonic crystals; Ion tracks; Latent damage; Track etching

1. Introduction

A beam of high energy MeV ions offers the potential to generate very high aspect ratio nanostructures. The latent damage track in a material following the passage of a single ion is cylindrical with a diameter between 10 and 100 nm and length of the order 10^4–10^5 nm. There is an extensive literature on track formation in solids and the formation of nanostructures, e.g. [1], use of ions for micromachining, e.g. [2] and many examples in the literature of studies of the tracks formed by high-energy ions [3–5] in polymers. There are also examples of using a focused beam of ions to write structures into a resist [6]. The emphasis in the present work is to use a specific number of well-oriented tracks, followed by development, to create structures at the ultimate resolution limit of a single ion. Using a precision positioning system, production of nanostructures with dimensions below the wavelength of light becomes possible. With irradiation at different tilt angles, even complex 3D nanostructures could be developed with useful applications [7–11].

There are four problems to overcome in order to achieve single ion resolution: (1) positioning a single ion impact in the right place, (2) detecting the passage of a single ion, (3) developing the latent damage along the length of the track to produce a hole and (4) imaging the high aspect ratio ion track. Problem (1) requires precision ion beam resolution and positioning. State of the art proton beam writing systems demonstrate a resolution of <100 nm in production of lithographic structures [12]. We propose nanometre precise positioning by use of a nanoaperture based on the method of Lüthi et al. [13], which is also being developed by Schenkel et al. [14] for highly charged keV ions. The spatial resolution limits imposed by ion scattering after passage through a nanoaperture is under investigation by Taylor et al. [15]. We overcome problem (2) by counting individual ion tracks using a substrate that acts as a detector onto which the resist film is spun. Problem (3) is addressed by studying the resist/developer combination in conjunction with different energetic ions. As a starting point the resist poly(methyl-methacrylate) PMMA was
chosen. Finally problem (4) remains to be fully solved but can be partially addressed by the use of high aspect ratio scanned probes as we demonstrate here.

2. Experimental

2.1. Film manufacture

PMMA films were prepared on various substrates using MicroChem 950 PMMA A2 and a spin coater with a spin speed of 5000 rpm. The resulting film thickness was approximately 60 nm after baking for 10 min at 180 °C. To expose the PMMA films to a precise number of ion impacts a method has been devised whereby a PMMA film is spun onto the face of a Hamamatsu S1223 Si PIN photodiode. After coating with PMMA the photodiodes were found to be fully functional and capable of producing signals from single MeV ion impacts that could reach the photodiode after passage through the surface PMMA layer. The PMMA layer was patterned with a grid of pitch 125 μm using conventional UV lithography to provide a location reference for subsequent exposures to single ion impacts.

2.2. Exposure

Exposures were performed utilising nuclear microprobe beam lines on accelerators in two laboratories: (1) The 5 MV Pelletron accelerator facility at the University of Melbourne, capable of accelerating H or He ions, with a beam resolution of ~1 μm. (2) The 10 MV ANTARES facility at ANSTO, capable of accelerating heavy ions, with a beam resolution of ~5 μm. The PMMA coated photodiodes were mounted in the target chamber of the nuclear microprobe system. The lenses were focused by viewing the ion beam on a glass slide with a beam current of ~1 nA. The incident beam current was then adjusted down to a few thousand ions per second and the beam brought onto a Cu grid mounted in front of a blank photodiode detector. The detector was used to measure the beam current and check the resolution of the beam by scanning the microprobe over the grid. The image of the grid was also used to calibrate the microprobe scan size from the known grid period. The data acquisition system was set to dwell on counts in the pulse height spectrum, each count representing a single ion impact on the photodiode. After a set number of counts a signal is sent to the microprobe scan coils to reposition the beam to the next irradiation region.

2.3. Developing

Samples were immersed in the developer, a mixture of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA), and agitated ultrasonically to etch to latent damage from the ion beam exposure. Next the samples were placed into IPA to halt the developing process. Samples were then dried with compressed N₂ gas.

### Table 1

Data used to calculate the etch rate of unirradiated PMMA using different developer combinations

<table>
<thead>
<tr>
<th>Developer</th>
<th>Time for complete removal of 60 nm film</th>
<th>Etch rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIBK</td>
<td>5 min</td>
<td>~10 nm/min</td>
</tr>
<tr>
<td>MIBK:IPA 1:1</td>
<td>50–100 min</td>
<td>~1 nm/min</td>
</tr>
<tr>
<td>MIBK:IPA 1:3</td>
<td>Film not removed after 100 min</td>
<td>Negligible</td>
</tr>
</tbody>
</table>

3. Developer study

Regions of latent damage are developed to form a structure making use of the contrast in etching rates between the irradiated and unirradiated regions of resist. In lithography the emphasis is usually focused on obtaining high contrast because irradiation sources typically have a penumbra that, if etched, will worsen the resolution of the process. Since we aim to use the passage of a single ion then there is no penumbra and contrast is not so important. However, if the latent damage from a single ion is below a certain critical threshold the track will not etch in which case the resist is not sensitive enough to form etchable tracks from single ions under the developing regime. We must configure the lithographic process for high sensitivity to allow etching of single ion tracks, but some level of contrast must be maintained so that the track does not become conical as the undamaged region near the ion track etches. Three developing combinations were tested to check the etch rate of unirradiated PMMA. The samples were developed until the entire film had been removed; results are shown in Table 1.

