

**Strategies for Secondary Ion Yield Enhancement in
Focused Ion Beam Secondary Ion Mass Spectrometry**

by

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Declaration

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions.

This work was done under the guidance of Dr. David McPhail, at the Department of Materials within the Imperial College London.

Libing Li

9th September 2009

不自是，故彰；不自伐，故有功；不自矜，
故器；亦唯不爭，故天下莫能與之爭！

To my Parents.

Abstract

Focused Ion Beam Secondary Ion Mass Spectrometry (FIB-SIMS) has the potential to provide crucial small-area elemental analysis by combining the high spatial resolution of FIB (5 nm) with the high elemental sensitivity of SIMS. Unfortunately, the sensitivity provided by the Ga^+ beam is orders of magnitude poorer than that found using a reactive source such as O_2^+ or Cs^+ . To increase the range of applications of FIB-SIMS it is essential that we produce larger secondary ion yield in order to achieve higher sensitivities.

This report reviews a study of methods of enhancing the secondary ion yield by changing the surface chemistry with reactive ion sources. Methods such as low energy oxygen or nitrogen implantation with the Atomika 6500 and oxygen flooding with the ION-TOF IV system have been studied. The chemically modified altered layers were then analysed in the FIB-SIMS system. The secondary ion yield was enhanced by the implantation of nitrogen and oxygen. The low beam energy was efficient to provide maximum ion yield enhancement which was more than two orders of magnitude. It has been shown that the ion yield enhancement provided by oxygen implantation was the same as that provided by oxygen flooding. The advantage of using oxygen implantation is that the implant area and depth can be precisely controlled. The disadvantage is the ion yield enhancement depth is finite. The thickness of the altered layers was also studied with cross-sectional transmission electron microscopy (TEM).

AlGaAs/GaAs test structures were used to investigate the damage of the altered layer induced by the low energy beam sputtering. The damage associated with primary ion implantation was obtained by TEM. The results have shown that at low energy oxygen and nitrogen sputtering, the damage was much compressed. For 1 keV Ar^+ ION-TOF IV bombardment sample rotation was used. Surprisingly, the depth profile was not improved by this technique simply because ion mixing remained a limiting factor.

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Chapter One

1. Introduction and Objectives

1.1 Introduction

The semiconductor industry has been revolutionised in terms of radios, phones, and computers since the invention of transistor in 1947 ^[1]. The dimensions of Complementary Metal-Oxide Semiconductor (CMOS) devices have been reduced exponentially for several decades as this leads to inherent advantages of increased speed, lower power consumption, lower cost-per-function, improvements of productivity and high performance. The most common description of the evolution of CMOS technology is known as Moore’s Law, ‘an exponential growth in the number of transistors per square inch on integrated circuit which have doubled every 18 months’ ^[2].

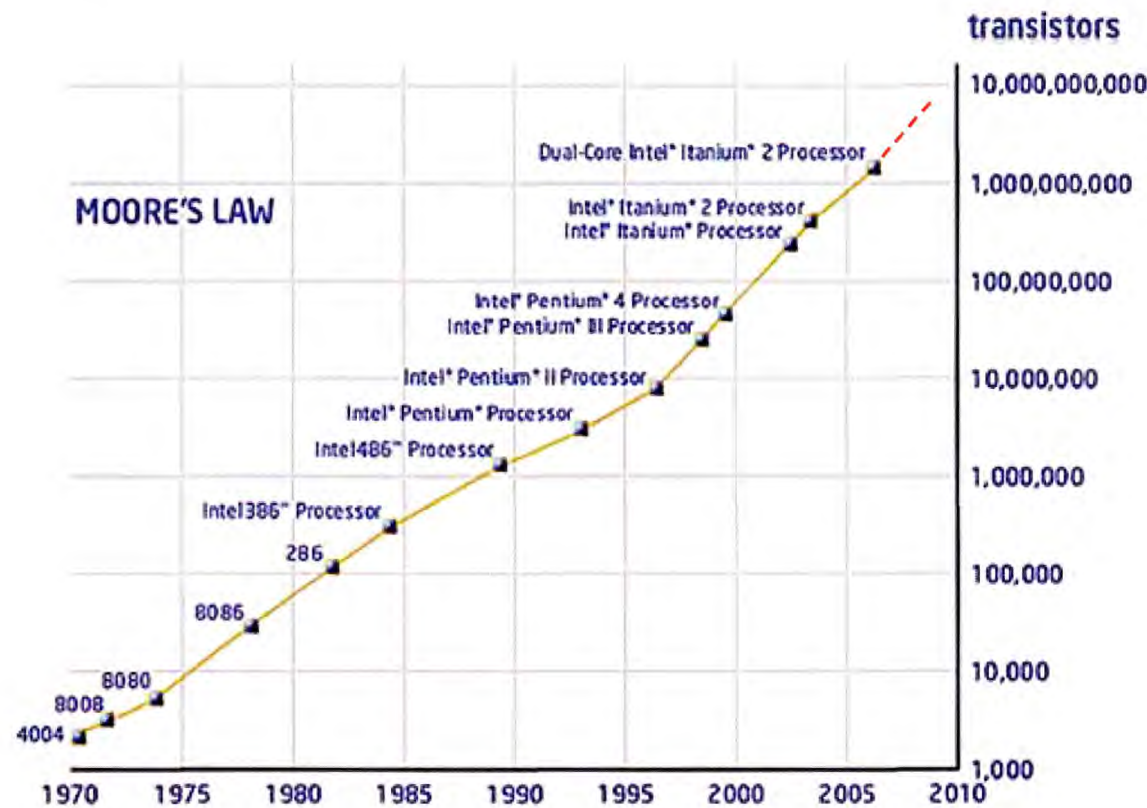


Figure 1.1 Moore’s Law – the actual number of components are shown to increase exponentially over the last 35 years, according to the manufacture of Intel’s microprocessors ^[3].

Scaling down devices leads to some major problems such as the Short Channel Effect (SCE). The SCE dominates them as a gradual effect as the gate length is decreased and causes several problems such as substrate leakage current, hot electrons, latch up, punchthrough, and leads to an increased junction sheet resistance. The Lightly Doped Drain (LDD) structure was necessary to improve hot carrier immunity of CMOS by reducing the electric field strength at the drain edge. By decreasing the Source/Drain (S/D) doping concentration the depletion layer becomes thicker and the electric field is reduced. In addition, a lower doping concentration leads to a shallower junction depth, which is also effective for improving SCE immunity. However, LDD went out of use after the quarter-micron generations because shallower and lower doping results in higher sheet resistance. The very shallow doped Source/Drain extension (SDE) was then modified to maintain the high performances of the devices. These junctions are referred to as ultra shallow junctions. The new generations of CMOS devices require an extension depth of 16-26 nm (the international technology roadmap for semiconductors (ITRS) predicted that by the year of 2014, the extension depth will be ~8-13 nm)^[4]. Furthermore, the gate oxide thickness must be reduced to maintain the gate field at the reduced gate voltage. However, this can lead to high gate leakage currents and boron penetration. New materials such as oxynitride films and oxide/nitride are considered as a good substitute for SiO₂^[5]. With the miniaturization of devices, quantitative determination of these shallow implanted device doping profiles is identified (ITRS roadmap) as one of the significant needs of the semiconductor industry^[6].

Secondary Ion Mass Spectrometry is an analytical technique used to characterise the surfaces of solids and has been used to measure doping profiles in semiconductors for many decades. It is one of the most sensitive elemental surface analysis techniques that provides trace element sensitivity, with a capability of sub-nanometre depth resolution for almost all elements. It provides various modes of analysis including depth profiles, imaging, isotopic analysis and three-dimensional (3D) SIMS. This technique uses a primary ion beam to bombard a sample surface followed by mass spectrometry of the emitted secondary ions. Figure 1.2 demonstrates the capability of SIMS for measuring shallow profiles with sensitivities down to 1×10^{16} atoms/cm³. Figure 1.2a shows an As implanted silicon wafer with implantation conditions of 3 keV implant energy and 2×10^{15} /cm² dose. The depth profile was gained with an ION-

TOF IV using a Cs primary beam (500 eV) with a sputter rate of 4 nm/min^[7]. Figure 1.2b shows the SIMS depth profile of the nitrogen concentration as a function of depth for six oxynitride films grown under different processing conditions^[8].

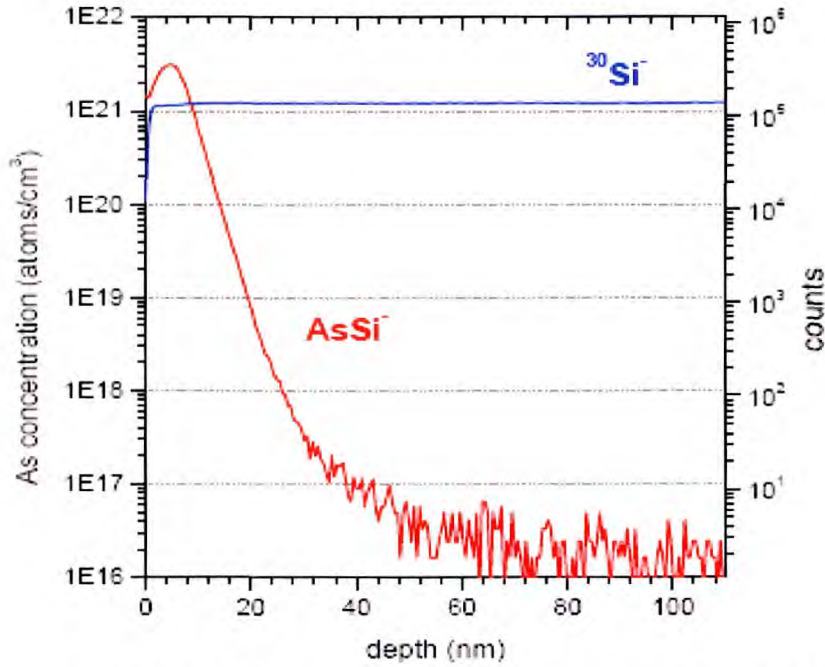


Figure 1.2a) Implant conditions: As implant, energy 3 keV, $2 \times 10^{15}/\text{cm}^2$, depth profiled by an ION-TOF IV, shallow profiling with sensitivities down to 1×10^{16} atoms/cm³^[7].

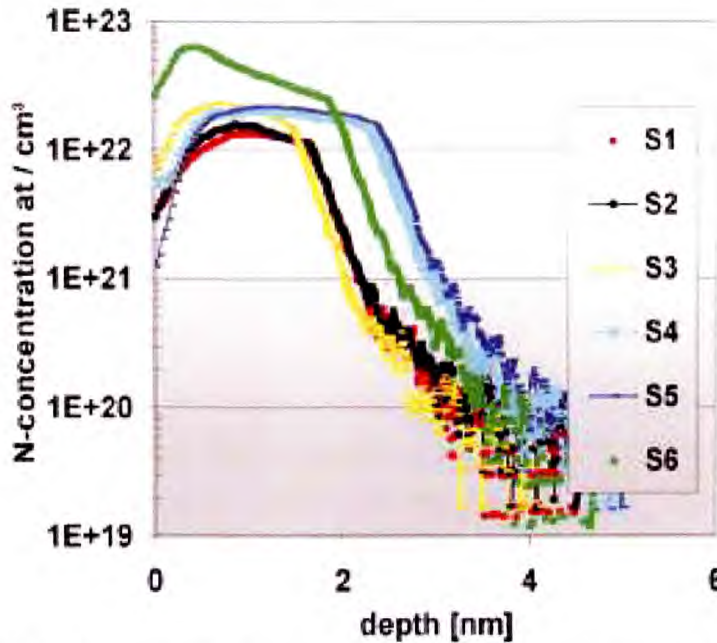


Figure 1.2b) The composition as a function of depth of six oxynitride films. The sample were analysed using a 250 eV oxygen beam at an angle of incidence of 70° on an Atomika 4500 at FEI Munich^[8].

The Focused Ion Beam (FIB) is an inherently destructive microanalytical tool that uses a focused beam of ions to scan the sample. It combines high resolution imaging in secondary electron and ion modes. Small probe sputtering is achieved by the Liquid Metal Ion Source (LMIS). Ga^+ is the most commonly used LMIS in the FIB systems, because of its reliability, reproducibility and stable beam for a reasonable lifetime which can exceed 1000 hours. The modern FIB system has become a very attractive tool for nanofabrication with a high spatial resolution of 5 nm. Its capabilities have expanded into many applications including lithography, wafer repair, TEM sample preparation, and metal alloys [9, 10].

Focused Ion Beam Secondary Ion Mass Spectrometry (FIB SIMS) involves the integration of a SIMS analyser into a FIB system. It potentially combines the high spatial resolution of FIB (~5 nm) with the high elemental sensitivity of SIMS. This has made it possible to provide crucial small area elemental analysis for some systems with examples from areas as diverse as semiconductors, superconductors, glass, stainless steel, solid oxide fuel cell components, museum artifacts, aerospace alloys and biomaterials [3-6].

However, despite the advantages of using Ga^+ LMIS in the FIB system, the sensitivity provided by the Ga^+ source is not as good as that found using reactive sources, indeed it is generally several orders of magnitude lower. This results in poor ion yields which lead to poor sensitivities. The sensitivity is defined in the literature as that concentration that will produce x counts per data point. Different authors [11] use $x = 1$, $x = 10$, or $x = 100$. Here we use $x = 1$. As the analysis volume gets smaller and smaller it becomes a big problem for conventional SIMS. The problem for the FIB SIMS is its low sensitivity. The relationship between the analytical volume and the ion yield can be simply expressed as:

$$I_x = Y_x * V * \rho_x \quad (1)$$

Where I_x is the ion intensity of type X^+ , V is the analytical volume, Y_x is the ion yield and ρ_x is the concentration of the monitored atom X . If $I_x = 1$, then equation (1) can be re-written as:

$$\rho_{\min} = \frac{1}{Y * V} \quad (2)$$

Figure 1.3 shows the main advantage and challenge for the FIB SIMS technique. As the figure shows, the analysis volume in the range of 10 nm to 100 nm is mainly the FIB SIMS territory which is its main advantage over other analytical techniques, but the ion yield is very low ($\times 10^{-6}$) which limits its detection capability to the bulk level. Hence, the challenge is to take advantage of the excellent lateral resolution of the FIB ion beam, and at the same time to bring that secondary ion yield (or sensitivity) at least below the level of part per thousand (PPT) or even in the region of part per million (PPM).

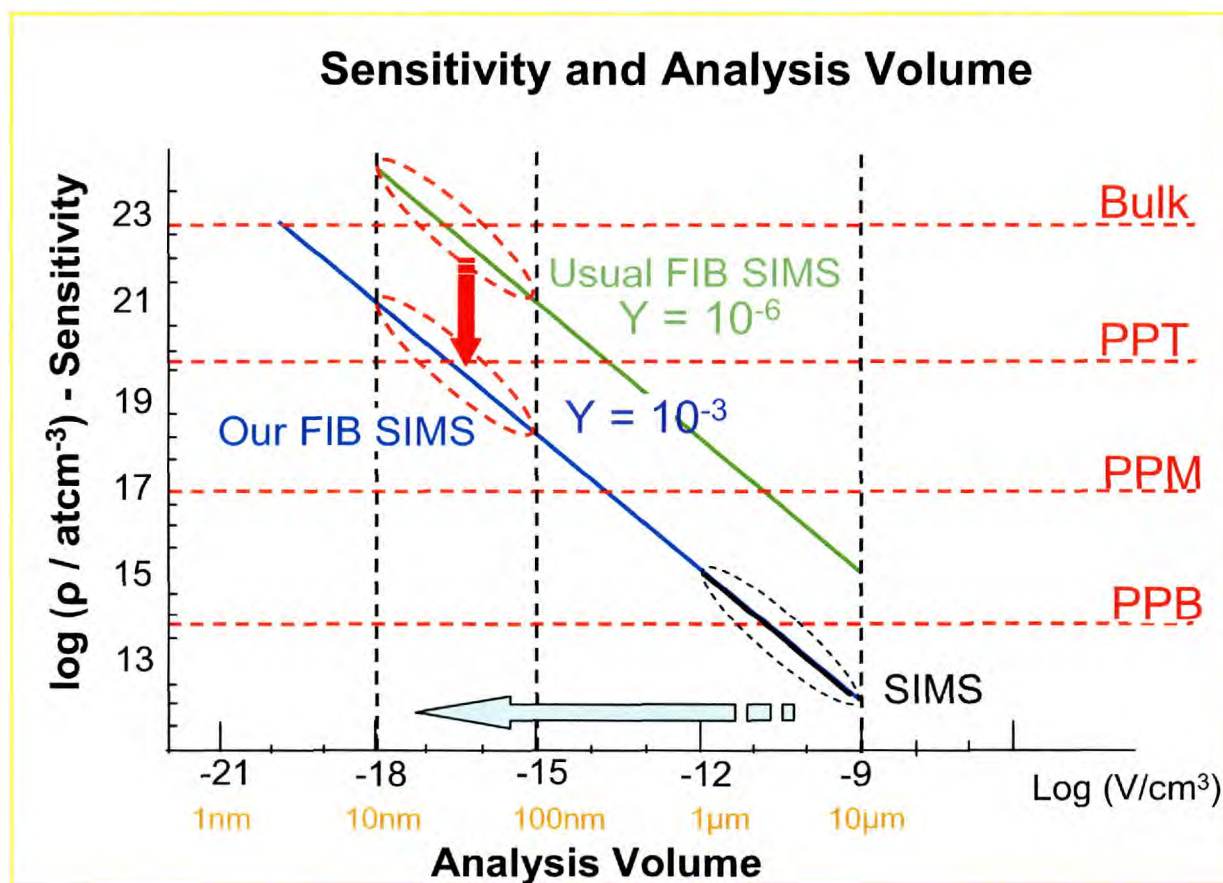


Figure 1.3 shows the sensitivity as a function of analysis volume. As the analytical volume continues shrinking down, the challenge for the FIB SIMS is to increase the sensitivity in order to extend its applications in Materials Science.

It is believed that methods of enhancing the secondary ion yield such as surface chemistry modification with reactive ion sources (e.g. oxygen, cesium deposition and oxygen flooding) and injection into the system of reactive gases can increase the secondary ion yield up to two or three orders of magnitude. Figure 1.4 shows FIB elemental map images of an Intel Pentium Microprocessor with/without oxygen pre-dosing. Clearly, the one on the right has much better contrast and brightness.

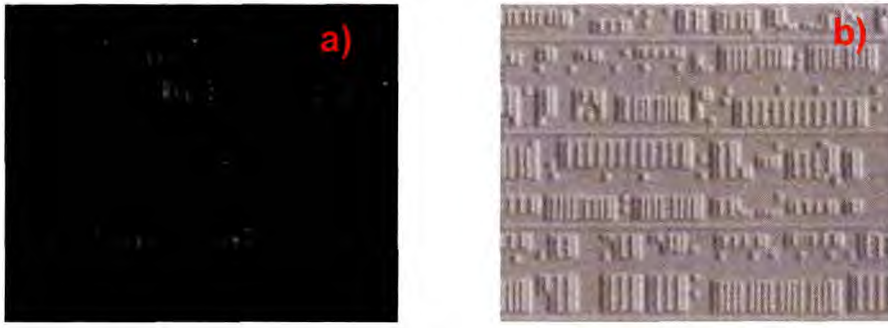


Figure 1.4 Elemental map images of a Pentium microprocessor obtained by monitoring the intensity of Si^+ ions produced as a result of 30 keV Ga^+ bombardment, a) with oxygen implantation, b) without oxygen implantation. Image dimensions: $60 \times 60 \mu\text{m}^2$ [12].

The other approach is to increase the analytical volume by scanning the beam in a series of annular rings, the analytical volume can be increased by two orders of magnitude, shown in figure 1.5 [13]. The third method one could try to do is to increase the secondary ion transmission, T.

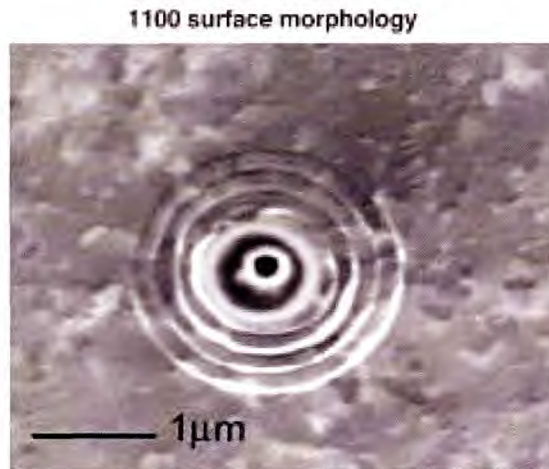


Figure 1.5 A FIB SEM image of an area of a manganese sulphide inclusion. A series of annular rings has been drilled in order to maximise the analytical volume. The SIMS analyser has been used to detect the intensity of the chromium and the iron signals. The 30 keV Ga^+ primary beam current during milling was 100 nA, FEI FIB 200, Imperial College [13].