4. Sensitivity determination

Holes with a diameter of a few tens of nm are difficult to image, especially if one is uncertain whether the holes have actually been formed owing to lack of resist sensitivity. A macroscopic method has been devised to measure the sensitivity of PMMA under different developing conditions. A PMMA film is exposed to a 3 MeV proton beam (LET = 11.2 eV/nm) in a 250 × 26 pixel array creating a rectangular exposed area of approximately 30 × 3 μm². The low LET proton beam is used to achieve uniform damage density across the irradiated area. By multiplying the measured particle fluence in the exposed area with the LET (calculated using SRIM [16]) the energy deposition density is determined with units eV/nm³. After developing, the average PMMA height in the exposed region is measured using non-contact AFM and plotted against the deposited energy. The results following 10 min development in MIBK:IPA 1:3 show that for complete removal of the PMMA film the deposited energy must be greater than ~2 eV/nm³ (Fig. 1). This number is defined here as the sensitivity of the resist/developer combination. It follows that to etch a hole along a single ion track the damage density inside the track must exceed this value. An accurate
determination of the radial damage profile combined with the LET of a particular ion should indicate whether the damage density inside the track meets the threshold value.

5. Identifying single ion tracks

The radii of ion damage tracks in PMMA are not well known. The passage of a 1 MeV/u ion through a material can produce up to 2 keV electrons. Using the range of a 1 keV electron in PMMA as a guide, we would expect to produce tracks of the order of 10 nm. For H and He with LET values <300 eV/nm, it is not certain that the damage deposited along a single track reaches the sensitivity threshold. In order to assure supra-threshold energy densities, heavier ions have been employed. We used 71 MeV Cu with a LET of 4850 eV/nm.

Exposures using the Cu ion beam consisted of $5 \times 5$ arrays of beam spots. The sample was developed in MIBK:IPA 1:1 for 5 min. The number of ions ranged from 50,000 down to 10 ions per spot. An image of the 50,000 ion per spot region reveals the beam spot size (Fig. 2(a)). The ions are not distributed evenly over the whole spot and there is some overlap between spots. The beam spot has been approximated as a rectangle 8 μm high and 7 μm wide. An AFM image of a beam spot containing 100 detected ions is shown in Fig. 2(b). A dashed line with the beam spot dimensions has been inserted to act as a guide to the beam spot. Approximately 90 holes have been identified inside the border and 100 holes in the entire image. The discrepancy between the number of detected ions and counted holes can be attributed to ions falling outside the defined beam spot area.

6. Hole analysis

Quantitative analysis of the holes has been performed with non-contact AFM utilising a Si nanowhisker type cantilever (NT-MDT, NSC05). Standard cantilevers were inadequate for this task. The high aspect ratio whisker at the cantilever tip enables imaging of the small openings to the etched ion tracks. The image of an area containing single ion impacts is shown in Fig. 3(a). To separate holes in the PMMA from the surface roughness a height discriminator of $\pm 4$ nm is chosen based on the pixel height histogram shown in Fig. 3(b). This discriminator is used to produce the one bit image displayed in Fig. 3(c). Sixteen holes are identified with a depth below the discriminator of 4 nm. A profile is taken through the deepest pixel of each hole and each profile used to find the average profile for an ion impact (Fig. 3(d)). The holes show an average depth of...
7 nm and width at FWHM of 45 nm. However the true hole is expected to be deeper as the measurement is limited by the width of the cantilever tip.

7. Conclusion

We have achieved counting of single MeV ion impacts into PMMA for low fluence exposures. Areas with homogeneous and exactly known fluence allow us to determine the sensitivity of a resist with respect to the developing conditions. We have performed the first step for single ion beam lithography by etching a counted number of single ion impacts.

References

Ion transmission through nano-apertures

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Abstract

Localisation of ion impacts with a resolution better than can be achieved with a focused ion beam microprobe may potentially be achieved by employing a high-aspect ratio nano-aperture mask. The present paper applies Monte Carlo methods to investigate the role of ion scattering and straggling through the aperture and the influence of these processes on the transmitted ion energy and intensity distribution. The objective of the investigation is to determine the potential of this method for delivering few or single ions to sub-100 nm locations on substrates. Simulation of 2 and 4 MeV He, 8 MeV F and 71 MeV Cu has indicated that the masking process is effective, with probabilities between 82% and 93% of obtaining single ions with full energy at the exit of the aperture. Possible applications include precision ion doping, single-ion machining and potentially ion beam analysis.

PACS: 07.05.Tp; 02.70.Uu; 61.18.Bn; 81.16.Nd

Keywords: Ion beam analysis; Ion beam lithography; High aspect ratio structures; Nuclear microprobe; Monte Carlo modelling; Nano-stencil

1. Introduction

Applications for ion beams requiring the precision delivery of few or single ions to high resolution are emerging [1–3]. There are two main methods for the delivery of ions to sub-100 nm resolution: focusing by means of electric or magnetic lenses or by collimation with apertures. For MeV ions, focusing is generally preferred because of the difficulty of making high aspect ratio apertures required, however focusing ions to sub-100 nm beam spots entails considerable technical complexity [4]. With the advent of methods for making sub-100 nm high aspect ratio apertures [5–8], we investigate the trajectories of ions emerging from such apertures with the goal of ultimately exploiting the trail of latent damage induced by the passage of a single ion, typically 20 nm in diameter. Ion scattering and straggling through the walls of the aperture and the fact that all materials are partially transparent to MeV ions will limit the spatial resolution for the delivery of ions regardless of the diameter of the aperture itself.

These phenomena can be modelled with a Monte Carlo (MC) ion transport simulation which is a useful technique for studying problems in which individual ion histories are relevant, or where the treatment of the ion beam as a continuous distribution is inappropriate. The passage of ions through a sample with a complex geometry such as an aperture is an example of such a problem and can be investigated with MC simulation.

2. Monte Carlo simulation

The MC approach involves modelling the interaction of the beam with the sample by explicitly calculating individual ion trajectories. A fast FORTRAN ion transport simulation code based on the TRIM code [9] has been adapted to the problem of ions passing through a high aspect-ratio aperture used as a collimator. The code is described in...
detail in [10,11], however, the recoil specific efficiency enhancements are not employed here. The code has been modified to model an aperture in a mask which has a thickness that exceeds the ion beam range by considering the aperture as a cylindrical void in the mask. The original modelled ion transport in a 2-D projection for efficiency reasons. The present code models the ion transport in 3-D which is required to model individual ion paths which intersect the aperture.

Ions that enter the aperture are transported, without electronic energy loss or nuclear scattering, to the point at which the trajectory intersects with the aperture wall or is transmitted beyond the mask. The points of intersection of the trajectory and the aperture wall are determined by equating and solving the parametric equations for a cylinder and a line of any free flight segment which enters the aperture.

As the sample is not laterally homogeneous, the ion positions relative to the aperture are tracked explicitly and ions may be made incident at any point relative to the aperture, with an incident angle consistent with the ion beam that delivers the ions to the mask.

The ions of primary interest are the fraction which are not transmitted directly through the aperture, but have a trajectory that intersects the aperture wall, or are incident upon the mask near the aperture and subsequently scatter into the aperture so that they are transmitted through the mask albeit with reduced energy. The net effect will be a beam broadening at the aperture exit analogous to the penumbra seen in radiotherapy and optical collimation of non-point sources.

3. Model and experimental configuration

Nano-scale apertures have been drilled by focused ion beam systems in silicon cantilevers. These structures are attractive for use as a nano-stencil [12] potentially allowing sub-1 nm control of the position of the aperture in the cantilever above the substrate as well as precision mapping of location markers on the substrate by scanning probe microscopy. SEM images of apertures in silicon cantilevers show a radius of the order of 100 nm can be achieved. We therefore apply our model to high-aspect ratio apertures in silicon masks.

We apply the MC simulation to various ion-energy combinations and model the mask as a uniform Si layer with a 100 nm radius cylindrical aperture through a slab whose thickness is chosen to be approximately twice the range of the incident ions used in each case. We also consider some alternatives for beam energy and aperture size to demonstrate their effects on the transmission spectra. In practice, we consider that the ion beam is delivered onto the mask by a focused ion beam system, such as a nuclear micro-probe, where the beam spot will be much larger than the aperture. For our simulations the beam is modelled with a one micrometer radius. To obtain insights into the influence of ion energy, mass and range we have run simulations for 2 MeV He, 8 MeV F and 71 MeV Cu ions, for which

![Fig. 1. Transmission of (a – i,ii) 2 MeV He, (b – i,ii) 8 MeV F and (c – i,ii) 71 MeV Cu through a 100 nm radius nano-aperture.](image-url)
experimental data will be available in the near future [5]. In our simulations, $10^7$ incident ions were modelled in each case except for $71$ MeV Cu which used $10^6$ ions due to the much longer simulation times associated with heavy ions.

4. Results

For each transmitted ion, the simulation calculates the energy, position and direction cosines at the point of exit from the mask. Fig. 1 shows the spatial distribution and mean energy of transmitted ions as a function of radial distance from the centre of the aperture. The distribution of transmission angles from the sample normal is also shown.

Table 1
Ion-energy systems: percent of ions transmitted with full energy, $T$, percent of transmitted ions scattered out of the aperture, $S_{out}$, scattered into the aperture, $S_{in}$, and the mean energy of the latter ions, $E_{in}$.

<table>
<thead>
<tr>
<th>Ion/Energy (MeV)</th>
<th>Aperture radius (nm)</th>
<th>$T$ (%)</th>
<th>$S_{out}$ (%)</th>
<th>$S_{in}$ (%)</th>
<th>$E_{in}$ (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He/2</td>
<td>100</td>
<td>86.44</td>
<td>3.51</td>
<td>10.05</td>
<td>0.990</td>
</tr>
<tr>
<td>F/8</td>
<td>100</td>
<td>82.22</td>
<td>4.54</td>
<td>13.24</td>
<td>3.240</td>
</tr>
<tr>
<td>Cu/71</td>
<td>100</td>
<td>90.26</td>
<td>2.15</td>
<td>7.59</td>
<td>31.582</td>
</tr>
<tr>
<td>He/2</td>
<td>40</td>
<td>92.79</td>
<td>2.42</td>
<td>4.79</td>
<td>1.015</td>
</tr>
<tr>
<td>He/4</td>
<td>100</td>
<td>89.84</td>
<td>3.16</td>
<td>7.00</td>
<td>2.110</td>
</tr>
</tbody>
</table>

For single ion applications, the radial intensity plot should be interpreted as a probability distribution. The mean energy per ion represents the expected transmission energy, as a function of position.
The percentage of transmitted ions which exit the aperture while retaining their full energy is denoted by $T$. Of all transmitted ions, a fraction, $S_{\text{out}}$, are scattered out of the aperture, and $S_{\text{in}}$ are scattered in to the aperture spot with reduced energy. The mean energy of these inwardly scattered ions is $E_{\text{in}}$. The remaining fraction are those that pass freely through the aperture. Table 1 summarises these quantities for each ion-energy-aperture system.

For a one micron radius ion beam centred on a 100 nm radius aperture (1% of the beam area), the total percentage of ions transmitted is 1.15%, 1.22% and 1.09% for He, F and Cu, respectively. These numbers are greater than 1% due to scattering in the walls of the aperture. From the data in Fig. 1((a)–(c))((i), it is evident that the great majority of ions are transmitted along the axis of the beam, with scattering of 8 MeV F resulting in the greatest distribution of exit angles. The conspicuous features of the energy distributions are the few high energy counts far from the aperture. These are single ion strikes following large angle scattering in the mask. While these are the counts that contribute the greatest deviations from the intended location of the ions, they are extremely rare events. Of the $10^7$ incident 2 MeV He ions, there are 79 beyond the tailing region at four aperture radii with $E > 100$ keV; compared to 111,481 within the aperture radius, i.e. only 0.07% of the transmitted ions. Although the tailing is narrower, this scattering effect is somewhat more pronounced for smaller apertures. For the 40 nm aperture of Fig. 2, the number of counts outside four radii and $E > 100$ keV is 59 compared to 16,596 counts within the spot, i.e. 0.36%.