1.2 Objectives

The objectives of this work are:

1) To investigate how the ionization probability might be improved by changing the surface chemistry by ion implantation prior to analysis. In these experiments, we will pre-dose the surface of the materials by low energy ion implantation with reactive ion species (N_2^+ , O_2^+). The secondary ion yields produced with different implantation conditions (e.g. energy, dose) will be compared.

2) To investigate how the ionization probability might be improved by changing the surface chemistry prior to analysis by oxygen flooding. The oxygen flooding method has been widely used to enhance positive ion yields. We will use different oxygen flooding pressures to study how secondary ion yields change with pressure. The secondary ion yield enhancements of ion implantation and oxygen flooding will be compared and the relative merits of the two techniques compared.

3) To investigate the ion beam induced altered layer by TEM. The thickness of the altered layers will be measured by using the Transmission Electron Microscope. How the altered layer thickness varies with the implant conditions will be studied.

4) To measure the altered layer by SIMS depth profiling on the FIB SIMS and the ION-TOF and to compare and contrast the results.

5) To measure the damage introduced during chemical modification of the surface using a specially grown AlGaAs test structure.

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Chapter Two

2. Experimental Theory

2.1 The Secondary Ion Mass Spectrometry (SIMS) Process

The first fundamental experiments on SIMS were pioneered by Herzog and Viehböck in 1949, at the University of Vienna, Austria. The instrument used electric fields to accelerate primary ions to the sample and an electric field parabola spectrograph to separate the secondary ions and record secondary ion mass spectra from metal oxides ^[1]. The first “Modern Day” SIMS paper was published in 1958 by Honig ^[2]. Then in the early 1960s two SIMS instruments were developed independently. One from an American project, led by Liebel and Herzog and a French project initiated by Castaing and Slodzian ^[3, 4]. The first commercial SIMS instrument, the CAMECA IMS-300, was introduced in 1968.

SIMS is widely used for analysis of trace elements in solid materials. In this technique a primary ion beam is bombarded onto a sample surface and mixes with target atoms in an ultra-high vacuum (lower than $\sim 10^{-9}$ mbar). When the primary ions strike the surface, a series of collisions will occur between primary ions and target atoms. Primary ions will finally come to rest, with many target atoms displaced from their original positions. This is often described as a collision cascade. Some of the atoms near the sample surface have enough energy to leave the surface. The majority of those emitted species are usually neutral, only a small fraction of the atoms are ionised either negatively or positively.

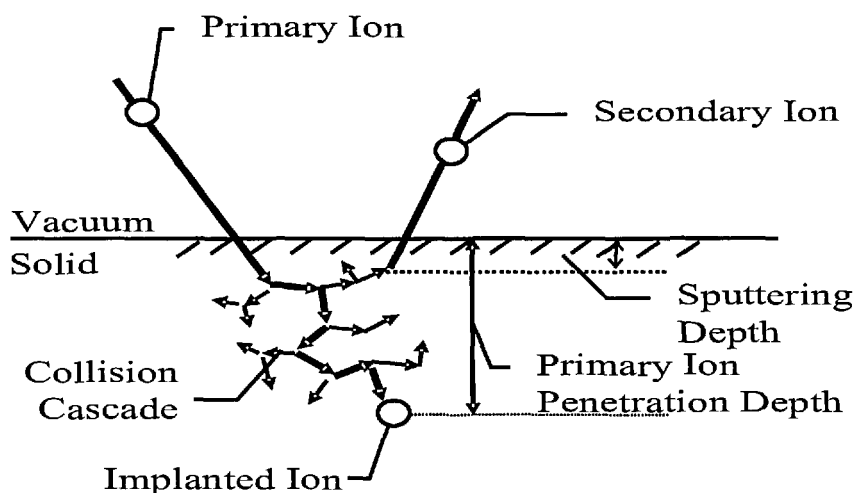


Figure 2.1 The collision cascade in SIMS ^[5].

The secondary ions are then extracted and accelerated into a mass spectrometer where the ions are separated according to the mass-to-charge (m/q) ratio. Ions of a specific m/q are allowed to pass (only for quadrupole systems) into an electron multiplier detector for pulse counting. The output of the detector is sent to the computer where the collected data can be displayed as a compositional depth profile, an elemental map of the analyzed surface, or a mass survey. Figure 2.2 shows the general synopsis of a SIMS analyser [6].

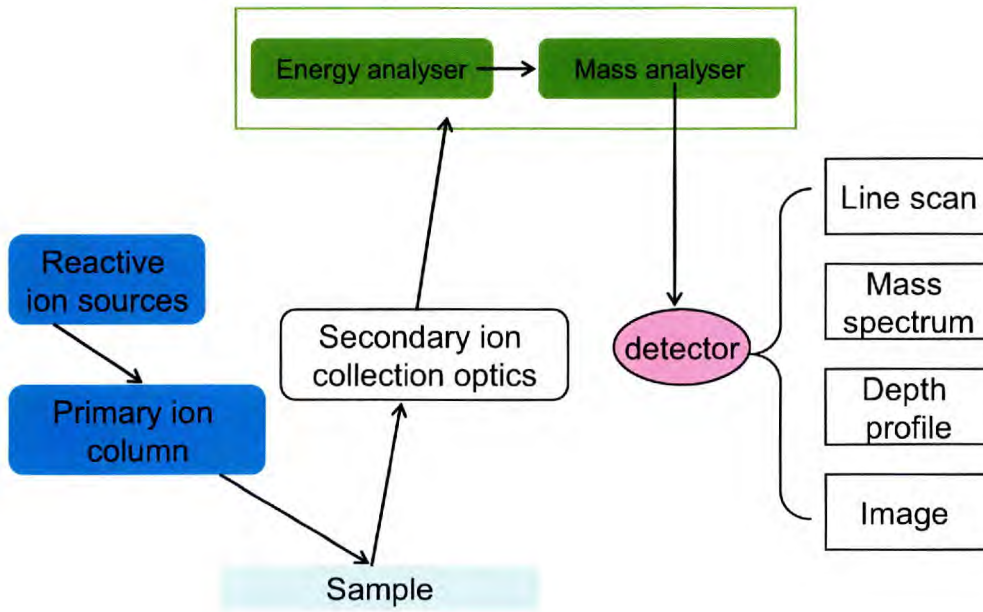


Figure 2.2 General synopsis of a SIMS analyser.

2.1.1 Quantification in SIMS

In the sputtering process, the analytical volume sputtered away by the ions is:

$$V = Az \quad (1)$$

where V is the total analytical volume, A is the sputtered area, and z is the sputtered depth. If the concentration of the monitored atom X is $\rho_{(x)}$ then the number of atoms removed is $\rho_{(x)} * Az$. Some of these atoms are ionised as positive (or negative) ions X^+ during sputtering, so the number of X^+ ions sputtered (X_{sp}^+) is:

$$X_{sp}^+ = \alpha_{(x^+)} \rho_{(x)} Az \quad (2)$$

Where α^+ is the ionisation probability. α^+ differs strongly across the periodic table (can be up to 10^4) depending on several factors (discussed in Chapter 3). The number of secondary ions that will actually pass through the mass spectrometer and be detected will depend on the efficiency of the secondary ion optics and the detector. *These*

factors are collectively known as the secondary ion transmission coefficient T . T can vary day to day on the same instrument, it can also vary from one species to another. Thus the number of X^+ ions detected $N(x^+)$ is:

$$N_{(x^+)} = (\alpha_{(x^+)} T_{(x^+)}) \rho_x A z \quad (3)$$

This is referred to as 'the basic SIMS equation' and can also be written as:

$$N_x = Y_x * V * \rho_x \quad (4)$$

The basic SIMS equation is the basis of the quantification process [7]. The central construct in SIMS quantification is useful ion yield, Y (ions/atom), the ratio of ions detected to atoms sputtered. Y is the product of the ionisation probability and the transmission coefficient, $Y = \alpha * T$. The improvement of useful ion yields leads to better sensitivity of the SIMS technique. In a SIMS depth profile to convert the SIMS raw data (ion intensity as a function of time) to quantified data (concentration as a function of depth), a profilometer is used to measure the total sputter depth. The total depth divided by the total sputter time is the sputter rate. A constant sputter rate is assumed for single matrix layer analysis. For multilayer analysis the sputter rate can vary for the different layers, corrections need to be made if changes of the sputter rate occur. Thus, to convert intensity to concentration on the Y axis, an ion-implanted standard is required. This is because useful ion yields for a given element or molecule may vary significantly depending on the chemical matrix. Therefore, it is necessary to have an ion-implanted standard which is produced by ion-implantation of the impurity element into a same matrix of the same chemical composition as the examined sample (for multilayer analysis it is necessary to have an ion-implanted standard for each dopant-matrix combination).

2.1.2 Modes of SIMS

There are two main modes of analysis in SIMS, static and dynamic. Static SIMS (SSIMS) emerged as a technique of potential importance in surface science in the late 1960s and early 1970s [8]. It is the process involved in surface atomic monolayer analysis. In SSIMS a surface is bombarded by a focused low energy ion beam with a very low dose of primary ions ($<10^{12}$ ions/cm²). The aim is to obtain sufficient signal to provide compositional analysis of the surface layer without actually removing a significant fraction of a monolayer (0.1-1%). A maximum efficiency of analysis and significant information level are required. Dynamic SIMS is used to analyse the

elemental composition of materials as a function of depth. In dynamic SIMS, a much higher sputtering rate (0.25 -50 keV) and primary ion dose ($>10^{12}$ ions/cm²) are used. The primary ion beam is rastered over an area to a certain depth producing hopefully a flat-bottomed crater. The secondary ion intensity as a function of time is plotted and may be converted to a profile of concentration versus depth using suitable quantification procedures.

When a primary ion beam is bombarded on a sample surface it mixes with target atoms to a depth beneath the sample surface. This causes cascade collisions between the primary species and target atoms. The relocation of material in the sample surface can be attributed to the effects of sputtering, atom mixing, radiation enhanced diffusion ^[9] and radiation-induced segregation ^[10], resulting in a chemically and physically modified region termed the altered layer. This effect is further complicated if the sputtering ions are reactive (O_2^+ , Cs^+) and create new compounds in the sample ^[11]. Oxygen is famously known for enhancing the positive ion yield, the oxidation of the beam induced altered layer can be beneficial. The degree of yield enhancement increases with increased oxygen doses until it became constant, indicating saturation of the oxygen concentration at the analysis depth ^[12]. The behaviour of silicon samples under O_2^+ bombardment at various energies and angles has been studied extensively ^[13] with regard to the shape and thickness of the modified oxide layer. It has been shown that oxygen bombardment of silicon gives an altered layer with a composition of SiO_x , where $x \leq 2$ depending on the analysis conditions (e.g. incident angle).



Figure 2.3 Firstly O_2^+ primary ions are implanted into silicon and then an ion induced oxide layer SiO_2 is formed.

Thus, the altered layer consists of three distinct regions: 1) for oxygen bombardment, ranging from normal to 18° angles of incidence the composition of the surface region is close to SiO_2 up to a depth of 1-1.13 time the projected range of the

oxygen primaries in silicon, 2) a region over which the oxygen content decreases over depth, 3) a third region - contains mostly radiation damaged silicon ^[14]. It has been shown that the layers produced from normal to 20° incidence beam appeared to be completely oxidized. Above this angle of incidence more of the implanted oxygen is consumed in the sputtering process making a complete oxidation of the altered layer impossible ^[15].

Imaging SIMS is used to obtain the lateral distribution of species with minimum possible damage to the surface. A primary ion beam is scanned over the sample surface in a scan pattern whilst monitoring secondary ion intensities as a function of beam position. The imaging SIMS can be divided into two modes depending on the mass spectrometer being used. In addition, secondary electrons are also released during the bombardment process, which allows secondary electron imaging to enable accurate positioning of small features for subsequent analysis. Figure 2.4 shows images of a pyrite (FeS₂) grain from a sample of gold ore with gold located in the grain boundaries of the pyrite grains ^[16].

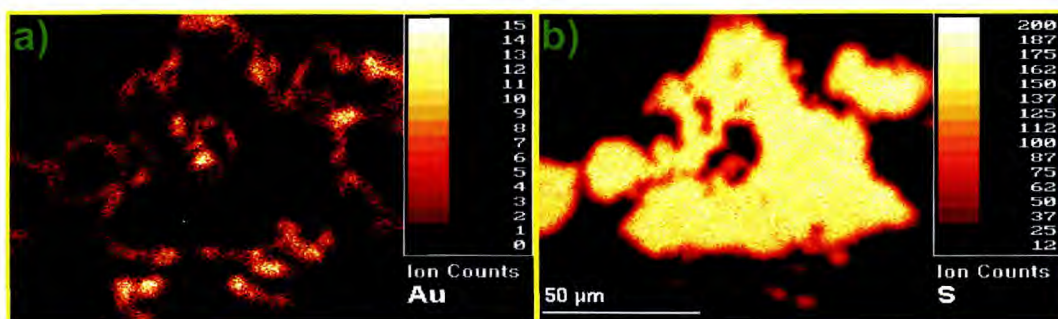


Figure 2.4a) ¹⁹⁷Au, b) ³⁴S. The imaging results are presented as images of secondary ion intensity. The numerical scales and the associated colours represent different ranges of secondary ion intensities per pixel ^[16].

Mass interference is a common problem that exists in the ion detection. That is an interfering signal can be superimposed to the signal of the searched ion: it occurs when two ions have the same nominal mass, e.g. ²⁸Si₂⁺ and ⁵⁶Fe⁺. Although the interfering pair has the same nominal mass, a mass spectrometer of sufficiently high mass resolution can separate them. The resolving power is the ability to yield distinct signals for two ions with a small mass difference ^[17]. If Δm is the smallest mass difference between ion with mass m and ion with mass $m + \Delta m$, the definition of the resolution is called mass resolution, $R = m/\Delta m$. Where m is the nominal mass at

which the peak occurs, and Δm is the mass difference. Figure 2.5 shows the mass spectrum observed from sputtering a silicon wafer. The mass resolution is sufficient to split the iron signal $^{56}\text{Fe}^+$ from the interference due to $^{28}\text{Si}_2^+$ and the $^{63}\text{Cu}^+$ signal from the interference due to $^{28}\text{Si}^{35}\text{Cl}^+$ [18].

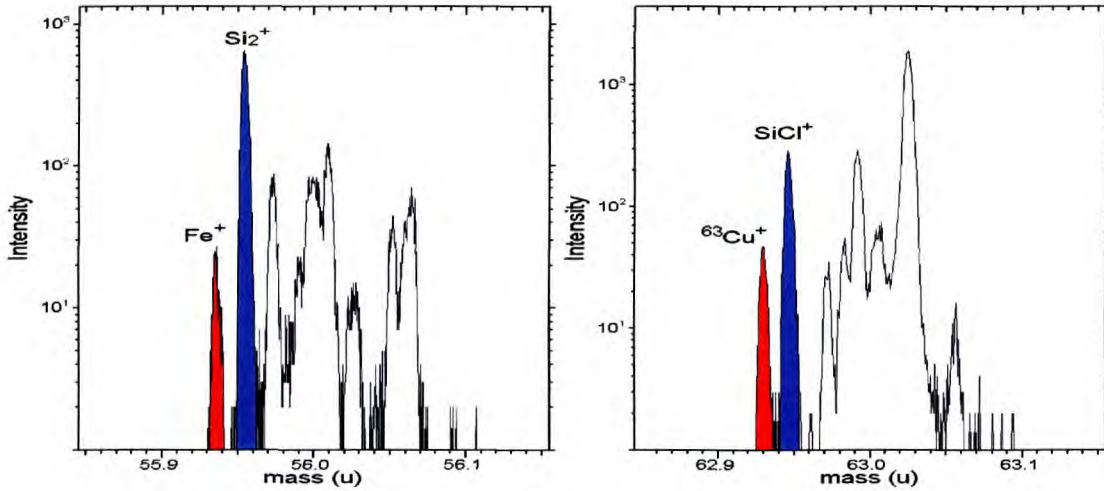


Figure 2.5 Shows an analysis of a silicon wafer using a high mass resolution from an ION-TOF V instrument, courtesy of Mr Colin Helliwell. This instrument uses a TOF mass spectrometer and can achieve mass resolutions in excess of 10,000 [18].

2.1.3 Mass Spectrometer

The semiconductor industry has made great demands for high performance SIMS instrumentation. A high quality mass spectrometer should enable one to gain full information. There are three main characteristics of a mass analyser, namely: upper mass limit, the transmission and mass resolution. The mass limit determines the highest value of the mass-to-charge (m/q) ratio that can be measured. The transmission is the ratio between the number of ions reaching the detector and the number of ions leaving the sample surface. The most widely used mass spectrometers are Quadrupole, Magnetic Sector and Time-Of-Flight (TOF).

2.1.3.1 Quadrupole (QMS)

The quadrupole mass spectrometer is a device that separates ions according to their mass-to-charge ratio. It is capable of transmitting only one mass at a time, only one secondary ion species can be mapped at a time, and the elements of interest must be mapped sequentially [5]. A quadrupole instrument is made up of source, focus lenses, four rods with circular, or ideally, hyperbolic section, and a detector. It uses oscillating electrical fields to selectively stabilise or destabilise ions passing through the radio frequency quadrupole field. The applied radio frequency potentials force

most of the ions that do not have the desired mass-to-charge ratio to describe unstable trajectories and to collide with the rods. Only desired ions follow a periodic trajectory with limited amplitude and are therefore transmitted. When the desired ions leave the mass spectrometer, the weak ion signal needs to be amplified. An electron multiplier allows those selected ions to be detected by converting secondary ion pulses into amplified electron pulses. This is done by the ions to be detected hitting the first dynode C of the multiplier where they produce secondary electrons. These electrons are then accelerated by a suitable voltage difference (200-300 eV) toward the next dynode where they release secondary electrons. In the pulse counting mode each electron current pulse corresponds to an individual ion arriving at the conversion dynode ^[19]. The intensity of ions as a function of m/q is plotted. Because quadrupole mass spectrometers are low transmission (1-10%) devices and only allow the sequential transmission of ions, the information loss is high. A typical quadrupole system has a mass resolution of about 300.

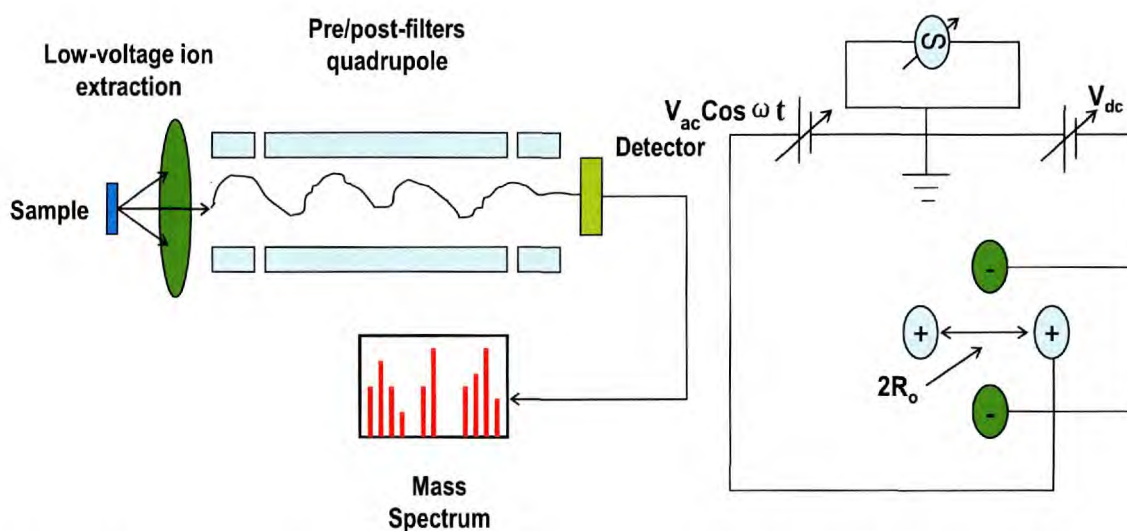


Figure 2.6 A diagram of operation of a quadrupole mass filter. a) Shows longitudinal cross-section, showing stable trajectories; b) Radial cross-section, showing applied voltages ^[18].