Ions which enter the mask at an angle to the normal are expected to undergo more significant scattering. In Fig. 3 we illustrate the scattering distribution for three different incident angles. The mask ‘closure angle’, $\theta_c$, is chosen as a characteristic angle of the system – the angle at which the path length through edges of the aperture becomes equal to the ion range. Plots corresponding to ions of normal incidence and half $\theta_c$ are also presented. The simulations in Fig. 3 show the skewing of the transmission spot, and the broadening of the scattered distributions illustrates the importance of the alignment between the beam and aperture axis. The reduction of the peak energy at greater angles verifies the experimental alignment technique of tilting the sample until the energy peak is a maximum.

5. Conclusion

Monte Carlo simulation is a very successful technique for evaluation of experimental systems and parameters, for specific outcomes or tolerances. The distributions for various ion-energy combinations are very similar and systems may be scaleable for appropriate choices of ion, energy, aperture size and mask thickness. The intensity distributions show that the masking process works well – the steep intensity at the aperture edge coupled with sharp energy reduction are the desired features for single ion lithography. Exploitation of these characteristics enables tailoring of lithographic processes where there exists a threshold damage density below which etching does not occur. Future work involves comparison with the SCATT technique employed by Adamczewski et al. [13], and further experimental investigation.

References

Ion beam lithography using a nano-aperture

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Abstract

A high aspect ratio nano-aperture mask was used to perform sub-micrometre lithography with MeV ions. Such a mask can localise ion placement in ion machining or doping, including the fabrication of high aspect ratio structures from ion beam damaged regions by subsequent etching. Ion scattering and straggling is the main limiting factor for the transmission with respect to transmitted energy, lateral intensity and angular intensity distribution of the ions. These limits are investigated by a 3D Monte Carlo modelling program based on the SRIM code; simulation of 1.5 MeV He incident on nano-scale apertures of various diameters indicates that the masking is highly effective. The simulation results were tested by experiments on the transmission of 1.5 MeV He ions through apertures that were machined using a focused ion beam of keV Ga ions in a 10 μm thick Si-cantilever. Firstly, the aperture was placed in front of a 50 nm thick polymethyl methacrylate (PMMA) coated photodiode and scanned by a microprobe. The photodiode gives an energy spectrum of the transmitted ions. Secondly, a nano-scale pattern was produced in an 800 nm thick PMMA sample by the step-and-repeat process, implementing a nanonics stage that facilitates precise three-dimensional orientation of the mask. The damaged PMMA was developed and the lateral distribution of ion impacts was imaged using non contact AFM.

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Keywords: Nanostencil; Step and repeat nanolithography; High energy ion lithography; Ion mask; Nano-aperture; Single ion machining and doping; Ion straggling

1. Introduction

Nuclear microprobe analysis has reached a beam spot resolution limit of around 0.3–0.9 μm [1]. With the exception of some work done in the low current regime (<1 pA), such as [2], no significant improvements in spatial resolution have been published over the past five years. Applications for high resolution beam spots are emerging though several restrictive factors exist, including (i) difficulty in manufacturing sufficiently accurate ion optic lenses, (ii) influences of vibrations and stray fields, (iii) focusing difficulties and (iv) brightness and chromaticity limitations [3].

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With recent developments in the construction of high aspect ratio nano-scale apertures (for example [4–9]) comes the prospect of using such apertures as masks for high energy ions. A previous study employed detailed Monte Carlo (MC) modelling to evaluate the potential of such masks to enable sub-micron resolution [10]. Experimental verification of that model in this work involves ion beam lithography in polymethyl methacrylate (PMMA) applied through a nano-aperture drilled in a Si cantilever by focused ion beam (FIB) milling, followed by atomic force microscope (AFM) imaging of the etched hole. There are growing applications for ion beams requiring the precision delivery of few or single ions to high resolution, and similar techniques have been adopted by Schenkel et al. with highly charged keV ions [11–13] and by Luthi et al. for nano-stencil deposition [14]. The initial motivation for this
work was the expectation that such a mask can localise ion placement in single ion applications, such as the etching of single ion damage tracks (refer to [15]). A wider range of applications involving nanometre beams is anticipated.

2. Sample and nano-aperture preparation

2.1. Sample preparation

A commercially available S1233 Hamamatsu™ photodiode, suitable for ion detection, was removed from its protective case and the sensitive region of the detector exposed. The photodiode was then cleansed with acetone in an ultrasonic bath for 10 min and rinsed with isopropyl alcohol (IPA). MicroChem 950 PMMA (2% in Anisole) was then spun onto the photodiode at 5000 rpm and subsequently baked at 180°C for 10 min, producing a film of approximately 50 nm thickness. Similarly, a second sample was fabricated with MicroChem 950 PMMA (8% in Anisole), producing a film approximately 800 nm thick. The detector acts as an active substrate to provide the number and energy of transmitted ions. Following irradiation, the radiosensitive 800 nm PMMA coating is etched using pre-mixed MicroChem MIBK:IPA 1:3 for 20 s to reveal the ion tracks via atomic force microscopy. This allows quantitative measurement of the irradiated spots.

2.2. Nano-aperture mask fabrication and Monte Carlo model considerations

The key element to this study is the transmission of MeV ions through nano-scale apertures that act as the mask. The apertures are drilled into atomic force microscope (AFM) cantilevers, which may in principle facilitate precision ion placement. Numerous apertures were drilled into a Si cantilever with a Ga ion beam. Scanning electron microscope (SEM) imaging of the 10 μm thick cantilevers indicates that the apertures are conical, with diameters typically of the order of 1.2 μm at the top and 200 nm at the base.

The cantilever containing the apertures was positioned above a 50–60 nm coating of radio-sensitive PMMA on a PIN photodiode, which acts as an ion detector (an idea first presented by [16]). This allows ion beam induced current (IBIC) measurements to be taken during irradiation of the sample, and subsequent imaging of the PMMA target to determine the magnitude of the lateral spread of transmitted ions. The sample was irradiated with 1.5 MeV He ions, the photodiode detector charge collection efficiency (CEE) for which has been shown to be 100% on the Melbourne system [17], though this can deteriorate over time with exposure to very high fluences.

The cantilever was fixed at a position approximately 300 μm above the substrate. The sample itself is effectively an ion beam induced charge (IBIC) detector, and was appropriately wired to the detection system before being irradiated with a 1 μm spot size beam of 1.5 MeV He ions on the University of Melbourne Pelletron MP2. The Monte Carlo model allows simulation of cylindrical apertures only; hence, qualitative comparison is achieved by modelling transmission of 1.5 MeV He ions through a 600 nm diameter aperture.

2.3. Precision stage

In order to evaluate the lithography possibilities of the nanometre beam, an 800 nm PMMA film on a PIN detector was mounted on a purpose-built nanonics stage, which enables movement of the mask independent of the sample. The piezo-electric scanning stage is a 70 × 70 mm Nanonics 3D Flatscanner™ with a 24 mm central opening, providing computer-controlled incremental movement in three dimensions with nanometre positioning accuracy. The housing structure was designed and built in house.

2.4. Atomic force microscopy

Conventional non-contact AFM imaging of the sample has been performed to allow quantitative characterisation of the holes left in the PMMA following etching of the latent damage regions. A Si nano-whisker AFM tip (NT-MDT, NSC05), with an aspect ratio greater than the standard cantilever type, was required to accurately determine the dimensions of the small openings.

3. Results and Discussion

3.1. Nano-aperture masking: comparison between simulation and experiment

Two apertures drilled in a Si AFM cantilever with keV Ga ions, henceforth referred to as Apertures (i) and (ii) (indicated by (i) and (ii) in Fig. 1), were raster-scanned with a ~1 μm beam of 1.5 MeV He ions. 1.5 MeV He was chosen because of its reduced range in Si and increased linear energy transfer (LET) in PMMA, compared to higher energy ions.

The energy spectra in Fig. 1 show a uniform background of full energy counts. These arise as a result of the halo around the beam spot reaching the detector around the edges of the cantilever. This halo is normally much weaker,
or absent, for beam currents typical of IBIC experiments. However, to obtain statistically significant counts in the beam reaching the detector through the apertures a relatively intense beam current (>10 pA) was required. The energy spectrum below the full energy peak indicates that the beam is more closely aligned with Aperture (i) than Aperture (ii), as evident from the greater number of high energy counts from the former. Fig. 2 shows the mean energy of the transmitted ions; the left image corresponds to the two aperture system under discussion, while the right image corresponds to a further set of three apertures on the same cantilever. The ions transmitted through the apertures appear to have a mean energy of about 0.9 MeV. Another interesting feature of the mean energy maps is the low energy ‘shadow’ on the right of each bright spot. This implies that the beam of incident ions was not precisely parallel to the aperture axis, a phenomenon successfully predicted by the Monte Carlo model, as shown by Fig. 3. When aligned correctly, Fig. 3(a) (i and ii), the masking is highly effective as indicated by the sharp drop in intensity outside the aperture region. By contrast, when significantly misaligned, Fig. 3(b) (i and ii), the model predicts significant spreading of the scattered ions. This effect is observed experimentally via AFM imaging of the substrate post-irradiation. It is made more pronounced by the fact that the cantilever mask sits at a height of the order of 300 \(\mu\)m above the detector, resulting in ions striking the substrate over a far wider region than if the mask and substrate were immediately adjacent. Bringing the mask closer to the substrate clearly reduces this undesirable effect significantly.

3.2. Nano-lithography with precision stage

A nanonics stage was implemented, allowing precise three-dimensional orientation of the cantilever mask inde-
pendent of the substrate. The mask was brought within approximately 15 μm of the PMMA surface and the step-and-repeat lithographic process was employed to develop a sub-micron pattern of damage regions. Exposure of PMMA to intense, high energy He ions causes chain scissioning of the polymer. The resulting locally damaged resist consists of polymer chains with a lower molecular weight, and are selectively removed via chemical etching at room temperature. Approximately $1 \times 10^4$ ions were used to ensure creation of each damage region – orders of magnitude above the damage threshold in PMMA [7]. The array was investigated using atomic force microscopy, yielding the results in Fig. 4.

From inspection of Fig. 4, it is clear that construction of periodic arrays of high aspect ratio nano-structures has been achieved with the use of a nano-aperture. The aperture in the mask is not a right cylinder but conical with the cone’s axis not quite perpendicular to the surface as a result of the FIB drilling, which gives rise to the triangular shaped damage regions in the PMMA. This shape may also be influenced by beam misalignment with the hole, which can yield the effects described in Fig. 3(b) (i and ii). A periodic array with sub-micron pitch of damage zones has been produced, where the damaged regions have lateral dimensions of approximately $100 \times 200$ nm. AFM imaging shows that the ion damage tracks go all the way through the PMMA coating, indicating nano-structures with an aspect ratio of almost 5:1. The tapering in the depth profile is a result of the limitations of the AFM tip shape.