2.1.3.2 Magnetic Sector (MS)

A magnetic sector instrument operates in double focusing mode. A high extraction potential extracts the ions from the sample to a series of lenses which focus the ions to the source slit of a double focusing sector. The ions then are deflected by the magnetic field, B , and exit with different trajectories depending on the mass to charge ratio only. That is the ions of mass to charge ratio have equal *centrifugal force* and *centripetal force*:

$$mv^2/r = BqV \quad (1)$$

Where, m is the mass of the ion, v is its velocity, r is the radius of curvature, q is the charge on the ion. The ions now have been separated only by their masses and exit the monitor slit into the electrostatic sector. The secondary ions are then deflected and exit with different trajectories depending on their kinetic energy:

$$KE = \frac{mv^2}{2} = qV \quad (2)$$

Where, V is the accelerating voltage. This enables one to gain good resolution by separating the ions according to their kinetic energies. Finally, the energy distributions of the ions with the same m/q are corrected and the ions are focused in direction and velocity onto the detector slit. By rearranging the equation and eliminating the velocity term using equation (1) and (2), the relationship between the m/q ratio of the ions and the magnetic field and the accelerating voltage:

$$m/q = \frac{B^2 r^2}{2V} \quad (3)$$

The equation shows that the mass to charge ratio of the ions that reach the detector can be varied by changing either B or V . The MS detect ions sequentially and have a transmission of about 10-50%. The mass resolution is about >5000 .

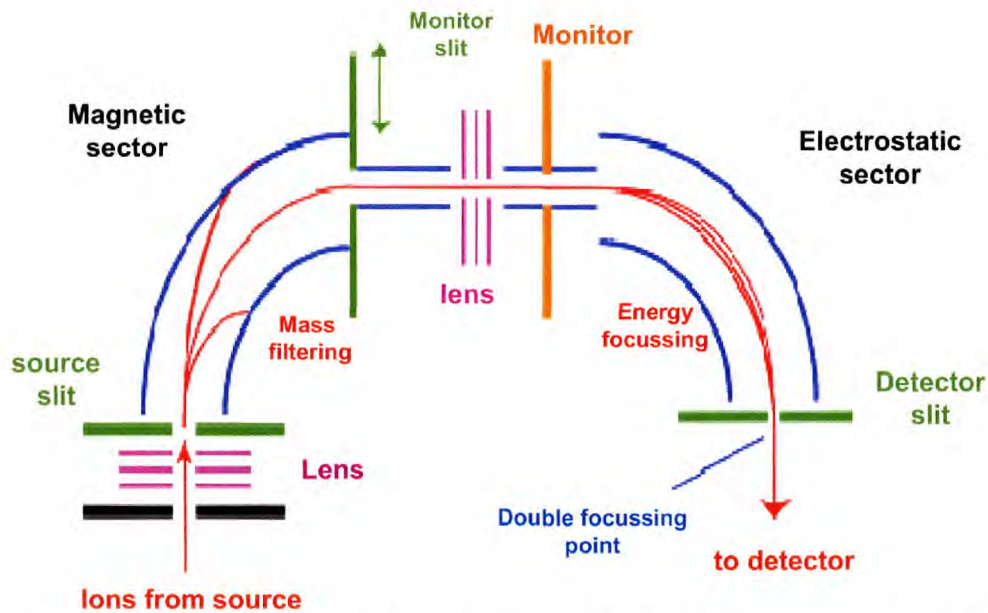


Figure 2.7 The combination of a magnetic and an electrostatic sector produces a double focusing instrument^[20].

2.1.3.3 Time of Flight (TOF)

A Time of Flight mass spectrometer uses an electric field to accelerate ions to a given potential such that all ions of the same charge possess the same kinetic energy. Thus, the time for ions to travel in a known field-free region and reach the detector will only depend on their mass-to-charge ratio. The lighter ions reach the detector faster and so the measured flight time t , of ions of mass-to-charge ratio, m/q , accelerated by a potential V down a flight path length L provides a simple means of mass analysis:

$$t = L \left(\frac{m}{2qV} \right)^{1/2} \quad (1)$$

The equation shows that m/q can be calculated from a measurement of t , q is the charge on the ion. Mass resolution is critically dependent upon the primary ion pulse. The shorter the ion pulse is, the better the mass resolution that can be gained. A pulse length of 1 ns can be achieved by using a device called a buncher. An ion mirror acts as an energy analyser in the flight tube to compensate for the initial energy spread. As a result, all ions of the same mass will reach the detector at the same time. The detection system is a combination of a channel plate, scintillator and photomultiplier, combined with a very fast electronic counting system.

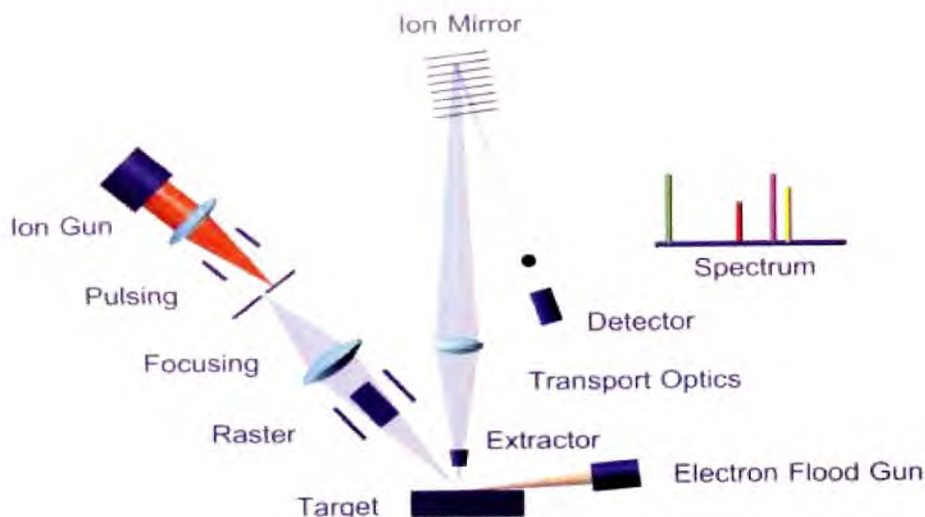


Figure 2.8 A schematic view of a TOF SIMS instrument ^[21].

The transmission of the TOF system is usually >50%, but the great advantage of TOF is that no secondary ions are rejected or lost, so that a mass spectrum of all the ions is generated from the flight time. The mass resolution is about 10000. Imaging

SIMS is better performed with TOF SIMS due to its high sensitivity and lateral resolution (burst mode). The TOF SIMS used for this project is an ION-TOF IV instrument. The system has dual beam mode, both guns operate quasi-simultaneously. After each analytical cycle pulse, the secondary ions travel, and during the time of flight, extraction is turned off and the sputter gun is switched on to erode the sample. Figure 2.9 shows the timing sequences for the ION-TOF IV system ^[18].

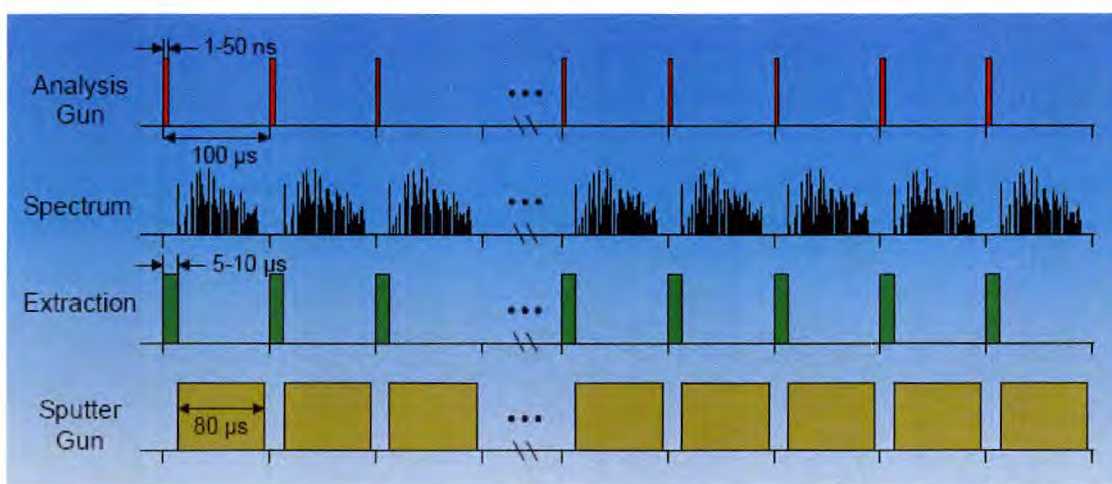


Figure 2.9 Interlaced mode, sputtering and analysis quasi-simultaneously. The primary ions reach the target and the secondary ions are extracted into the analyser, the extraction voltage is off. The sputter gun is switched on. This mode is usually used for conductor and semiconductor materials ^[18].

The key difference between a quadrupole SIMS instrument and the TOF SIMS is that the latter uses parallel acquisition. All the interesting profiles can thus be recorded and later examined. For a detailed mass spectrometer description, see “Surface analysis – The Principle Techniques” edited by John C. Vickerman ^[8].

2.2 Focused Ion Beam (FIB)

The Focused Ion Beam instrument uses a focused beam of ions to scan the sample. In 1973, Seliger and Fleming investigated the possibility of focusing an ion beam for micro-fabrication ^[22]. The results showed that a beam diameter of 3.5 μm was achieved with a conventional implanter. In the late 70's, Seliger was able to produce a probe diameter of 100 nm at a current density of 1.5 A/cm² (~0.12 nA) with a gallium Liquid-Metal Ion Source (LMIS) ^[23]. The instruments are now specified at 5 nm. Over the past few years, the capabilities of FIB instrument have been expanded into many applications such as failure analysis, lithography, device modification, metal alloys and biological materials ^[24-26].

A FIB system consists of a vacuum system, liquid metal ion source (LMIS), ion column, stage, detector, gas inlets, and a computer. The FIB can also be incorporated into other analytical instruments such as an SEM or SIMS for different types of analysis. In a basic FIB system, the ions which are emitted from the LMIS are focused in the ion column onto the sample in a vacuum chamber. There are three vacuum pumping regions, the source and ion column vacuum chamber ($\sim 10^{-8}$ mbar) is required to avoid contamination of the source and to prevent electrical discharges in the high voltage ion column. The sample chamber vacuum works in the 10^{-6} mbar range to prevent collisions between ions and gas molecules. The electron multiplier detector is orientated at an angle of 45° to the incident beam to detect either secondary electrons or secondary ions emitted from the sample.

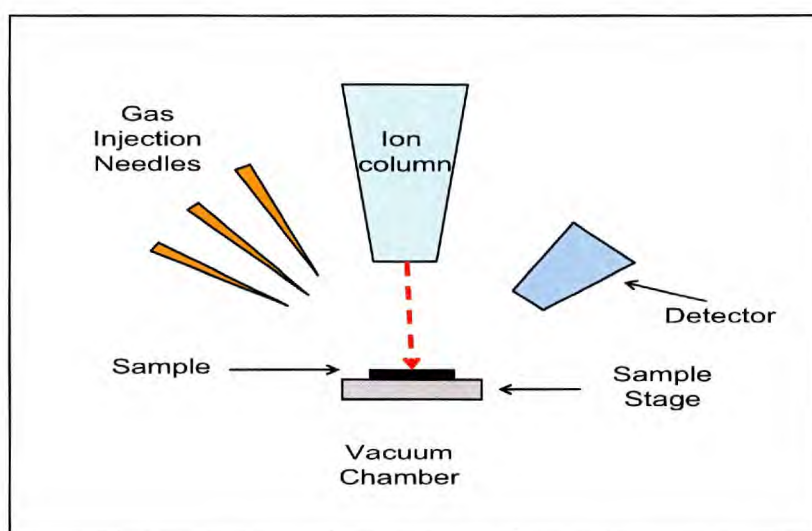


Figure 2.10 A basic description of a FIB system.

2.2.1 The Liquid Metal Ion Source (LMIS)

There are several metallic elements or alloy sources such as Al, Cu_3P , Au/Be/Si that can be used in a LMIS. Ga^+ has been used widely due to its many advantages such as room temperature operation, long source time (~ 1000 hours), low melting point ($\sim 29.8^\circ\text{C}$) and high angular intensity with a small energy spread (~ 5 eV). The basic principle of the LMIS is that when the electrical field is applied to the liquid metal (electrically conductive), the shape of liquid will deform from the shape caused by surface tension. As the voltage increases the effect of the electrical field on the liquid metal is more prominent and finally it approaches exerting a similar amount of stress on the liquid metal as the surface tension does a cone shape is formed. When a certain threshold voltage is reached and the ions are pulled from the tip.

The focused ion beam operates as described below: 1) a liquid metal is maintained at one end of a tungsten needle (tip radius $\sim 2\text{-}5\text{ }\mu\text{m}$), the metal is then heated by the coil heater to wet the needle and the liquid metal flows down to the tip, 2) a high extraction electric field ($\sim 10^8\text{ V/cm}$) is applied to the end of the wet tip to exert a stress on a liquid surface, the liquid metal is then pulled into a sharp cone ('Taylor cone', was described by Sir Geoffrey Taylor in 1964^[27]) shape whose radius can be as small as 2-5 nm, 3) the metal is held by surface tension balance between the heater and the shank of the needle, when a certain extraction voltage has been reached the slightly rounded tip inverts and emits a jet of liquid (Ga^+). A flow of Ga to the cone continuously replaces the evaporated ions, if the extraction voltage is changed, the energy of ions entering the ion column is changed, and the lens voltage may need to be adjusted to maintain beam focus. The emission current of the source varies with extraction voltage. A low emission current is often used to maintain the beam stay focus and stable.

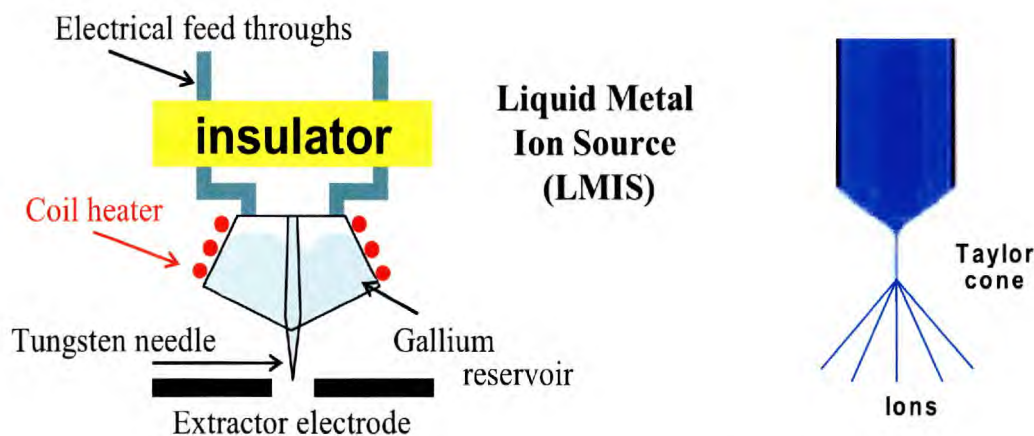


Figure 2.11 Shows schematic view of a Liquid Metal Ion Source.

2.2.2 The Ion Column

In the ion column, extracted ions are firstly accelerated to an energy of 5-50 keV, and are then focused onto the sample by an electrostatic lens. Two or more very precisely machined washer-shaped electrodes allow ions to pass through a high potential and electric fields and deflect and accelerate the ions to the surface. The probe diameter can be changed using different beam defining apertures. Cylindrical octopole lenses may be used to perform multiple functions such as beam deflection, alignment, and stigmation correction. In addition, the scan field can be rotated using octopole lenses^[7]. When the ion beam is writing over a selected area, beam blankers

are used to prevent any unwanted erosion of the sample by applying a voltage $-V_d/2$ and $+V_d/2$ to a pair of electrodes which are located on opposite sides of the beam, and the beam is deflected sideways. The FIB ion column is shown in figure 2.12.

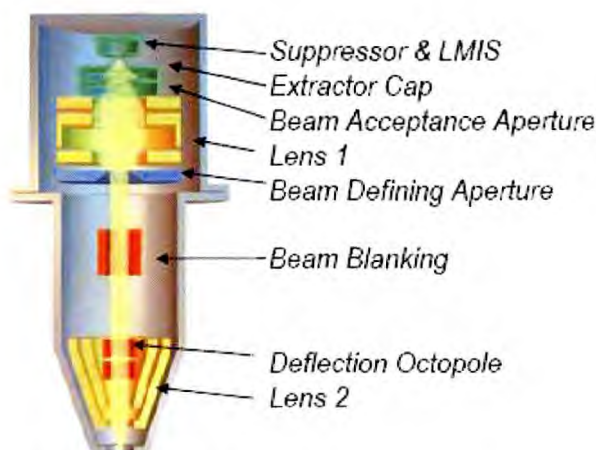


Figure 2.12 Schematic of a basic FIB ion column^[28].

2.2.3 The Stage, Imaging Detectors, and Gas Inlet

The sample stage provides 5-axes movement (x, y, z, tilt-0-55° and rotate), and is capable of positioning the large sample precisely under the beam. This is useful for device repairs that involve multiple layers of materials analysis. A laser interferometer plays a central role in the measurement of the position of the stage. It reflects laser light from the x and y directions and is aligned to the axis of motion of the stage. The stage is then driven by computer controlled motors to a desired location. The sample stage also has thermal stability to hold the sample during FIB milling or deposition. Secondary electrons that are emitted from the sample surface are collected by either a multi-channel plate or an electron multiplier to form images. Small beam currents (<100 pA) are normally used to minimize material removal during imaging. The bombardment of insulating samples undergoes charge build-up on the sample surface. Thus, any emitted secondary electrons will be attracted back to the surface and will not reach the detector. This greatly limits the detection efficiency. Any sample charging can be reduced by grounding the inputs of a semiconductor device. Sample coating and an electron flood gun can also be used to reduce sample charging. A gas inlet is used in conjunction with the ion beam for gas-assisted etching or ion beam induced deposition. A detailed description of the FIB technique can be found elsewhere^[28].

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Chapter Three

3. Literature Review

The ion yield Y is the product of ionisation probability α and secondary ion transmission coefficient T . α is different for every element, m , in every matrix, M , and also depends on various factors such as primary beam type, the beam energy, and angle of incidence of the primary beam with respect to the surface normal. It can vary by several orders of magnitude across the periodic table and is very dependent on the chemical state of the surface. Therefore, the optimisation of sputtering conditions can lead to better secondary ion yields. Other factors such as topography, temperature, and escape velocity can also have an effect on the ion yields ^[1-4]. In this chapter we will look at some of the work that has been done to enhance the ion yields.

3.1 Reactive Ion Source Effect

Many primary beam species have been employed for SIMS analysis. The choice of primary species depends on many factors: secondary ion yield, depth resolution, lateral resolution, and charge neutralizer ^[5]. Reactive primary ions provide chemical reactions with the surface that enhance the secondary ion yield. When a sample surface is bombarded with a reactive ion beam the ion yields can be maintained at a high level by controlling the surface chemistry. This is because the ion yield is a function of surface chemistry. Instead of destroying the chemical compounds the reactive ion source can reconstitute them. In a SIMS sputtering process, only a small fraction of the sputtered atoms from the layer near the surface are ionised either negatively or positively. Oxygen and cesium are the two most commonly used reactive ion source to enhance the positive and negative ion yield.

A negative ion is produced by transferring an electron from the surface to the sputtered atom. This requires a low work function, i.e. the minimum amount of energy required to transfer an electron from the solid to form a negative ion. The work functions of many materials are known to be reduced by the adsorption of electropositive ions. Cs is the most electropositive element and generally lowers the work function ^[6]. Therefore, Cs can increase the availability of electrons and lead to enhanced negative ion yield. The high secondary negative ion yields for Groups 5 and 6 and the noble elements were observed under Cs^+ bombardment by Andersen *et al* ^[6]

in the late 1960s and a few years later, Storm *et al* [7] obtained enhanced negative ion yields for Group 7 and H^- and carbon with an improved Cs^+ source. The degree of ion yield enhancement depends on the Cs surface concentration, which has a huge influence on the work function [8]. Yu *et al* [9] studied the negative secondary ion yields of Mo^- , O^- , H^- and D^- under Ne^+ bombardment. Cesium was applied to a clean surface of Mo (100) to form a submonolayer to modify the surface work function. Figure 3.1 shows the work function change and the Mo^- yield as a function of Cs deposition time. It was found that the negative ion yield increased with decreasing work function until the work function reached the minimum. This had a good agreement with Gnaser's *et al* observation, the ion yield enhancements increased with increasing dose until the critical dose was reached. After reaching the maximum, the Mo^- yield dropped significantly as the Cs deposition time continued to rise.

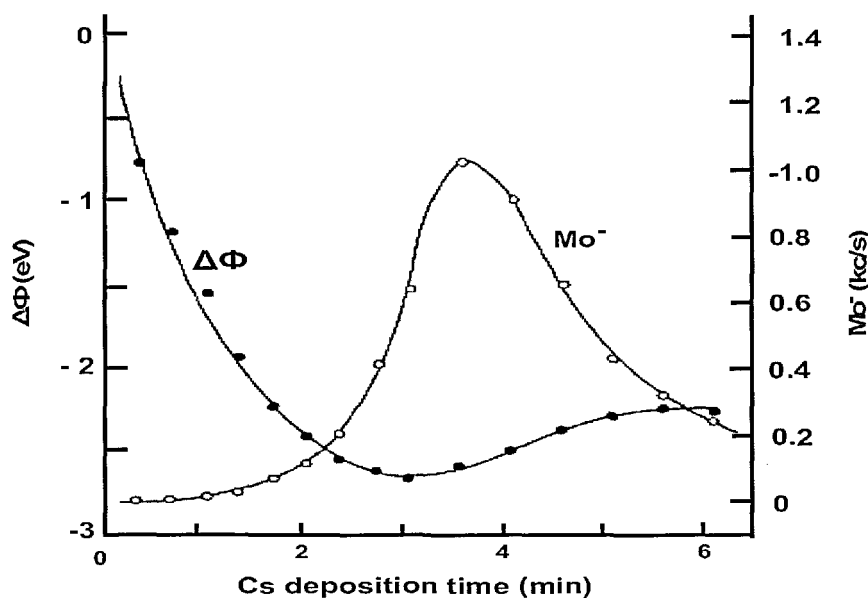


Figure 3.1 Variation of work function and Mo^- yield with Cs deposition time. The Cs dependence of H^- , D^- , and O^- production was also very similar. The yield maxima correlate closely with the work function minimum [9].

Gnaser *et al* [10] studied the relationship between several negative ion emissions (C^- , Si^- , Ge^- and Au^-) and Cs surface concentration. The experiment showed that for all secondary ions (i.e. C, Si, Ge, and Au) the ionisation probability of negative ions was enhanced upon Cs buildup, and saturated for steady state sputtering, and the work function variations were $\Delta\Phi = 2.75$ eV for C, $\Delta\Phi = 2.3$ eV for Si, $\Delta\Phi = 0.84$ eV for Ge, and $\Delta\Phi = 0.62$ eV for Au. Figure 3.2a exemplifies the gradual Cs incorporation for pyrolytic graphite bombardment with 14.5 keV Cs^+ . The C^- intensity started

increasing from a Cs^+ dose of $9 \times 10^{15} \text{ Cs}^+/\text{cm}^2$ and reached a maximum at a dose of $2 \times 10^{16} \text{ Cs}^+/\text{cm}^2$. On the other hand, the work function started decreasing from $9 \times 10^{15} \text{ Cs}^+/\text{cm}^2$ and reached the minimum at a dose of $2 \times 10^{16} \text{ Cs}^+/\text{cm}^2$. The figure clearly showed that the ion yield increased with increasing Cs surface concentration. At a dose of $2 \times 10^{16} \text{ Cs}^+/\text{cm}^2$ the steady state was reached with this critical dose. Figure 3.2b shows the correlation between the secondary ion (C^-) intensity and the work function. That is, the C^- intensity increased with decreasing work function.

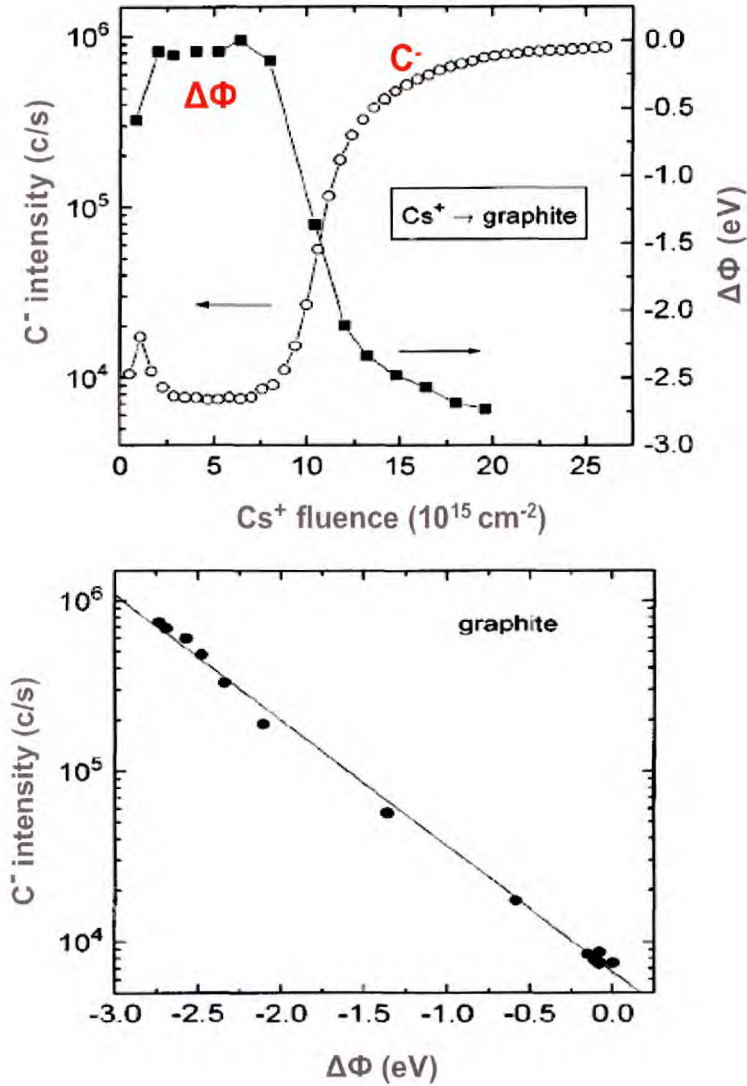


Figure 3.2a) C^- intensity and work function variations as a function of dose for 14.5 keV Cs^+ bombardment of graphite, b) Intensity vs work function variation^[10].

Doucas *et al*^[11] observed the changes in the cesium surface concentration by monitoring the shifts in the energy distribution of the negative ions $^{12}\text{C}^-$ and $^{24}\text{C}_2^-$ as a function of target temperature. The negative ion yields increased with increasing

temperature from 80K up to about 500K, and decreased from 500 K down to 880 K. The decrease in negative ion yields was thought due to the reduction of the surface cesium concentration because of thermal desorption. In the temperature interval 500 - 880 K, the work function of the surface is estimated to increase by 1.3 eV. This can be considered as:

$$g = \frac{1}{\tau_0} \exp\left(\frac{-E_d}{kT}\right) \quad (1)$$

Where $\tau_0 \sim 10^{-13}$ s, E_d is the binding energy of the cesium atom to the surface, T is the temperature and k is the Boltzmann constant. The concentration of cesium near surface is determined by the rate of thermal desorption g and sputtering $J_0 \sigma$:

$$c = \frac{J_0}{g + J_0 \sigma} \quad (2)$$

Where, J_0 is the incidence ion flux. At relatively high temperatures g dominates the denominator of equation (2) and cesium concentration decreasing with increasing g (i.e. increasing temperature). This explains the decrease in negative ion yield with temperature above 500 K. However, at lower temperature (<500 K) the sputtering term $J_0 \sigma$ is more dominate, the cesium concentration is independent of temperature and negative ion yield increases up to temperature 500 K. Figure 3.3 shows the work function plotted against the target temperature both for the C^- and C_2^- ions.

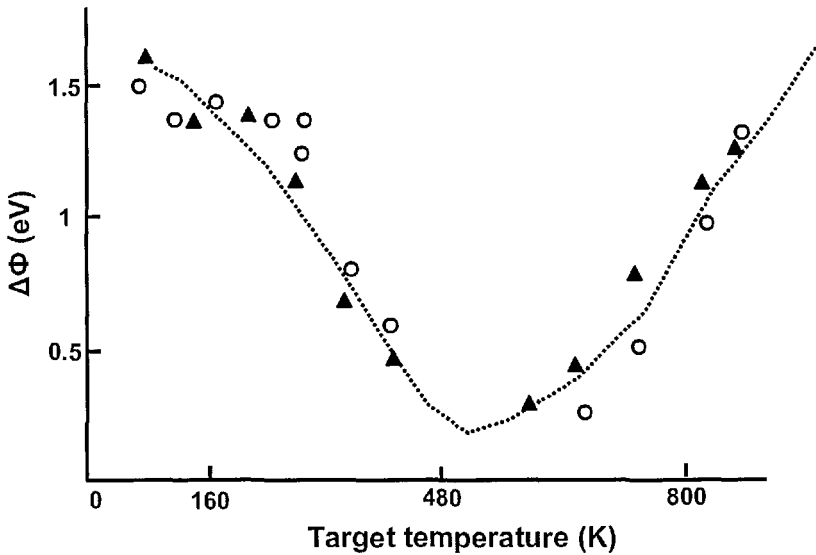


Figure 3.3 Change in work function as a function of K. (○) C^- ions, (▲) C_2^- ions ^[11].

The two monitored ions showed a similar trend. The work function decreased with increasing temperature, the lowest was gained at a target temperature of 500 K.

In both cases, the maximum estimated change in work function was 1.3 eV. Figure 3.4 shows the peak position of the energy spectrum peak E_m and the negative ion current as a function of target temperature.

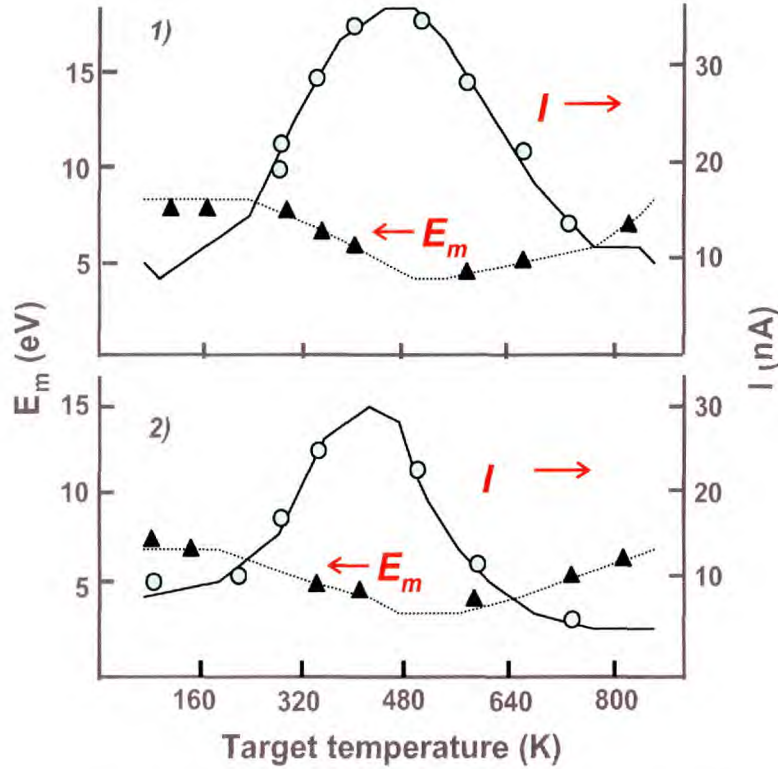


Figure 3.4 Energy spectrum peak position E_m and negative ion current I as a function of temperature for 1) the C beam and 2) the C_2^- beam. Primary beam density = 6.3×10^{13} particles/s/cm², intensity = 0.22 μ A. (full symbols for increasing temperature, open symbols for decreasing temperature) The curves are to guide the eye only^[11].

Thus, it is clear that the Cs^+ surface concentration is crucial for the negative ion yield enhancement. As it increases, the work function decreases and the ion yield increases until the critical dose is reached. Further deposition of Cs^+ ions results in reduction of ion yield.

In the case of positive ion yield enhancement, the ionisation probability α^+ increases with increasing work function. Oxygen has been widely used to enhance the positive ion yield. The effect of adsorbed oxygen is chiefly chemical in origin while the effect of Cs comes mostly from a change of surface work function due to the formation of a surface dipole layer^[12]. During normal incidence oxygen implantation the ionisation probability increases roughly exponentially with increasing dose until the steady state is reached, i.e. I_x^+ , is proportional to α_x^+ ^[13]. Ga^+ FIB SIMS offers

great lateral resolution but poor ion yields. It was reported that the positive ion yield under Ga^+ bombardment was lower than that of the O_2^+ primary bombardment by two or three orders of magnitude ^[14]. Oxygen implantation prior to SIMS analysis and oxygen flooding can dramatically enhance the positive ion yield, by up to two orders of magnitude ^[15]. Figure 3.5a shows typical depth profiles of boron-implanted Si measured with a Ga^+ FIB SIMS primary beam. The boron intensity with oxygen implantation is much higher than that without prior oxygen implantation. Figure 3.5b shows the dependence of the enhancement effect of boron secondary ions from an Si matrix on oxygen dose $^{16}\text{O}_2^+$. The boron intensity increased with increasing oxygen dose and became constant when the oxygen dose reached $1.5 \times 10^{16} \text{ atoms/cm}^2$.

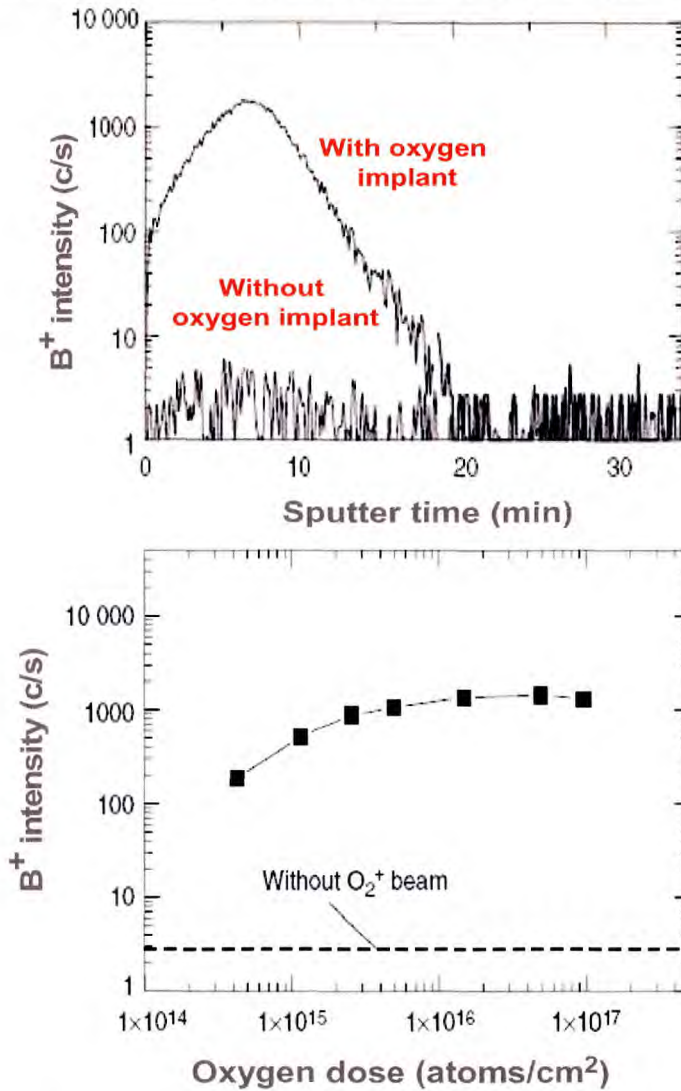


Figure 3.5a) B^+ intensity with prior oxygen implantation at 3 keV oxygen beam energy, a dose of about $2 \times 10^{16} \text{ atoms/cm}^2$ was implanted, and without prior oxygen implant, b) the dependence of the B^+ ion yield enhancement on oxygen dose; oxygen beam energy 3 keV; raster area $150 \times 195 \mu\text{m}^2$; Ga^+ beam energy: 25 keV at 700 pA, normal incidence ^[15].

For ambient oxygen incorporated Ga^+ FIB SIMS, the ion yield can be enhanced by increasing the oxygen gas pressure in order to raise the oxygen concentration on the sample surface ^[16] ^[17]. The angle and energy of the oxygen beam also have a strong impact on the ion yield (section 3.3). Figure 3.6 shows the change of secondary ion intensities from a Cu sample during oxygen flooding. Solid symbols represent the intensities when the oxygen pressure was increased to 5.6×10^{-5} torr ($\sim 7.4 \times 10^{-5}$ mbar) within 150s. It clearly shows that the Ga^+ and Cu^+ intensities increased with increasing oxygen pressure. However, the ratio of Ga^+/Cu^+ intensities stayed constant which indicated that the Ga^+ and Cu^+ intensities behaved in the same way in relation to the incorporated oxygen. The oxygen pressure was then decreased toward the base pressure. The two intensities (open symbols) decreased in the same way.

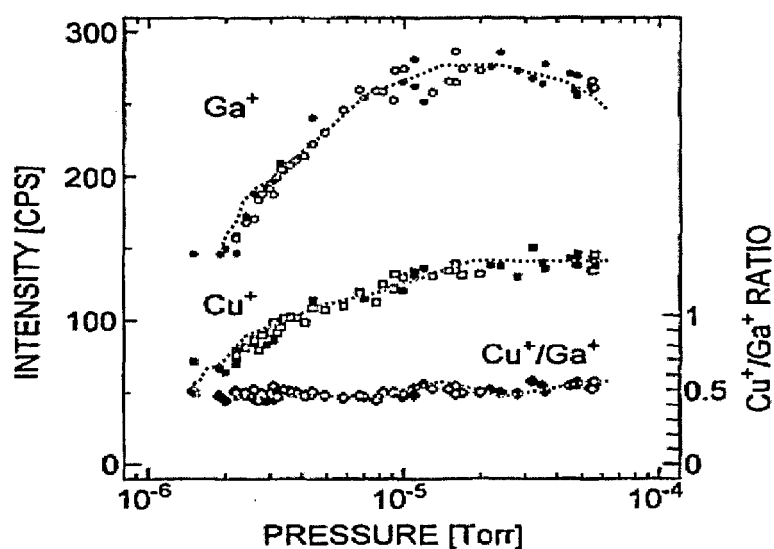


Figure 3.6 Shows the variation of the secondary ion intensities from a Cu sample during oxygen gas introduction. Solid and open symbols represent the intensities with the pressure increasing or decreasing, respectively. The FIB conditions were 30 keV, 230 pA, $19 \times 19 \mu\text{m}^2$ scanning area and an incident angle of 10° ^[16].

In addition to the ion yield enhancement, oxygen flooding reduces matrix effects in multi-layer analysis, and also the transient in the oxygen buildup region ^[18-20]. The fast surface oxygen coverage allows quick stabilisation of the steady state.

As we have shown, the positive ion yield in Ga^+ FIB SIMS is enhanced by the surface chemistry modification by oxygen implantation and oxygen flooding. The positive secondary ion emission is directly proportional to the oxygen concentration on the sample surface and the amount of ion yield enhancement showed a

characteristic dependence both on the oxygen dose/pressure and the beam scanning area. Hence, it is very important to find out how the sputter yield, which is a critical factor in the relationship between the ion yield and the surface oxidation, changes with the oxygen concentration on the surface.

Franzreb *et al* ^[21] studied how the Si sputter yields changed under Ar^+ and O_2^+ bombardment at beam energies 8 keV and 17 keV at incident angles of 25° and 39° with oxygen flooding. It was found that the Si^+ sputter yield decreased dramatically with increasing oxygen pressure, and that the oxygen/silicon ratio, O/Si, increased. Comparing the $\text{Si}^{+/-}$ sputter yields observed at two different incident angles, the higher incident angle led to a higher sputter yield despite the higher impact energy, figure 3.7.

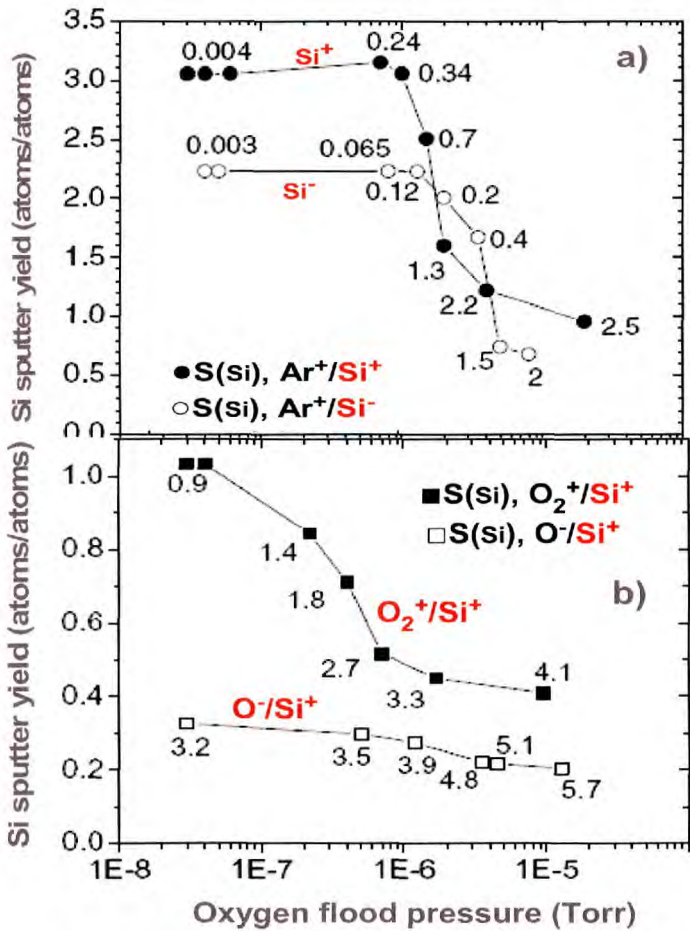


Figure 3.7a) Oxygen pressure dependence of the silicon sputter yield for Ar^+ sputtering of Si, monitoring positive (full symbols: 8 keV impact, 39° incident angle, 50 nA) and negative (open symbols: 17 keV impact, 25° incident angle, 50 nA) sputtered ions, b) oxygen pressure dependence of the silicon sputter yield for $^{16}\text{O}_2^+$ (full symbols: 8 keV impact, 39° incident angle, 50 nA) and ^{16}O (open symbols: 17 keV impact, 25° incident angle, 175 nA) sputtering of Si, monitoring positive ions. The numbers next to the data points denote the O/Si values ^[21].