4. Conclusions

The experimental work undertaken here indicates that the masking of MeV ions using nano-scale apertures in AFM cantilevers is indeed achievable. This supports the results of the Monte Carlo simulations which indicate that well fabricated masks and accurate beam to mask alignment can potentially provide nano-scale ion beam resolution. The Monte Carlo model shows that it is the diameter of the nano-aperture mask that determines the resolution obtainable. The influence of the ions scattered outside this diameter from the nano-aperture mask is small provided the aperture has good angular alignment with the direction of propagation of the ion beam. We have demonstrated ion beam lithography using a piezo driven scanning stage to move the sample relative to the nano-aperture. Counting of single ion impacts into an active substrate is used as a precise method of dose normalisation. AFM has been used to image the structures fabricated by this technique and confirmed sub-micron resolution. This resolution can be improved further by optimising angular alignment of the beam with the mask; future work is planned to incorporate the beam rocking technique as described in [18–20].

References

Characterization of ion tracks in PMMA for single ion lithography

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Abstract

The ultimate resolution in ion beam lithography (IBL) can be achieved by etching tracks modified by the passage of a single ion impact which has a diameter in the order of 10 nm. For precise counting of single ions, a Si photodiode is used as a substrate onto which a PMMA film is spun. We have macroscopically investigated the sensitivity of PMMA using 3 MeV H and found that a deposited energy density of greater than 1 eV/nm³ is required to remove the PMMA film for 60 s developing in a water:IPA 1:4 solution. From this sensitivity measurement we have determined that 8 MeV F, 71 MeV Cu and 88 MeV I ions should produce enough damage in a single ion strike to create a hole etched along the latent damage track. We have used AFM imaging to quantitatively characterise the hole diameter as a function of the incident ion and the developing time. It was found that for up to 8 min development in a water:IPA solution holes were created for the F, Cu and I ions. SEM imaging has also been used to verify the holes seen by AFM imaging.

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1. Introduction

Lithography using high energy ions (around 1 MeV per nucleon) is an emerging technique that allows the fabrication of extremely high aspect ratio structures. The passage of such ions through a material produces electronic energy loss that is two orders of magnitude larger than the nuclear energy loss. Large angle scattering events between the incident ion and the target nuclei are mostly limited to the end of range. The resulting damage path is considered to be cylindrical where the diameter is defined by the range of the scattered electrons, the damage density by the linear energy transfer (LET) divided by the cross sectional area and the length is defined by the range of the ion. The highest energy transfer in a binary collision between the ion and an electron is of the order of 1 keV per electron. This gives a diameter in the order of 10 nm and the length in the order of 10⁴ nm. A description of the models proposed for track formation is given by Toulemonde et al. [1].

Track etching is the process whereby the material containing the latent damage of the ion track is removed via chemical dissolution of the damaged volume. The process of etching a track as a means of detecting and identifying the incident ion has been well researched and is covered by the book by Fleischer et al. [2]. A two etch rate model is proposed, the etch rate of the damaged volume $V_T$ and the etch rate of the bulk material $V_B$. The utilisation of this can be seen in [3]. The initial damage track defines the location of the hole and the etching of the bulk material over time increases the hole diameter to a size suitable for easy characterisation (greater than 1 μm allows easy viewing under an optical microscope).

To apply nuclear track etching to the field of lithography the bulk etch rate $V_B$ must be kept at a minimum to preserve the high aspect ratio of the initial latent damage and the nano-scale of the damage track. Our study is...
focused on the commonly used electron beam resist poly methyl methacrylate (PMMA) with a small bulk etch rate compared to the common nuclear track detecting material, CR-39. Fromm [3] gives values for variants of CR-39, Tastrak and Baryotrac, of between 1.6 and 1.9 μm/h (~30 nm/min). Alves et al. [4] show that the bulk etch rate of PMMA varies from 1 to 10 nm/min depending on the developer, mixtures of MIBK and IPA. Well established procedures for spin casting and developing (the process of etching the latent damage) migrated from electron beam lithography make PMMA an ideal starting point resist for studying ion beam lithography (IBL), in fact PMMA has already been widely used by the IBL community. The work of van Kan et al. [5] has shown the ability to write structures into PMMA with a focused beam at a resolution of 100 nm. In their work the damage path is created using the overlapping paths of 2 MeV protons. We aim to identify the conditions required for the production of a hole in PMMA using a single ion and therefore reaching the ultimate resolution limit for ion beam lithography. The use of a nano aperture, as seen in [6,7] with keV ions, and peizo driven precision scanning stage is proposed as a means of positioning the ion strike with an accuracy greater than conventional beam focusing. Aperture fabrication and the passage of high energy ions through the aperture is the subject of another paper submitted to these proceeding by Taylor et al. [8].

2. Experimental

The experimental work was grouped into three parts: (1) Macroscale – the resist response curve was determined by exposing the PMMA to a 3 MeV proton beam in a well defined macroscopic area to allow measurement of the sensitivity as a function of developing parameters. (2) Nanoscale – PMMA films were exposed to F, Cu and I ions with a low enough particle fluence so that single ion strikes would not overlap. This allowed the study of hole formation for the three separate incident ions. (3) Imaging – analysis of macroscopic areas and etched single ion tracks were performed with non-contact atomic force microscopy (AFM). Further imaging was performed with scanning electron microscopy (SEM).

2.1. Film manufacture

PMMA films were spun at 5000 rpm onto Hamamatsu S1223 Si PIN photodiodes and baked for 10 min at 180 °C. For macroscopic sensitivity measurements MicroChem 950 PMMA A2 produced films 55 nm thick. For single ion track experiments MicroChem 950 PMMA A8 produced films 800 nm thick. After coating with PMMA the photodiodes were found to be fully functional and capable of producing signals from single MeV ion impacts after passage through the surface PMMA layer. A grid of pitch 100 μm was patterned into the PMMA using electron beam lithography to provide a location reference for subsequent exposures.