Figure 3.7a shows that in the low oxygen pressure range, the $\text{Si}^{+/-}$ sputter yield stayed roughly constant up to O/Si ratio 0.24⁽⁺⁾ and 0.12⁽⁻⁾, then dropped by about a factor of 2 within the intermediate pressure range and carried on decreasing as pressure increased. Figure 3.7b shows similar results under oxygen bombardment. The oxygen content exceeded the stoichiometric SiO_2 value while the sputter yield continued to drop. This could be due to the shallow sputtered atom escape depth, for most atoms were ejected from the outermost atomic layer of the solid and at elevated oxygen pressure this outermost layer was fully oxidised. The positive ion yield of Si^+ , B^+ and Al^+ under Ar^+ bombardment was plotted as a function of O/Si in figure 3.8. As the O/Si ratio increased, the positive ion yields increased. Also, the ion yield enhancements showed a strong element dependence, the ion yields were enhanced 500 times more for Si^+ , 2000 for B^+ , and only 7 for Al^+ .

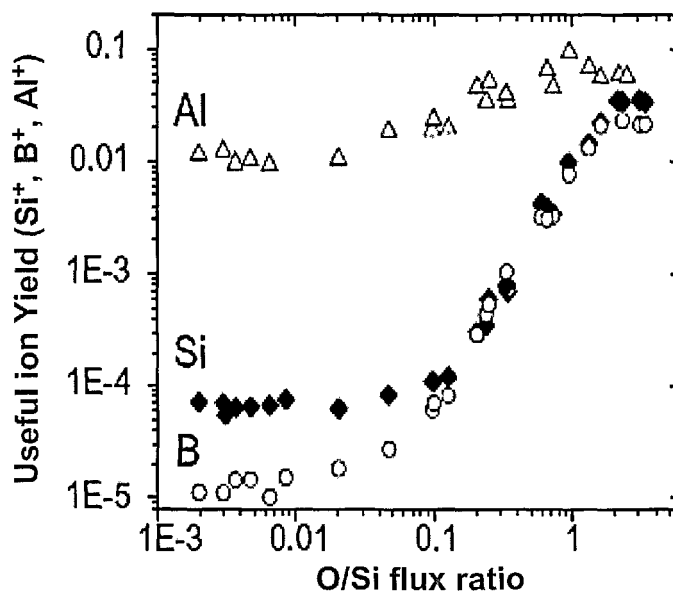


Figure 3.8 Positive ion useful yields $UY(X^+)$ of Si^+ , B^+ and Al^+ as a function of O/Si. 8 keV Ar^+ , 39° incident angle [21].

It was also worth noting that in the low oxygen coverage regime (>0.6 O/Si ratio), the ion yield of Al^+ was much higher than that of Si^+ and B^+ . But the ion yield enhancements of Al^+ due to oxygen flooding were much lower compared to the rest. The reason was thought to be that the Al^+ ion yields were intrinsically enhanced by silicon. It was clear that the degree of the ion yield enhancement was affected by the surface oxygen concentration and the sputter yield. However, under the same sputtering conditions the ion yield of different elements behaved differently, so the matrix effect must be taken into account when measuring the ion yield.

As mentioned above, the oxygen flooding technique reduces the transient region in the oxygen buildup region. Under high oxygen pressure, the matrix signal reaches the steady state fairly quickly, and the oxide thickness is thicker than that under intermediate oxygen pressure [22]. A systematic study of the oxide thickness and matrix signal under various oxygen pressures can be a great asset for the ion yield and beam damage measurement. Figure 3.9 shows how the oxide thickness changed under various oxygen pressures.

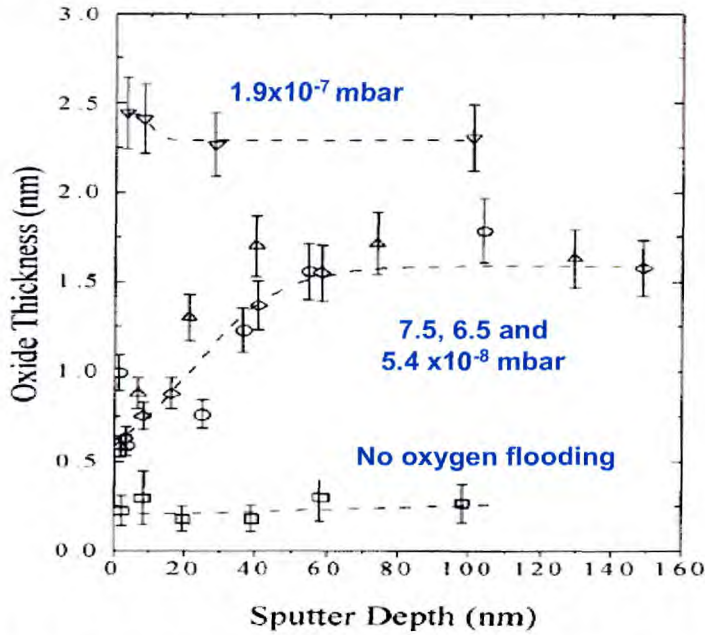


Figure 3.9 Oxide thicknesses as a function of depth of sputtering without and with flooding under various pressures. The silicon sample was bombarded by a 1 keV O_2^+ beam at an incident angle of 56° to the surface normal [22].

The oxide thicknesses increased with increasing oxygen pressure and could be divided into three regimes. The thickest was observed at a pressure of 1.9×10^{-7} mbar, (2.3 nm), the lowest was observed without oxygen flooding (0.2 nm). At intermediate values (e.g. 6.5×10^{-8} mbar) the oxide thickness increased gradually and saturated at about 1.6 nm after a depth of 60 nm. Figure 3.10 shows the changes in the $^{30}\text{Si}^+$ signals with depth during sputtering with/without oxygen flooding. The $^{30}\text{Si}^+$ intensity increased with increasing oxygen pressure. The highest intensity was gained at an oxygen pressure of 1.9×10^{-7} mbar. When sputtering with oxygen flooding under 1.9×10^{-7} mbar and/or no oxygen flooding, the signal quickly reached the steady state. However, under intermediate oxygen pressure the matrix signal underwent a transition in the ion yield. This is because at intermediate oxygen pressure, the surface is not fully or uniformly covered by the oxygen, the sputter rate is different at the surface

and resulting onset of surface roughening arising from the formation of a ripple-like topography on the crater bottom, shown in figure 3.11.

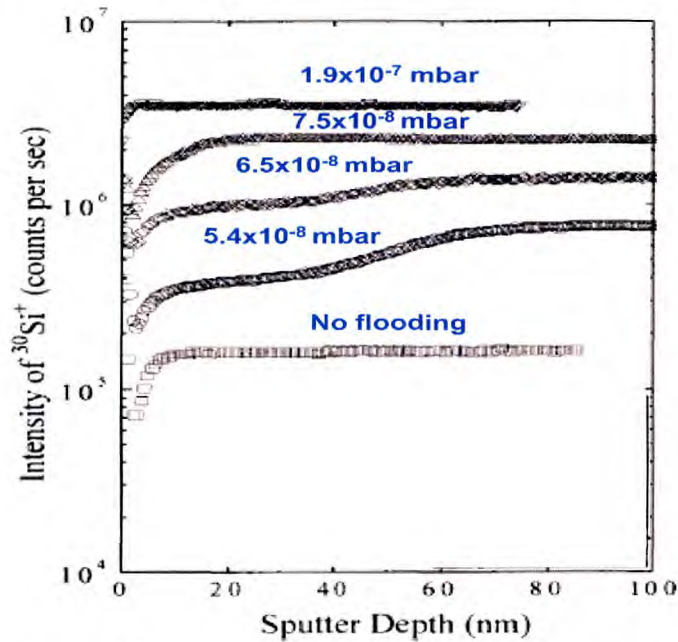


Figure 3.10 Intensity of $^{30}\text{Si}^+$ as a function of depth for sputtering without and with flooding under various pressures ^[22].

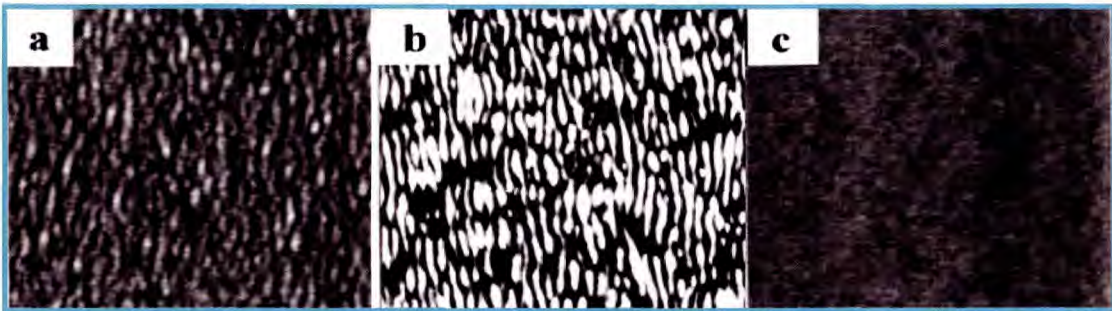


Figure 3.11 $2 \times 2 \mu\text{m}^2$ AFM images of the crater surface after SIMS profiling with a) no oxygen inlet; b) intermediate pressure (6.5×10^{-8} mbar); c) 1.9×10^{-7} mbar of oxygen ^[22].

For some metal elements that form a weak oxide bond such as Ni, Mo or Cu, oxygen may not enhance the ion yields but highly charged ions (HCI) can be used ^[23]. When solid materials are irradiated by HCI, a strong electronic interaction occurs between the primary ions and the target atoms causing atomic displacements. As a result, secondary ions form, and the ion yield increases with increasing charge state of the primaries ^[24]. Terasawa *et al* ^[25] used the highly charged heavy ion Xe^{q+} as a primary beam for bombardment of carbon thin films. The secondary carbon yields were measured as a function of charge state in the broad range of $q = 8$ to 44. TOF spectra were shown in figure 3.12 and 3.13. In figure 3.12, the highest intensity was

H^+ which was about 2.8×10^2 cps, the lowest was C^+ . When the charge state increased to 31 (figure 3.13), the intensity of all the secondary ions was increased by more than an order of magnitude (e.g. C^+ increased almost two orders of magnitude).

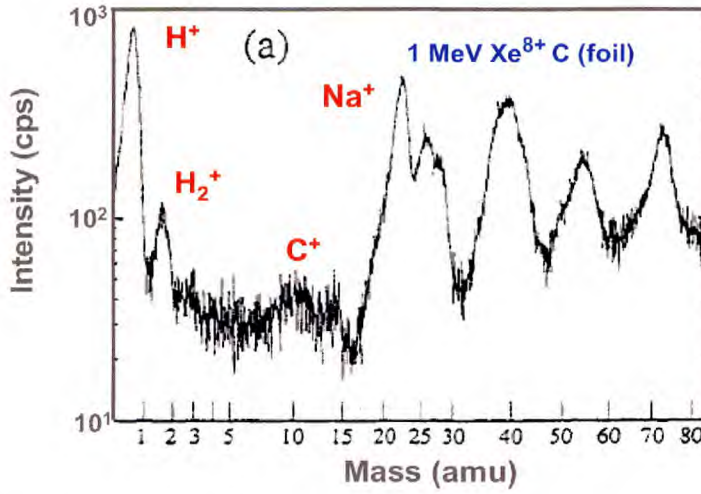


Figure 3.12 Mass spectra of the secondary ions emitted from carbon foil bombarded with high charge state Xe ions; 1 MeV Xe^{8+} [25].

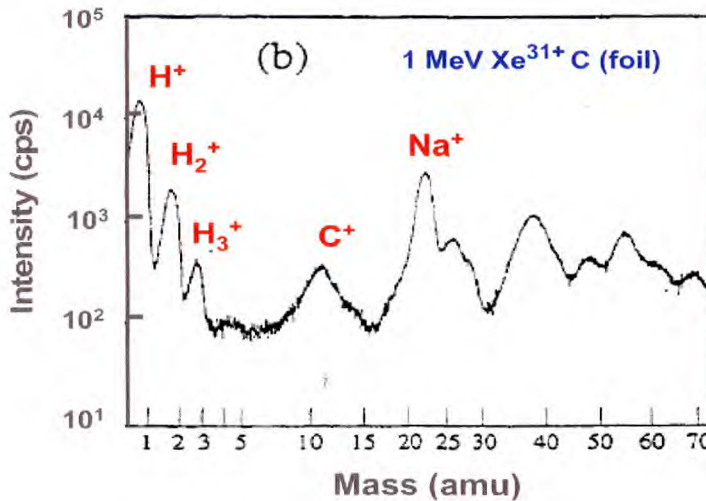


Figure 3.13 Mass spectra of the secondary ions emitted from carbon foil bombarded with high charge state Xe ions; 1 MeV Xe^{31+} [25].

Figure 3.14 shows the ion yields of H^+ , H_2^+ , H_3^+ and C^+ , as a function of the charge state of incident 1 MeV Xe^{q+} ions. The ion yield of each secondary ion increased gradually with the incident charge state in general. When q increased from 26 to 31-38 a huge increase in the ion yield was observed. Saturation appeared afterwards. This is evidence that the charge dependence of the ion yield is a consequence of the strong electronic interaction of HCI with target atoms.

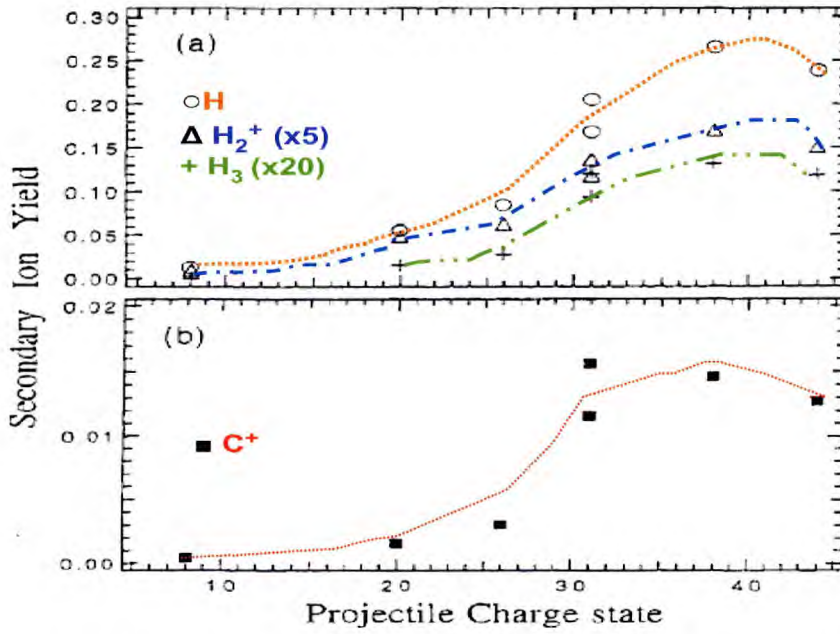


Figure 3.14 Ion yields of: a) H^+ , H_2^+ and H_3^+ , b) C^+ , as a function of charge state of projectile 1 MeV Xe ions ^[25].

Figure 3.15 compares the charge dependence of the second ion yield of the projectile Xe^{q+} for Al, Si, Ni, Cu, Ag bombarded by 1 MeV Xe^{q+} . For the semiconductor Si, a linear increase of the ion yield from Si started already at $q = 15$. However, for metal targets (Al, Ni, Cu), the ion yield was rather moderate at $q \leq 35$ but showed a prominent increase at $q \geq 35$ ^[26]. This clearly demonstrated the electronic excitation effect on the ion yields of metals. The differences of the secondary ion yields between target materials are correlated with the mass of the target atom.

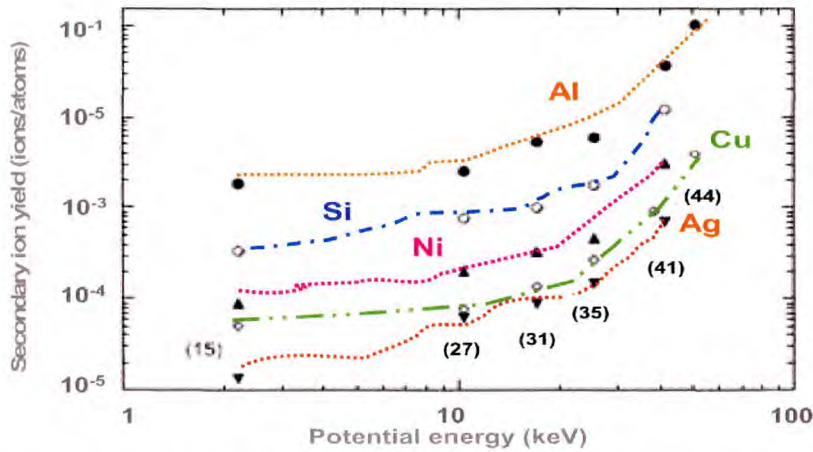


Figure 3.15 The charge state dependence of the ion yield as a function of the potential energy of the projectile Xe^{q+} for Al, Si, Ni and Cu bombarded by 1 MeV Xe^{q+} ($q = 15-44$) ^[26].

3.2 Polyatomic Source Effect

For TOF SIMS, polyatomic ions have often been used as the primary source ^[27, 28]. There has been a big debate about the polyatomic primary ions increasing the ion yield (by increasing the ionisation probability) or, just simply they increase the volume of material sputtering. Some manufacturers claim this is because ion yield has increased but others suspect more sputtering volume. Here we use ion signal intensity instead of ion yield. The use of polyatomic projectiles in sputtering has been investigated since the 1960s ^[29]. The early polyatomic ion sources had many drawbacks such as large spot size and were difficult to maintain. The newly developed polyatomic ion sources can be focused to a spot size of 100 nm and have other advantages such as long lifetimes and high brightness. When a polyatomic ion strikes the substrate, its constituent atoms stay near each other, and a substrate atom is struck simultaneously by multiple atoms. There is therefore more energy deposited into the substrate atoms close to the surface, which leads to high sputtering efficiency.

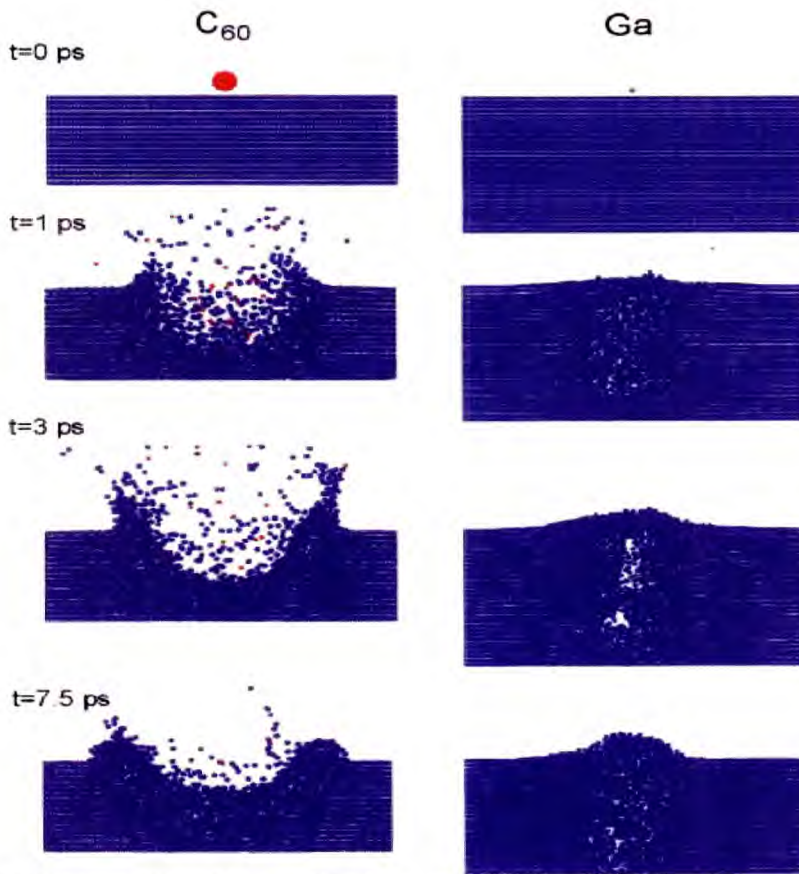


Figure 3.16 Cross sectional view of the temporal evolution of a collision event leading to ejection of atoms due to 15 keV C_{60} and Ga sputtering of a $Ag\{111\}$ surface at normal incidence. Blue, red and green represents silver, carbon and Ga atoms, MD simulations ^[30].

Figure 3.16 shows typical collision events leading to ejection of atoms during 15 keV C_{60} and Ga bombardment of a $Ag\{111\}$ surface at normal incidence ^[30]. Compared to the polyatomic ion C_{60} the penetration depth of the Ga ion into the crystal was much deeper, and the damage area had a more cylindrical rather than hemispherical symmetry. A significant amount of primary energy was buried deep in the crystal and only a small portion of this energy was deposited in the vicinity of the surface, causing sputtering.

Kotter *et al* ^[31] compared the signal intensity of polymer surfaces bombarded by Xe^+ , Ar^+ and SF_5^+ sources on the TOF SIMS. It was found that the increase (up to 1,000 times more) in signal intensity (X_i^+) occurred when changing from Ar^+ to Xe^+ and to SF_5^+ primary ion bombardment. A section of the positive secondary ion spectra in the mass range 145–185 amu obtained from spin coated polystyrene under Ar^+ , Xe^+ and SF_5^+ bombardment is shown in figure 3.17. The peak intensities in the three spectra were very similar, the intensity for SF_5^+ bombardment exceeded that for Xe^+ by a factor of 10 and that for Ar^+ by a factor of nearly 100 in this mass range. A broader mass range also showed that the effect is more pronounced for a higher mass range.

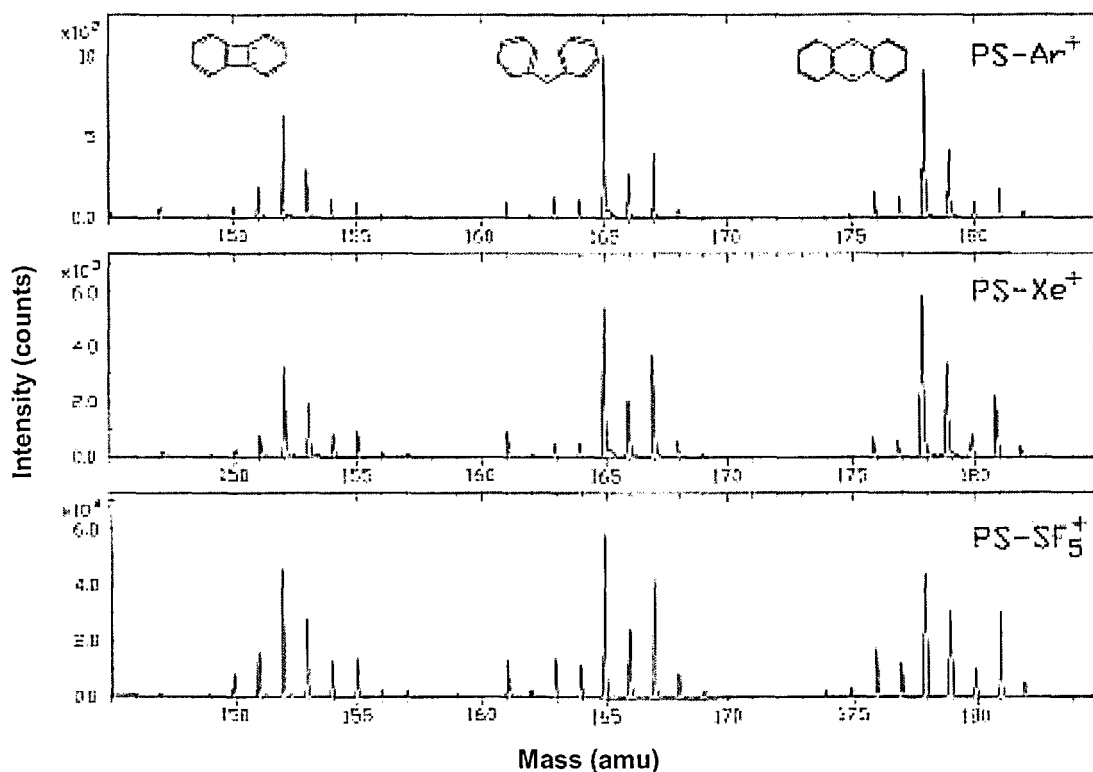


Figure 3.17 Positive static SIMS spectra of PS under Ar^+ , Xe^+ and SF_5^+ bombardment in the mass range 145–185 amu. Bombarded area: $100 \times 100 \text{ mm}^2$ ^[31].

The same result was found by bombardment of Cu (001) and Si (100) surface [32]. Those observations have demonstrated the effect of overlapping collisions of the atomic components of the polyatomic ions on the ion yield. The probability for overlapping cascades is much higher when two or more atoms are bound together in a polyatomic projectile. However, Fuoco *et al* [33] suggested that in the sub-keV range (<1 keV), the sputtering mechanism of SF₅⁺ and Ar⁺ is similar which could be the reason that no signal intensity enhancement was found for bombardment of methylmethacrylate (PMMA) film.

Gold and bismuth are also commonly used in the TOF SIMS to enhance the ion signal intensity. The sputtering mechanism of the two ions is very similar [2, 34, 35]. As the signal intensity increases with polyatomic ion bombardment due to overlapping collision cascades, the larger the projectile size, the higher signal intensity (up to its maximum value). A polycrystalline indium surface under bombardment with Au, Au₂, Au₃, Au₅ and AuCs₂ projectiles also showed that the signal intensity (sputter rate) enhancement increased with increasing projectile size up to Au₃ and then levelled off. The clusters ions appeared more sensitive to the polyatomic ion bombardment than that of atomic ions [36]. For semiconductor materials, the emission of secondary cluster Si_n⁺ ions (n = 1-11) under bombardment by Au_m⁺ was studied [28]. The results showed the signal intensity of Si⁺ cluster ions increased with Au_m (m = 1-5). This had a good agreement with the Ar cluster bombardment [37]. For a given Au_m primary ion, the signal intensity was lower for larger n (n = 1-11) of Si_n. Figure 3.18 shows the mass spectra of the secondary cluster Si_n⁺ ions measured under silicon bombardment. The signal intensity of cluster Si_n⁺ increased with increasing m. The highest was observed at m = 5. Comparing the Si_n⁺ intensity with Au⁺ bombardment at different primary energies (4, 6 and 9 keV Au⁺), the difference was little and negligible. However, this is not the case when the number of atoms in the primary ion increased or Si_n⁺ (n>1), signal intensity increased with increasing primary energy. For all Au₁⁺ bombardment, the signal intensity of different Si_n⁺ clusters stayed constant despite the increasing primary energy. Figure 3.19 shows the dependence of the signal intensity of Si_n⁺ ions on the primary ion energy. As we can see, the primary energy has a larger effect on the signal intensity of Si_n⁺ under polyatomic ion bombardment than that under atomic bombardment. Moreover, the cluster signal intensities appeared more sensitive to the polyatomic ion bombardment than that of atomic ions.

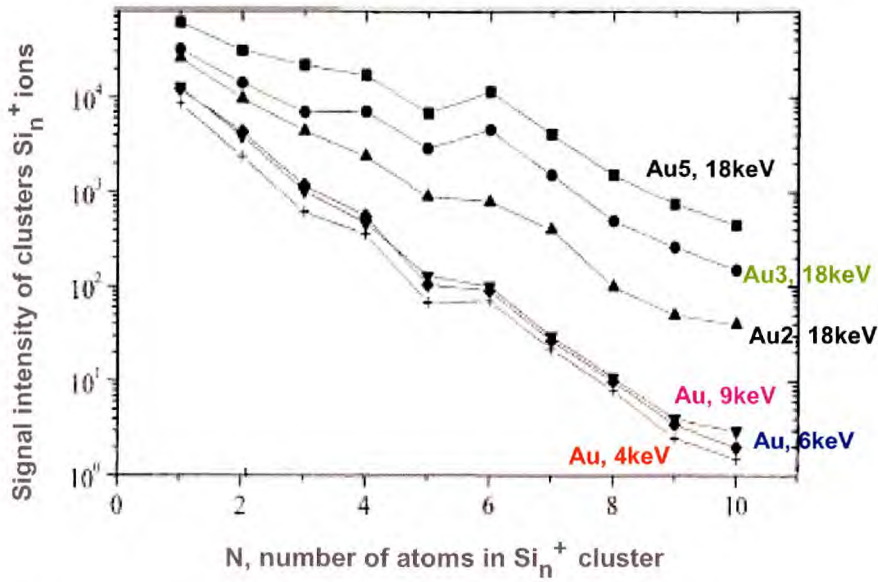


Figure 3.18 Mass spectra of the secondary cluster Si_n^+ ions sputtered by Au_m^- projectiles^[28].

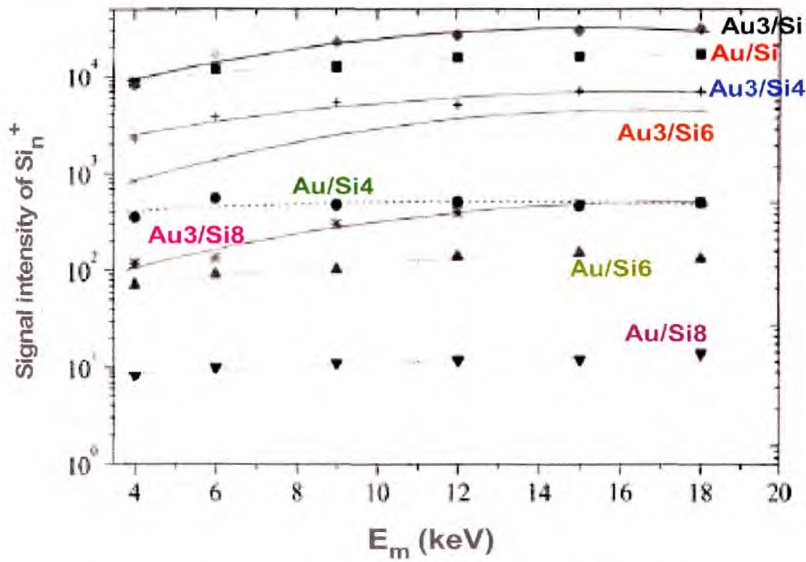


Figure 3.19 Dependence of the Si_n^+ intensity on Au_m^- primary energy^[28].

Nagy *et al*^[38] investigated the signal intensity of DL-phenylalanine, Irganox1010 and polystyrene – absorbed on Al, Si and Ag substrates under Bi_n^+ ($n = 1-6$) bombardment. Figure 3.20 shows the signal intensity of the Irganox1010 molecular ion and several fragment ions under Bi_n^+ bombardment. The signal intensity increased with n , and the maximum signal intensity enhancements were gained at $n = 3, 4$, the lowest were $n = 1$. The big changes in signal intensity were from Bi^+ to Bi_2^+ and Bi_2^+ to Bi_3^+ . Above $n = 3$, the enhancement increments were moderate. For a given Bi_n^+ primary ion, the signal intensity increased linearly with the incident kinetic energy per Bi atom. This was very similar to Au_m sputtering^[2, 36].

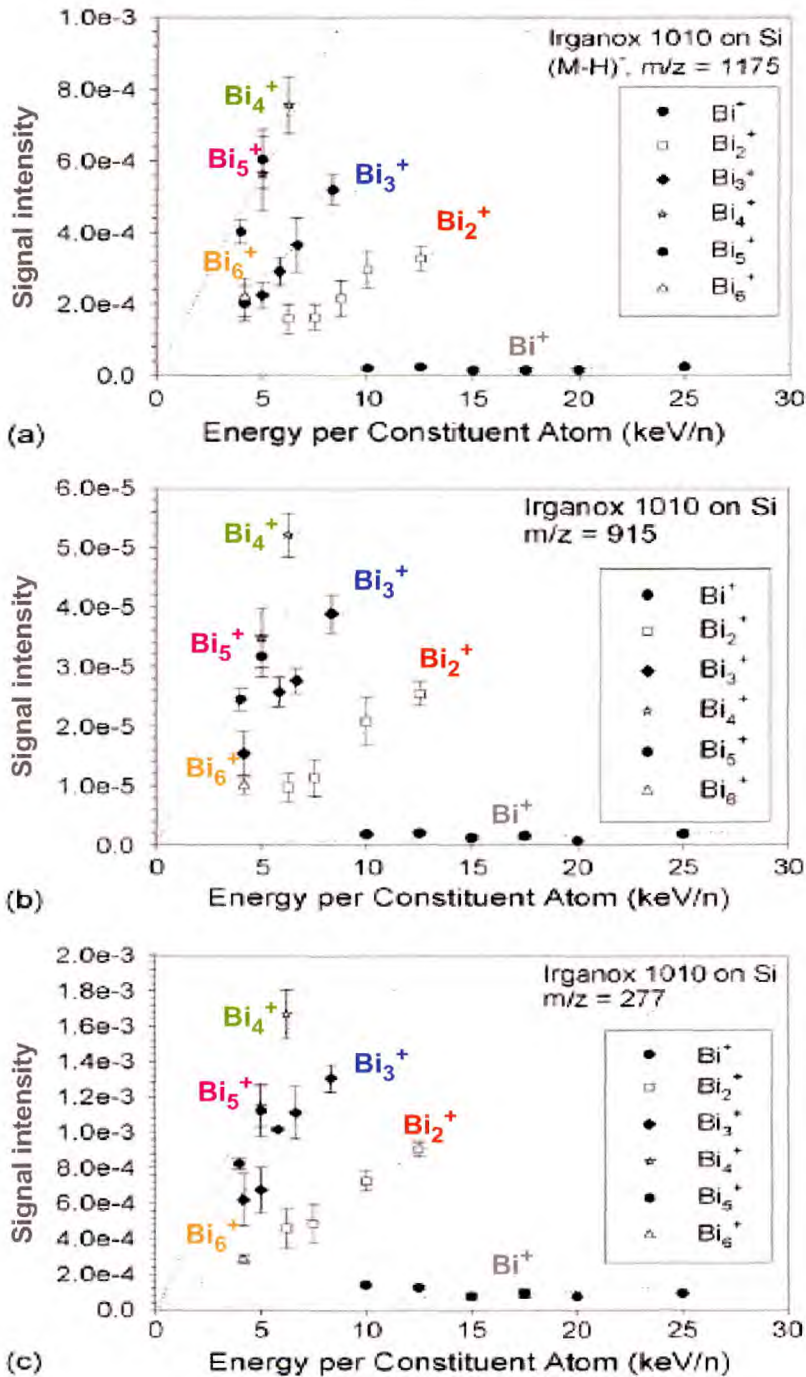


Figure 3.20 Shows the signal intensity enhancement of Irganox1010 spin-coated on a Si substrate from negative ion mode spectra presented as function of the kinetic energy per constituent atom of the primary ion (which is proportional to v^2 , where v is the primary ion velocity). a) $m/q = 1175$, b) $m/q = 915$ and c) $m/q = 277$. Signal intensity enhancements from Bi^+ primary ions are shown as filled circles, Bi_2^+ open squares, Bi_3^+ filled diamonds, Bi_4^+ open stars, Bi_5^+ filled hexagons and Bi_6^+ open triangles ^[38].

Compared with Bi_n^+ , Au_m^+ provides a slightly higher signal intensity enhancement than Bi does, which could be due to that the ion ionisation probability of

Bi is lower than that of Au (the ion mass of ^{208}Bi is higher than that of ^{197}Au). Bi_n^+ LMIS emit larger clusters and higher cluster ion currents which allow data acquisition quicker with Bi_n^+ . In addition, Bi produces Bi^{2+} , which can be used to image the surface with a higher lateral resolution (<400 nm).

Satoshi *et al* [37, 39] investigated the secondary ion emission from a Si target under larger Ar cluster and monomer ion bombardment. Si_n^+ ions with n values up to $n = 8$ were detected under Ar cluster bombardment, whereas, with Ar monomer ions the Si cluster ions produced were only Si_3^+ and the signal intensities were much lower than that produced by Ar cluster ions, shown in figure 3.21. The relationship between the so-called cluster ion yield $Y_{(n)}$ and the Si cluster size is plotted in figure 3.22, and is described by $Y_{(n)}$ is proportional to $n^{-\delta}$, where n is the number of Si atoms. The exponent δ for Ar clusters and monomer ion irradiation is about 2.1 and 6.8 respectively. A similar power law dependence has been also reported including, SF_5^+ , Xe^+ and F^+ primary sources [40]. Signal intensity enhancements due to cluster ion bombardment were clearly shown above. The signal intensity provided was much larger than that found with monomer ion bombardment. For a bigger Si cluster size, it is more likely to be seen in the cluster ion bombardment but the signal intensity was not as large as the smaller Si clusters.

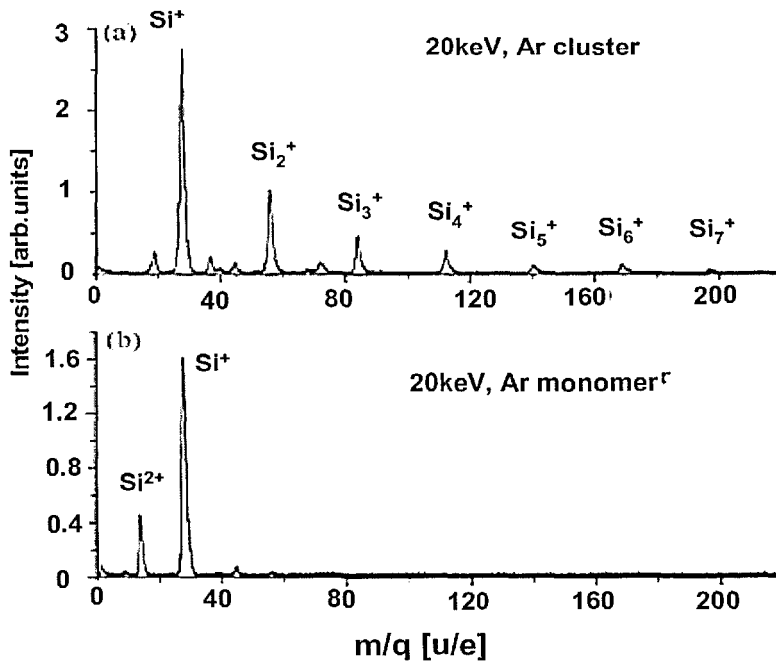


Figure 3.21 Mass spectra of secondary ions emitted from Si under bombardment by a) 20 keV Ar cluster ions, b) 20 keV Ar monomer ion [37].

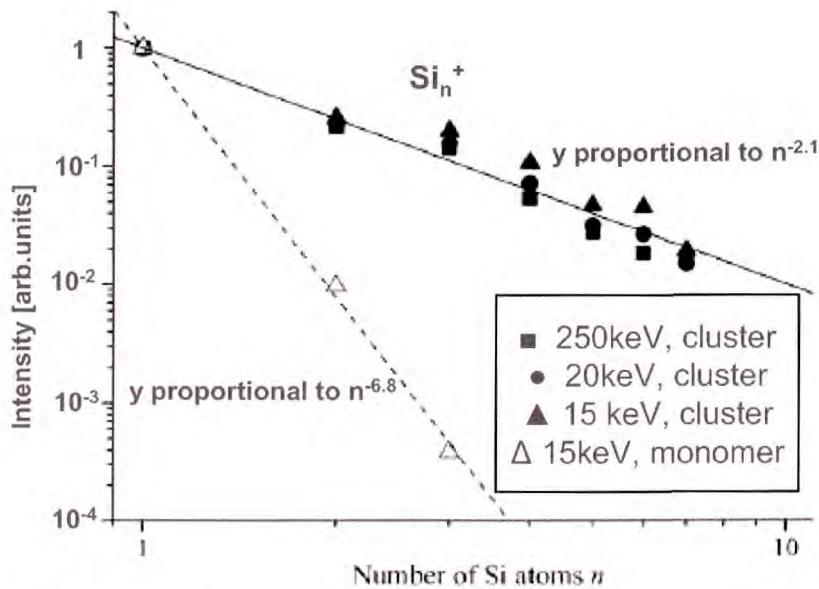


Figure 3.22 Size dependence of the signal intensity enhancement of Si cluster ions produced by Ar cluster and monomer ions [37].

A C_{60}^+ primary ion beam system in a TOF SIMS instrument has been investigated for organic material yield enhancement. The results have shown signal intensity enhancements of at least 30 to 100-fold, as compared to the signal intensity observed under Ga^+ bombardment at the same energy due to enhanced sputtering [41]. Figure 3.23 shows a positive TOF SIMS spectrum of PS-2000 using 10 keV C_{60}^+ and Ga^+ . Higher signal intensities were gained using C_{60}^+ compare to that for Ga^+ bombardment.