2.2. Exposure

Exposures were performed as described in [4] on two nuclear microprobe beam lines. The 5 MV Pelletron accelerator facility at the University of Melbourne was used to produce a 3 MeV H beam focused to ~2 μm. The 10 MV ANTARES facility at ANSTO was used to produce 8 MeV F, 71 MeV Cu and 88 MeV Iodine beams focused to ~5 μm. The data acquisition system was set to dwell on counts in the pulse height spectrum of the photodiode detector, each count representing a single ion impact. This allowed exposure to a preset number of ion impacts in an array created by positioning the beam with XY scanning coils.

2.3. Developing

Samples were immersed in the developer solution and agitated ultrasonically to etch latent damage from the ion beam exposure. Next the samples were placed into IPA to halt the etching process. Samples were then dried with compressed N₂ gas.

2.4. Sensitivity determination

To test the sensitivity under different developing conditions PMMA was exposed to a 3 MeV proton beam. The LET was calculated using SRIM [9] to be 11.2 eV/nm. The low LET proton beam was used to achieve a rectangular region of uniform damage density across the irradiated area. The irradiated areas comprised of a series of 250 × 25
beam spot arrays with an area of $25 \times 2.5 \, \mu m^2$. The fluence can be considered uniform in the long axis of the exposed rectangular region but probably has some non-uniform profile along the short axis. The PMMA depth was measured using non-contact AFM in a line along the centre of the exposed region, along the line of uniform fluence.

Fig. 2. Non-contact AFM images acquired using a Si nanowisker cantilever tip of regions containing single ion impacts from three different ion species. With increasing developing time, from left to right, the PMMA surface roughens and the width and depth of the holes increases.

Fig. 3. Comparison of imaging with an AFM and a SEM. An area containing single ion impacts from 71 MeV Cu ions developed with MIBK:IPA 1:1 for 5 min. A low electron beam voltage of 100 V is required to avoid damaging the PMMA surface during SEM imaging. The SEM image provides confirmation that both techniques can image the tracks from single ions. The main advantage of AFM imaging is that it offers the ability to quantitatively analyse the topography of the altered PMMA layer.
The non-uniform profile has been calculated by convoluting a single beamspot function with the beam spot array. Two types of beamspot function have been used, square and Gaussian, representing the two limits of the actual function. Error bars have been added to the plot to take into account these limits and to also include the uncertainty in the counts due to dead time fluctuations. Multiplying the measured particle fluence in the exposed area with the LET gives the deposited energy density in units eV/nm$^3$. Following development, the average PMMA height in each exposed region was plotted against the deposited energy density. Two developer combinations have been investigated, MIBK:IPA 1:1 and water:IPA 1:4. Yasin et al. [10] give a comparison between developer combinations for electron beam lithography. The developing solution water:IPA 1:4 was chosen for maximum sensitivity to best allow the etching of single ion tracks. The response curve (Fig. 1) shows that a deposited energy density of greater than 1 eV/nm$^3$ is required to remove the 55 nm film after 60 s of developing in the water:IPA 1:4 solution.

2.5. Holes etched along single ion tracks

For single ion strikes in PMMA the radii of the damage tracks are not well known. We estimate a radius by considering that the passage of a 1 MeV/u ion through a material can produce up to 2 keV electrons which when modelled with the electron Monte Carlo package CASINO [11] have a range perpendicular to the ion path in the order of 10 nm. An integrated Monte Carlo model for ions and electrons is being developed by Udalagama et al. [12] to accurately determine the radial damage profile of a single MeV ion in PMMA. For H and He with LET values less than 300 eV/nm, it is not certain that the damage deposited along a track (LET/$p^2$) reaches the sensitivity threshold of 1 eV/nm$^3$. We first ensure that the energy densities are

![Image](image-url)
3. Imaging

Non-contact atomic force microscopy (AFM) has been used to image the ion irradiated areas. A high aspect ratio Si nanowhisker tip (NT-MTD, NSC05) allowed higher resolution and image depth than a standard tip. Areas containing less than 300 ions in the 5 μm beam spot showed no overlap between the single ion impacts. Fig. 2 shows the evolution of single track etching over increasing developing time in a 2 × 2 μm² area containing 30 ions per beam spot. It can be seen that as the etching occurs the PMMA surface is roughened and the width and depth of the holes increases. Image quality was monitored by re-imaging previously imaged areas. An observed loss in measured topographic height necessitated the selection of a new tip. Further imaging of the etched ion tracks was performed by low voltage (100 V) scanning electron microscopy (SEM) and offered a comparison to the AFM images (Fig. 3).

3.1. Image analysis

An algorithm to automatically identify ion impacts was adopted as follows. For each 2 × 2 μm² image (Fig. 4(a)) containing holes a pixel height histogram is generated (Fig. 4(b)). A Gaussian curve is fitted to the distribution of pixels at the PMMA surface, $A_i \exp\left(-\frac{(z - \mu_i)^2}{(2\sigma_i^2)}\right)$, the subscript, i, indicates a curve fit to the hole. The amplitude, $A_i$, is subtracted from the entire image to set the PMMA surface equal to a height of 0 nm. A surface roughness discriminator level is set at the pixel height, $z$, where the Gaussian fit intersects the y-axis equal to 1 pixel. As each sample has a different surface roughness the discriminator level is dependent on the Gaussian fit. This level is used to create a one-bit image showing the location of holes (Fig. 4(c)). A depth profile is found for a select number of holes in the image (an example profile is shown in Fig. 4(d)). A second Gaussian curve is fitted to the AFM depth profile, $A_h \exp\left(-\frac{(z - \mu_h)^2}{(2\sigma_h^2)}\right)$, the subscript, h, indicates a curve fit to the hole. The amplitude, $A_h$ and sigma value, $\sigma_h$, are used to quantify the measured hole depth and width. If the holes are sufficiently deep, beyond the probed depth, we anticipate that the measured depth and width are related solely to the shape of the AFM tip, with the consequence that when plotting width verses depth all of the data should lie on a unique curve. However, if the