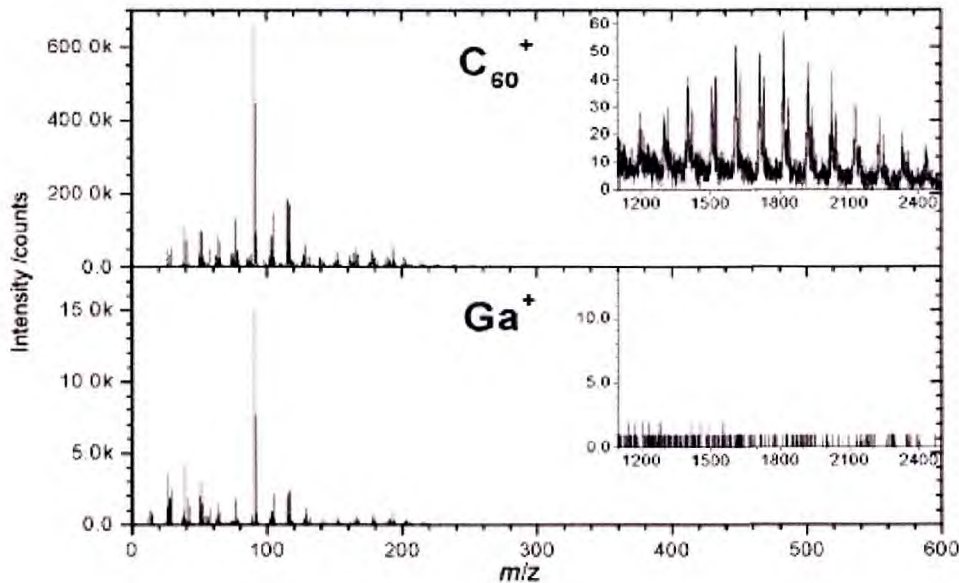


Figure 3.23 A positive TOF SIMS spectrum of PS-2000 [41].

Mondt *et al* ^[42] compared the signal intensity enhancement gained by using Ga^+ , SF_5^+ , C_{60}^+ , Bi^+ , Bi_3^{2+} and Bi_5^{2+} projectiles under static conditions. The monoatomic Ga^+ and Bi^+ sources exhibit consistently lower signal intensity than the cluster projectiles. Ga^+ ions offers worse signal intensity enhancements than Bi^+ does, whereas, SF_5^+ clusters provides lower signal intensity than the recently developed projectiles C_{60}^+ . The study of ion yields of model biological membranes using different primaries (Au^+ , Au_3^+ and C_{60}^+) also showed that the C_{60}^+ beam produces the highest signal intensity from these model cell systems, and it is the most sensitive to the change in surface ^[43]. The ion yields are found greater from thick films as compared to think films, and molecular dynamics and experimental studies on ice show that C_{60}^+ has a significantly shallower information depth than Au_3^+ and Au^+ .

Other techniques such as a post-ionisation technique and combined electron and focused ion beam systems have been developed to ionise the neutrals in order to improve the ion yield ^[44, 45]. At a certain optimized electron energy, the electron impact ionisation takes place and the ionisation rate can be significantly increased by increasing the electron current. Figure 3.24 shows the ratio I_s/I_i (I_s secondary ion current, I_i primary ion current), which is proportional to the secondary ion yield, plotted as the function of electron source biasing voltage V_e . When the electron biasing voltage is negative, the electron impact ionisation takes place which leads to secondary ion yield enhancements. Compared with the low electron current, the peak secondary ion yield for the higher electron current is five times more.

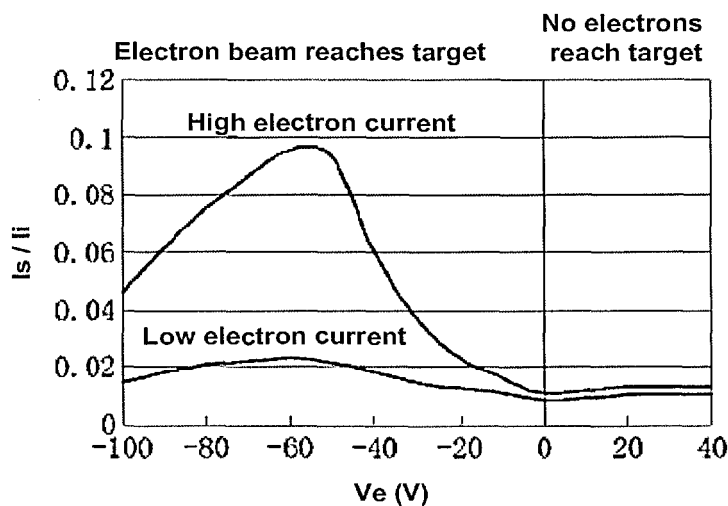


Figure 3.24 Shows I_s/I_i as a function of electron source biasing voltage V_e . When V_e is positive, no electrons reach the target; when V_e is negative, secondary ion yield enhancements are observed ^[45].

3.3 Summary

In the last two sections, we mainly concentrated on the primary ion beam effect on the ion yield enhancement. We have shown that the ion yield can be enhanced by surface chemistry modification by reactive ion implantation. Cesium has been widely used to enhance the negative ion yield by lowering the work function. The positive ion yield enhancement is mainly related to the increased ionisation probability, for which oxygen is mostly used as oxygen provide chemical reactions with the surface form SiO_2 , which increases ionisation probability. The ionisation process by definition is the physical process of converting an atom or molecule into an ion by adding or removing charged particles such as electrons or other ions. Ga^+ FIB SIMS offers great spatial resolution but low ion yield. Oxygen pre-dosing prior to SIMS analysis enhances the ion yield of FIB SIMS dramatically. Oxygen flooding also is commonly used and the degree of the ion yield enhancement depends on the oxygen pressure. In addition, it reduces the crater bottom roughness and transient depth in the oxygen build-up region. For some metal elements, the electronic excitation effect plays a big role in the ion yield enhancement. The strong electronic interaction between the primary ions and the target atoms leads to secondary ion formation, and in consequence, the ion yield increases. Polyatomic ions (e.g. C_{60} , bismuth) have been a very popular source used in the TOF SIMS technique to enhance the signal intensity (or ion yield – debatable). One of the main advantages of the polyatomic ions is that the bombardment of multiple atoms of the polyatomic ions results in more energy deposition onto the sample surface, this leads to more secondary ion ejection. From the instrumental point of view, a post-ionisation technique can be employed such that neutrals can be ionised by combining an electron gun and a focused ion beam. Furthermore, analyses of insulator materials are much easier. Finally, the ion yield can vary hugely depend on different combinations of instruments, materials and primary ion sources.

3.4 Angular and Energy Effect

Secondary ion yield enhancements involve the surface or near-surface chemistry. The surface concentration of the reactive bombarding species changes inversely with the sputter yield, S . The sputter yield is defined as the number of atoms of the material removed, per incident primary species, ions/atoms. Thus, the ion yield and sputter yield correlation can be interpreted in terms of variations in the surface concentration of the primary species. The effect of sputter conditions such as primary incident angle and energy on the relationship between sputter yields and surface concentration have been studied by many researchers [46, 47]. Matsunaga *et al* [48] investigated the relationship between negative ion yield (Y) and sputter yield (S), and that between ion yield and the surface density of Cs^+ . The C, Si and Ge implanted InP samples were bombarded with a Cs^+ beam at 15 keV at different incident angles ($0^\circ - 60^\circ$, 7.5° interval). Figure 3.25 shows that the ion yield of C^- , Si^- , Ge^- increased with increasing $1/S$ (i.e. ion yield changes inversely with sputter yield). As the sputter yield decreases, the Cs surface density increased and as a consequence, the ion yield increased.

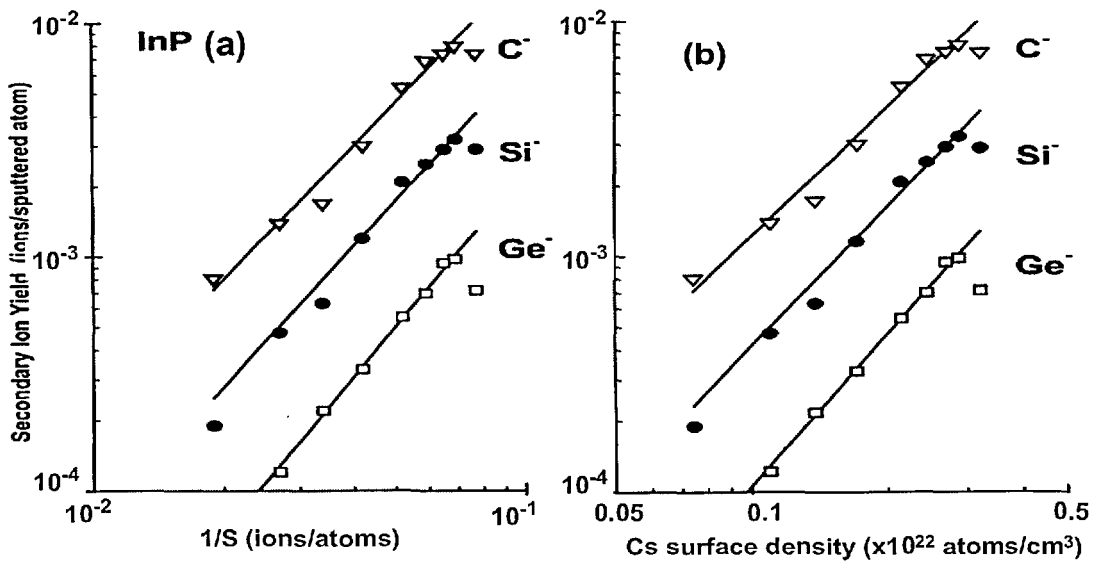


Figure 3.25 Relations between sputtering yields and secondary ion yields, and that between ion yields and surface density. Ion incident angles used for Cs^+ bombardment were 0° to 60° at intervals of 7.5° . a) data for normal incidence was excluded. The straight lines show that the negative secondary ion yield of these elements changes inversely with $1/S_{\text{InP}}$, b) shows secondary ion yields of C^- , Si^- and Ge^- versus Cs density at the InP surface. For every element, the ion yield rises in proportion to the power of the Cs surface density [48].

Wittmaack *et al* [49] investigated the effect of the angle of incidence on the $\text{Si}^{+/-}$ ion yields of oxygen-bombarded solids. A silicon sample was bombarded with Ar^+ at

5 keV and O_2^+ at 10 keV, the incident angles used were from 0° to 60° . For Ar^+ bombardment, the variation in ion yield was not very significant with increasing incident angle. Under 10 keV oxygen bombardment, the $Si^{+/-}$ ion yield was much higher, the highest $Si^{+/-}$ ion yield occurring at normal incidence, because of the full oxidation of the silicon layer, SiO_2 . As the incident angle exceeded 20° the ion yield decreased more rapidly with increasing incident angles. It is clear now, that the ion yield of negative ions or positive ions is affected by the surface concentration. As a fully oxidised layer can be achieved at normal incidence, a higher ion yield is expected. When the incident angle increases, the sputter yield becomes high which leads to a lower surface concentration of oxygen or cesium. In consequence, as we revealed in the previous section, the surface work function/ionisation probability is not optimised to enhance the ion yield. Figure 3.26 shows the ion yield of $Si^{+/-}$ as a function of incident angles. The Si^+ ion yield under oxygen bombardment decreased by a factor of 2×10^3 as the incident angle changes from 0° to 60° . Almost the same ion yield reduction was found with negative ions. As the angle of incidence increased, less oxidation occurred and a significant decrease in the ion yield was observed. Compared to oxygen bombardment a much lower ion yield of $Si^{+/-}$ was observed under 5 keV Ar^+ bombardment, and the variation in ion yield was less dramatic. The observation demonstrated the dependence of ion yield on the surface concentration of the reactive ions.

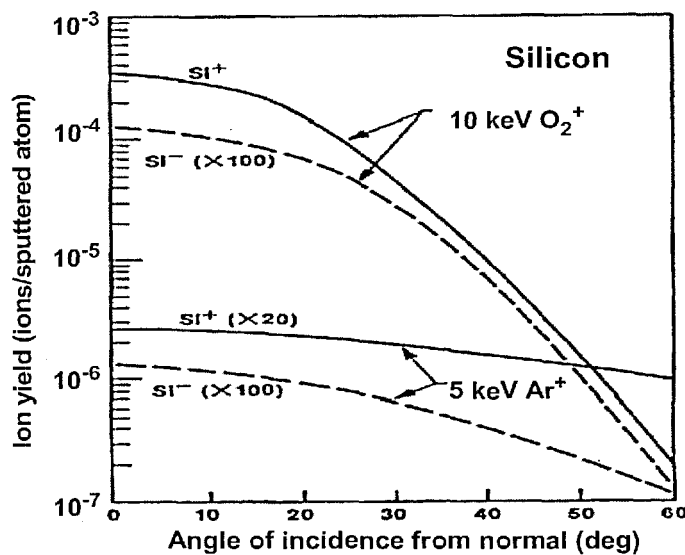


Figure 3.26 The dependence of $Si^{+/-}$ ion yield on incident angle from normal for primary Ar^+ and O_2^+ beams ^[49].

However, this can be different if a different matrix (e.g. Ge, GaAs) is used. It was reported that with bombardment of Ge and GaAs with a 10 keV O_2^+ beam at angles from 0° to 60° that the intensity of Ge^+ , Ga^+ and As^+ was reduced by only one order of magnitude, but that the Si intensity was reduced by two orders of magnitude. This was partially due to the high initial sputter yield of Ge^+ (or Ga^+ , As^+) under high primary oxygen energy which resulted in low oxygen incorporation. In addition, Ge does not react with oxygen as well as Si does. This can be described as a matrix effect. The oxygen incorporation can be improved by lowering the primary energy or increasing the incident angle above 45° where the matrix effect becomes less effective [50].

Beyer *et al* [51] reported the variations in the thickness of oxygen formed altered layers at various angle of incidences. The silicon was firstly bombarded with 14 keV $^{18}O_2$ at various angles from 0° to 60° . The crater bases were subsequently depth profiled using a 3 keV Xe^+ beam to reveal the oxygen distribution. He found that the layer thickness dropped at an incident angle, $\theta > 10^\circ$, which was accompanied by a further increase of the sub-stoichiometric oxide region at the back interface of the altered layer. The projected range of the primaries in silicon, the sputter rate and the diffusion of oxygen in the altered layer (oxygen is very diffusive in oxide) were mainly responsible for the change in oxide layer thickness. The total range which equals projected range plus straggle was calculated by TRIM [52]. They found that at angles from 0° to 10° the layer thickness and total range ratio did not change; above 10° the ratio dropped and at 20° the ratio was close to 1 thus indicating that diffusion only plays a minor role in terms of the altered layer thickness. The partial sputter yield of silicon only started to increase above 10° , this caused a reduction in the layer thickness. At incident angles above 20° the partial sputter yield of oxygen was high and a full layer oxidation was not achievable. The altered layer thickness and the interface width with various incident angles are plotted in figure 3.27. The altered layer/substrate interface width has been measured between the 84 and 16% drop off point of the normalised $^{18}O^- / ^{28}Si^-$ ratio. The larger interface width of the ion beam induced altered layer is indicative of a partially oxidised region that follows the completely oxidised region [51]. As seen, the interface width at 25° is almost 2.5 times larger than that at near normal incidence.

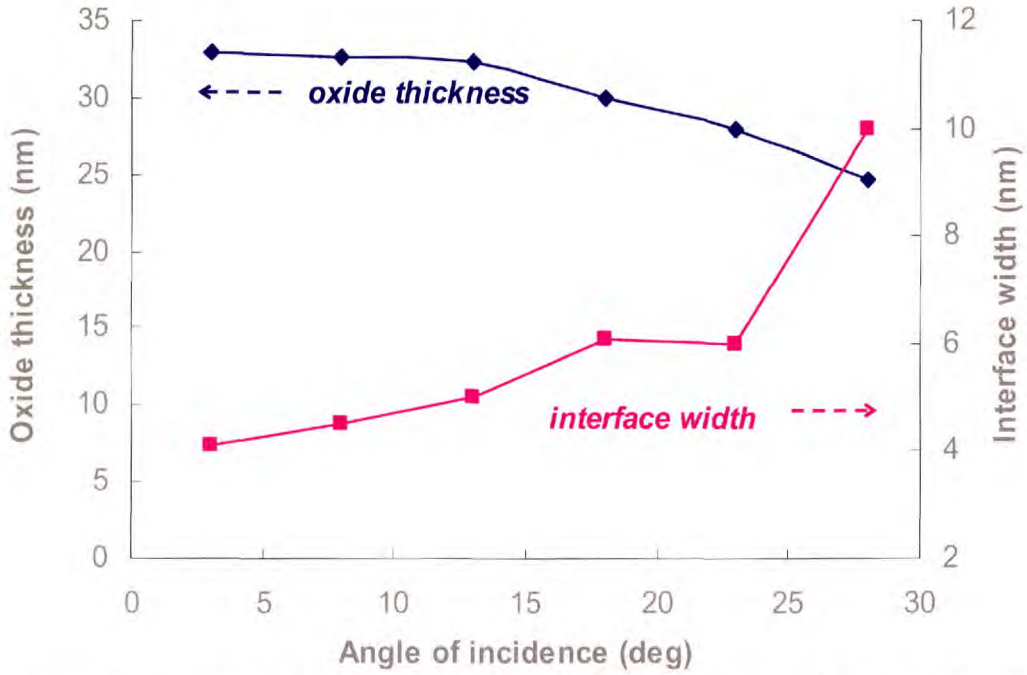


Figure 3.27 Oxide thickness and interface width as a function of $^{18}\text{O}_2^+$ incident angle, the oxygen implantation energy was 14 keV, the altered layer was depth profiled by a 3 keV Xe^+ beam at normal incidence ^[51].

Beyer *et al* ^[53] also demonstrated the dependence of the oxide layer thickness on primary $^{18}\text{O}_2^+$ beam energy. The bombardment of silicon with $^{18}\text{O}_2^+$ at energies ranging from 2 to 14 keV at normal incidence resulted in complete oxidation of the altered layer. The in-situ profiles were obtained by Xe^+ depth profiling. There was a clear increase in the thickness of the oxide layer as the primary beam energy was increased from 2 keV upwards. The thickness of the oxide layer was larger than the total range (determined by TRIM ^[52]) at all energies. This was due to the diffusion of excess oxygen in the silicon. It should be clarified that the fully oxidised layer can be formed at normal incidence with oxygen bombardment. For a given oxygen beam energy, the dose required to achieve full oxidation is named as the critical dose. The oxide layer thickness and the ion yield enhancements are related to this dose. Kilner *et al* ^[54] studied the relationship between the altered layer formation and the oxygen implant dose. It was found that the oxide layer increased with increasing oxygen dose until the critical dose was reached, and a fully formed oxide layer was formed. Figure 3.28 shows the oxygen buildup with different oxygen doses. Various $^{18}\text{O}^+$ primary doses were implanted into a clean Si(100) surface at 15 keV primary energy. The oxygen induced layers were then analysed by 3 keV Xe^+ bombardment, and $^{18}\text{O}^+$ ions were monitored.

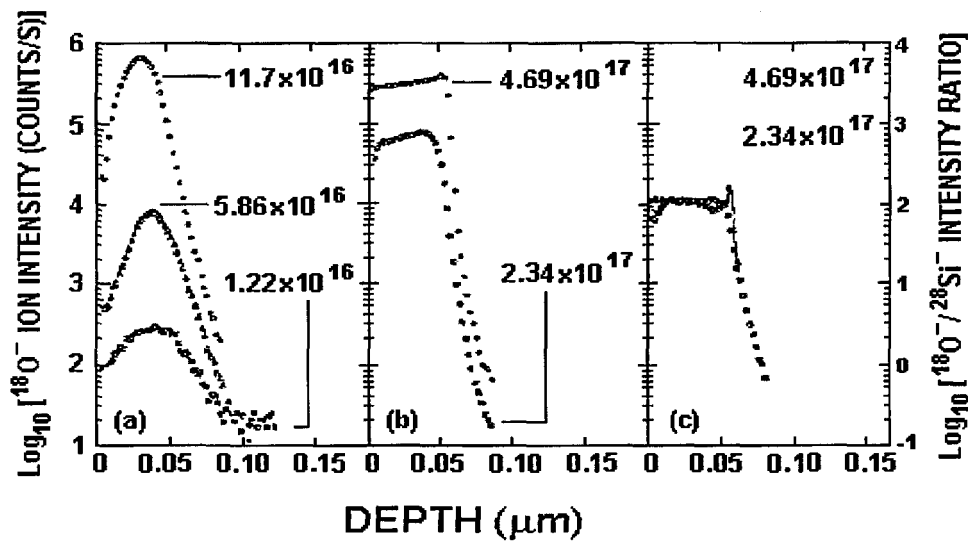


Figure 3.28 Oxygen buildup curves for 15 keV O^+ bombardment of silicon obtained by subsequent 3 keV Xe^+ profiling: a) doses of 1.17×10^{17} (●) 5.86×10^{16} (▲) and 1.22×10^{16} ions/cm² (■), b) for doses of 4.69×10^{17} (●) and 2.34×10^{17} ions/cm² (■), c) the ^{18}O profiles in (b) are plotted as $^{18}O/^{28}Si$ intensity ratios in (c). Depth profiling conditions: 3 keV Xe^+ [54].