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**Fig. 5.** (a) For each set of holes created using the ions F, Cu and I the mean value of $A_h$ is plotted against the mean value of $\sigma_h$. Where $A_h$ and $\sigma_h$ are proportional to the depth and width of the hole. Shaded discs surrounding each point represent the characteristic spread of data points. The developing time is written next to each data point. (b) Variation in the surface roughness of the PMMA with increasing etching time, each data point representing one 2 × 2 μm² image. It was not possible to use that same AFM tip for each image, it is therefore possible that the roughness of the surface could be affected by the tip chosen. As expected it can be seen that the roughness increases with developing time over 1, 2 and 4 min yet the surface is smoother after 8 min. We conclude that this is an artefact of the different tip used.
holes are not sufficiently deep then the measured depth will be equal to the actual hole depth and the depth and width will be uncorrelated. Therefore, a change in the damage density brought about by a different ion would lead to a difference in the probed depth for each ion species.

Fig. 5(a) shows the mean value for the width verses depth for every hole of the data set. A shaded disc surrounding the data points signify the characteristic spread of values. For the F ion impacts only the 8 min developing data set is shown and for developing times less than 8 min the holes were not well formed enough to allow quantitative analysis. For Cu and I ion impacts the data shows that the depth of the holes continues to increase as the development time increases. A width below \( \sigma_h \approx 10 \text{ nm} \) was not measured and it is believed that this is due to the finite width of the cantilever tip. The depth of holes etched along the Cu ion tracks are marginally shallower than those etched along the I ion tracks even though the widths are the same. This indicates that the depths and widths are uncorrelated and the Cu ion tracks have not been fully etched. This effect however is only slight and not beyond the tolerance imposed by the measurement uncertainties. It can also be observed that the hole widths do not increase from 4 to 8 min developing time indicating that the latent damage radius is not larger than when \( \sigma_h \) is equal to 30 nm.

Fig. 5(b) shows a comparison of surface roughness, defined by the width of the Gaussian fit, \( \sigma_h \), as a function of the developing time. The lower surface roughness value for the 8 min development is attributed to the different tip that was used. It was not possible to use the same tip for each AFM image because it was observed that tips degraded after multiple images.

4. Conclusions

Single ion tracks can produce etchable holes in PMMA for ion energy densities greater than 1 eV/nm\(^3\). Such tracks have been observed following irradiation with 8 MeV F, 71 MeV Cu and 88 MeV I ions, however, H and He single ions cannot deliver these energy densities and do not produce single ion tracks under the developing conditions used here. Imaging of the holes has been demonstrated using AFM and low voltage SEM. The AFM data has been analysed to determine depth and width of etched holes as a function of development time. This analysis shows that holes caused by 8 MeV F tracks are smaller than those caused by 71 MeV Cu and 88 MeV I ions. The Cu ion tracks have a smaller depth than I ion tracks while having the same width indicating the Cu ion tracks have not been etched along the full thickness of the film. Whether the I ion tracks extend through the full film thickness remains an open question and will be the subject of further work.

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References

Geochemical compositions of Miocene marine fossils and their embedding sediments were investigated from a number of circum-Alpine localities in order to determine the changes in climate and oceanography during an active phase of Alpine upliftment. 

$^{87}\text{Sr}/^{86}\text{Sr}$ of most fossilized shark teeth indicate that the marginal seas adjacent to the emerging Alps had good connections to the open oceans. However, some deviations from the Sr-evolution curve of the open ocean exist but can be related to a local influence by the hinterland lithologies. $\delta^{18}\text{O}$ values of teeth from the north Alpine Molasse basin, the Vienna and Pannonian basins, parallel the relative changes in $\delta^{18}\text{O}$ values observed for the global record (Zachos et al., 2001). Exceptions to this are given by $\delta^{18}\text{O}$ values of two shark teeth that are compatible with a formation while the sharks frequented a freshwater habitat, but that experienced diagenesis under conditions identical to those of the other teeth. These “freshwater” teeth can be used to estimate a Miocene paleoelevation that was similar to that of the Alps today. $\varepsilon_{\text{Nd}}$ values of marine fossils vary considerably ($-3.9$ to $-12$), but these values as well as their REE patterns differ from those of the embedding sediments, supporting fixation of the REE in the fossils during early diagenesis in the presence of a marine-dominated embedding sediments, supporting fixation of the REE in the fossils.

We report an approach to obtain new insights into fission track development and its etching behaviour close to the nanoscale in fluorapatite and mica using an atomic force microscope (AFM). In the present work, fission tracks were implanted in mica and fluorapatite using a 50 keV $^{252}\text{Cf}$ source and imaged with an AFM.

In our work we studied unetched fission tracks in micas and fluorapatite. It was found, that fission track openings are crater-like structures in the mineral surface with diameters between 16 and 28 nm. Some openings have a pronounced raised rim that may represent the region of strained lattice around the track core. Besides the large variation, a general increase by about 1.5–2 $\varepsilon_{\text{Nd}}$ units is observed for the Lower and Middle Miocene in the north Alpine area and the Paratethys, reflecting increasing Atlantic influence on the marginal Alpine basins. $\varepsilon_{\text{Nd}}$ units of the southern Alpine region have a range of between $-8$ to $-9$ with a minimum at 16 Ma (Mühlstrasser, 2001). To further constrain the variation of these Tethys-Mediterranean $\varepsilon_{\text{Nd}}$ values and the connection between these basins and the Paratethys, additional sections from Italy and Slovenia are being investigated.

Climatic and oceanographic changes during the deposition of circum-Alpine Miocene marine sediments

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Atomic force microscopy of fission tracks in fluorapatite and mica: A tool for nanoscale investigations

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