It showed that at low oxygen doses a Gaussian distribution of the oxygen was obtained up to a dose of 11.7×10^{16} O/cm². Above this level, saturation of the oxygen signal took place suggesting the formation of SiO₂. The flat $^{18}O/^{28}Si$ intensity ratio confirmed the observation. However, comparing 2.34×10^{17} with 4.69×10^{17} O/cm², the saturated oxygen signal is only seen in the central part of the depth profile, this indicates that a buried layer has been formed and complete oxidation of the immediate surface had not yet been achieved. Figure 3.29 shows calculated oxygen concentration profiles with different oxygen implant doses, diffusion also takes place in both directions. The results agree well with the experimental data.

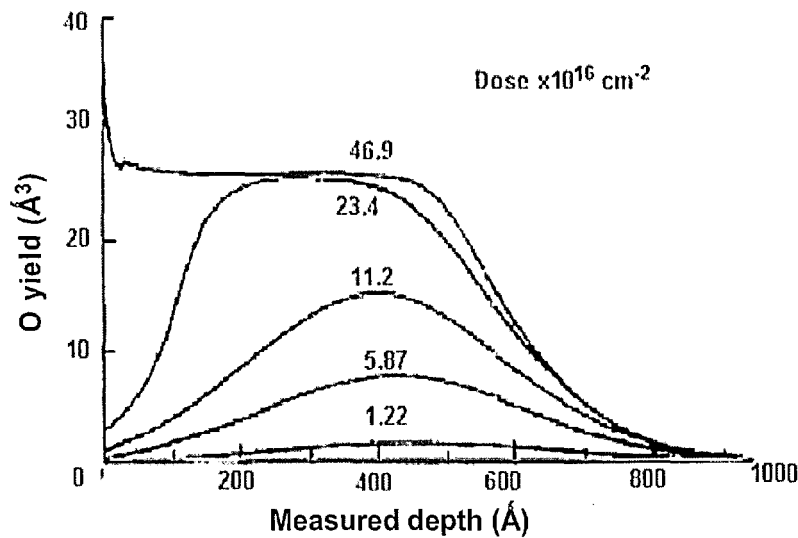


Figure 3.29 Calculated oxygen concentration profiles in silicon bombarded with 15 keV O^+ to various doses. The SIMS profile was gained using a simulated 3 keV Xe^+ primary beam [54].

The same results were observed by Williams *et al* ^[55]. He used Rutherford backscattering (RBS) and channeling to study the dependence of surface oxides on primary oxygen energy and dose. All craters made on the silicon sample were analysed by RBS and channeling (RBS-C) using 2 MeV He^+ ions. A linear dependence of oxide thickness with oxygen energy was found between 3 and 40 keV, and a stoichiometric SiO_2 layer was formed. This dependence agreed well with TRIM ^[52] calculations of the total range for oxygen bombardment of SiO_2 . Figure 3.30a shows the thickness of the oxide layer as a function of incident energy. Over the 3-40 keV energy range covered, the oxide thickness data fits a linear energy dependence rather well as shown by the least squares fit. The crosses are obtained from the TRIM calculations.

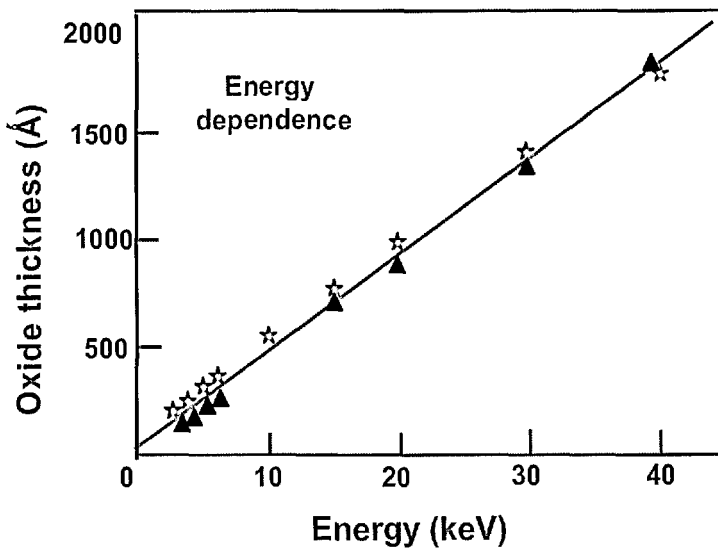


Figure 3.30a) The energy dependence of the oxide thickness. Triangles correspond to O_2^+ and O^+ SIMS bombardment (4-12 keV) and 10 keV, respectively and O^+ bombardment in an ion implanter (15-40 keV) at 0° . Stars are obtained from a TRIM simulation ^[55].

Figure 3.30b shows the thickness of oxide layer as a function of oxygen dose at a fixed primary energy of 8 keV O_2^+ . Compared with the critical dose gained for an 15 keV $^{18}\text{O}_2^+$ beam reported by Littlewood *et al* ^[56], the critical dose of a 8 keV beam measured in this experiment is much smaller, at 1.5×10^{17} atoms/cm² (for a 15 keV oxygen energy, the critical dose was 4.5×10^{17} atoms/cm² which is very similar to that gained by Littlewood). Hence, the beam energy effect on the altered layer formation is shown.

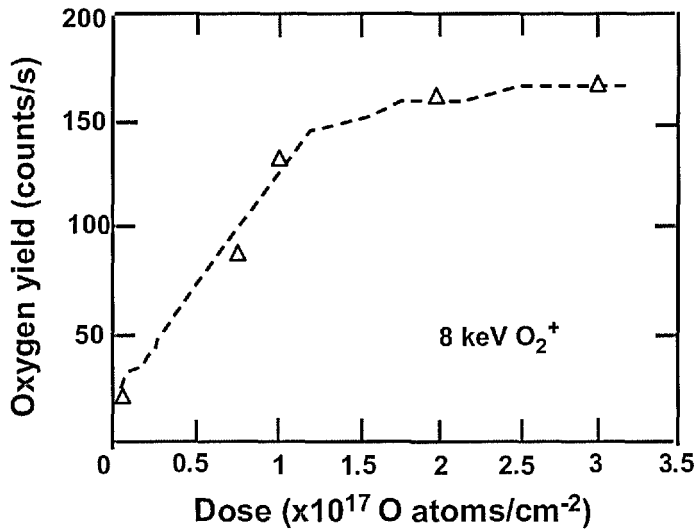


Figure 3.30b) Shows the measured oxygen incorporation as a function of dose. Build-up of incorporated oxygen, measured by RBS-C, is shown for several doses of 8 keV O_2^+ bombardment at 0° . A continuous SiO_2 layer forms at a dose of about 1.5×10^{17} oxygen atoms/cm² [55].

The dependence of ion yield of $Si^{+/-}$ on primary ion energy under various primary species namely: Ar^+ , Xe^+ , O_2^+ and Cs^+ was reported by Wittmaack *et al* [57], shown in figure 3.31. Under Xe^+ and Ar^+ bombardment, the increase of primary ion energy has produced more ions such that the ion yield of $Si^{+/-}$ increased. Under O_2^+ bombardment the Si^+ ion yield reduced slightly as the primary ion energy increased from 2 to 8 keV, this indicated that a thin oxide layer was formed in the lower energy range. The most pronounced change in Si^- ion yields was observed under Cs^+ bombardment. As the primary energy increased, much more Cs^+ was sputtered off and as the cesium surface concentration decreased, the ion yield decreased. Looking at the oxygen surface concentration, it varied little with the beam energy. This was due to the high sticking coefficient of oxygen. It is also interesting to note that the ion yield of the singly charged Si^+ ions were higher than that of the doubly charged ions Si^{2+} , since chemical enhancement effects are negligible for $n = 2$ unless the reactive atom content in the altered layer is high. For silicon delta-doped layers in GaAs, the ion yield enhancements of Si^+ are most pronounced at the low bombardment energies, whereas at high primary ion energies with normal incidence the Si atoms are spread out more and dilution of the local Si concentration is maximised, reducing the ion yield to the values for Si in GaAs [58].

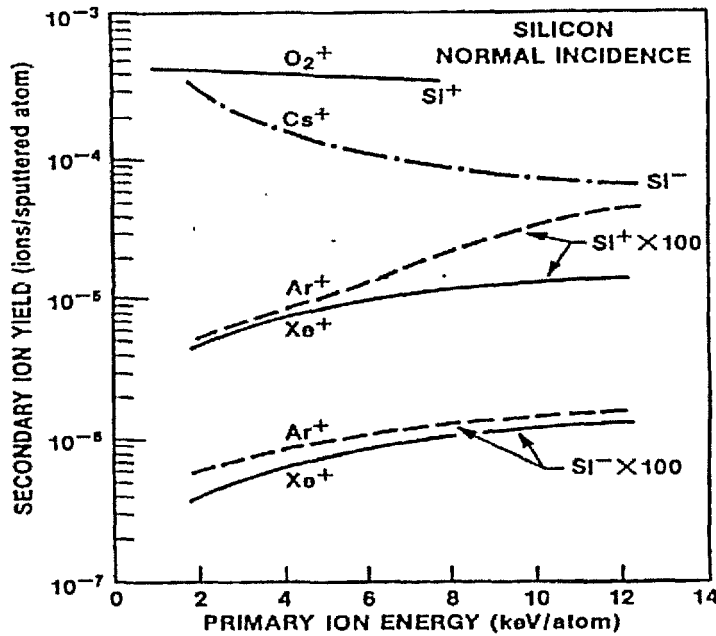


Figure 3.31 Shows the dependence of $\text{Si}^{+/-}$ ion yield on primary ion energy under various primary ions: Ar^+ , Xe^+ , O_2^+ and Cs^+ [57].

In the case of metals, Wittmaack *et al* [59] studied the relative ion yields of 12 metals as a function of Ar^+ primary ion energy between 2 and 15 keV. The secondary ion intensity was found to increase with increasing energy for all elements investigated and the differences in intensities for the various elements was less than two orders of magnitude. The difference between the highest relative ionisation probability (Al) (the ionisation probability is the probability that the sputtered flux is ionised) and the lowest relative ionisation probability (Au) was just two orders of magnitude.

The Zn^+ and Cd^+ ion bombardment of polycrystalline copper and molybdenum showed that the ion intensity increased almost linearly with the primary ion energy, attained a broad maximum and subsequently declined [60]. Figure 3.32 shows the ion yields of various ion-target combinations, e.g., Zn^+ -Cu, Cd^+ -Cu and Cd^+ -Mo. The ion yield increased with increasing primary energy until the critical incident energy and then decreased. The author suggested that this subsequent decline in secondary ion emission was due to the effect of channeling of incident ions within the crystal lattice. The ion induced preferential orientation in polycrystalline targets transforms a non-textured target into a textured one.

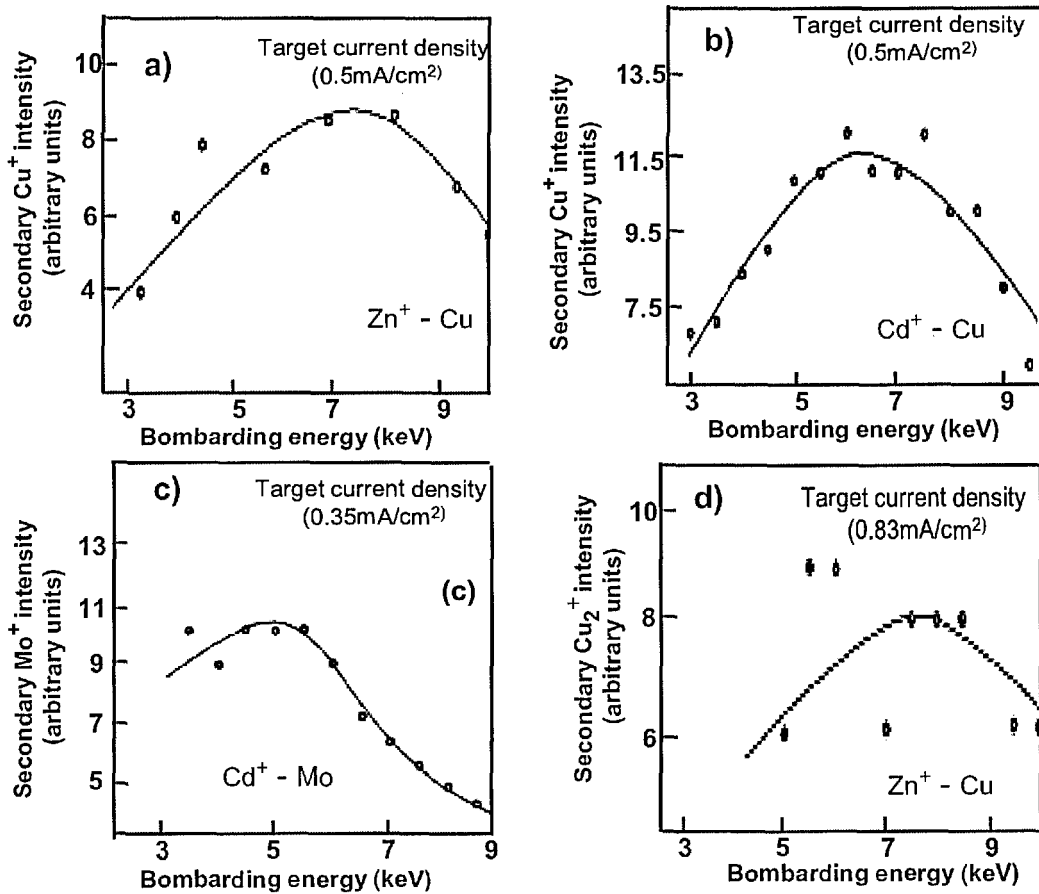


Figure 3.32 a) Cu⁺ intensity with primary Zn⁺, b) Cu⁺ intensity with primary Cd⁺, c) Mo⁺ intensity with primary Cd⁺, d) Cu₂⁺ intensity with primary Zn⁺ [60].

3.5 Summary

In this section, we have shown how the surface concentration of the reactive primaries affects the ion yield. The ion yield changes inversely with the sputter yield. The surface concentration (e.g. Cs⁺, O₂⁺) decreases with increasing primary incident angle. At oxygen oblique incident angle, a fully oxidised (refers to the overall chemical composition of the altered layer) altered layer is not achievable. At near normal incidence, the ion yield increases with increasing oxygen dose until the critical dose, when a fully oxidised layer is formed. The thickness of the oxygen induced altered layer also depends on the primary energy, i.e. the thickness increases with increasing oxygen energy. For Cs⁺ bombardment, the high primary energy reduces the surface concentration of the Cs⁺ ions, and in consequence, the ion yield decreases. To achieve high signal intensities from an inert gas source (e.g. Xe⁺) a high primary energy should be used. This allows a high sputter yield and more secondary ions are produced which leads to a high ion yield.

To summarise, for commonly used semiconductors (e.g. Si) oxygen and cesium enhance the positive and negative ion yield greatly. The degree of the ion yield enhancement largely depends on the Cs/O₂ surface concentration. To gain maximum ion yield enhancement, a low bombarding energy combined with normal incidence of the primary beam seems appropriate.

3.6 Topography Effect

During the sputtering process, ideally the receding sputtering surface should remain smooth, with no topographic variations in the base of the sputtering crater. In practice, topography often occurs and this effect comes from a fundamental interaction (physical or chemical) between the energetic primary ions and the sample surface. The sample surface region is amorphized and become rough with sputtering depth, even if it is completely smooth at the beginning of primary ion exposition ^[61]. The ripple formation is a result of the variation in sputter rate with the angle of incidence of the primary beam with the sample, and the growth of ripples is exponentially dependent on sputtered depth. The changes in surface topography can strongly enhance ion yields. The ion intensity before ripple formation is given ^[62]:

$$I(\theta_0) = K * S(\theta_0) * Y(\theta_0) \quad (1)$$

Where $I(\theta_0)$ is the secondary ion intensity before ripple formation, θ_0 is the primary ion incident angle (uniform everywhere on the surface before ripple formation), K is a constant, Y is the secondary ion yield, S is the sputtering yield. The ion intensity after ripple formation is approximated by:

$$I(\theta_1, \theta_2) = K[S(\theta_1)Y(\theta_1) + S(\theta_2)Y(\theta_2)] \quad (2)$$

Where $I(\theta_1, \theta_2)$ is the secondary ion intensity after ripple formation. The primary ion incident angles to the plane face normals of the two plane faces are denoted by θ_1 and θ_2 . θ_1 and θ_2 are constant during sputtering after ripple formation.

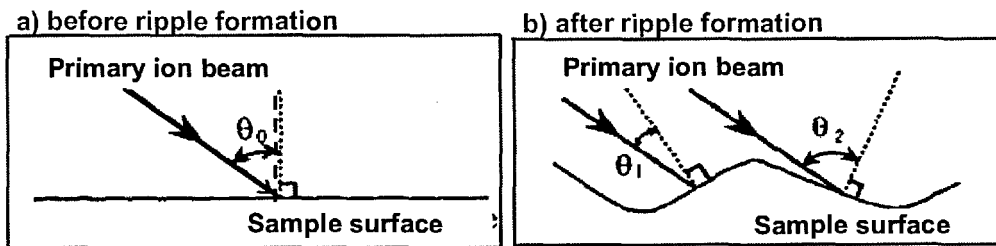


Figure 3.33 Sample surface and microscopic primary incident angle a) before and b) after ripple formation ^[62].

Under reactive ion bombardment (e.g. Cs^+ and O^+), the beam energy plays a crucial factor in the ripple formation mechanism. The impact energy must exceed a critical value in order to record measurable ion yield changes during ion bombardment. Shichi *et al* ^[63] observed the variation in ion yield of Si using a Cs^+ primary beam at higher energies, namely 17.5 keV and 14.5 keV. The incident angle was 45° . The change in ion yield was explained as a result of surface roughening, which was commonly observed with oblique oxygen bombardment. At lower Cs^+ beam energy there was no variation observed in the Si ion yield. They suggested that the impact energy was an important factor in producing the ion yield changes during Cs^+ ion bombardment. Figure 3.34 shows SEM micrographs of the crater bottom in Si after 17.5 keV Cs^+ sputtering at four different depths: (a) 0.2 μm , (b) 0.6 μm , (c) 1 μm and (d) 1.6 μm . The topography of the bottom changes from smooth to rippled with increasing sputter time. A yield increase of 38% occurred for Si at a depth of 0.6 μm .

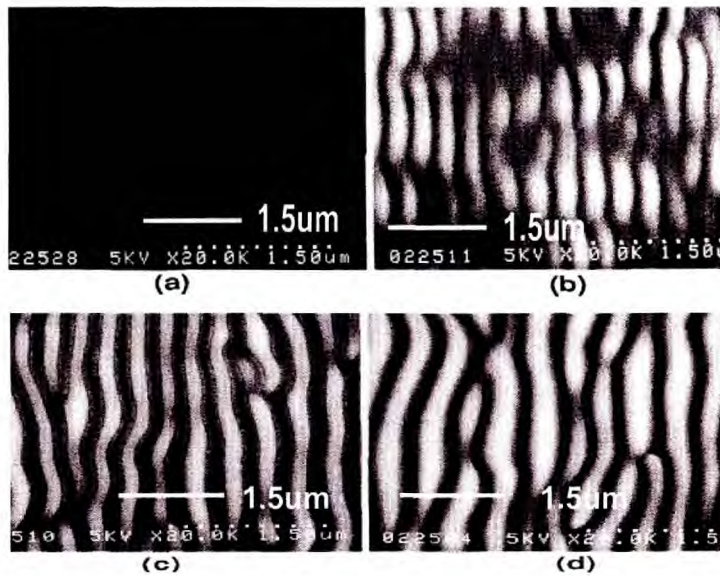


Figure 3.34 SEM micrographs of crater bottoms at different depths; a) 0.2 μm , b) 0.6 μm , c) 1 μm and d) 1.6 μm ^[63].

Stevie *et al* ^[64] investigated the ion yield changes in Si and GaAs during O_2^+ and Cs^+ bombardment at different energies and angles. In GaAs, under O_2^+ bombardment an enhanced ion yield was clearly observed over a certain depth range for high beam energies (i.e. 5.5 and 8 keV), and the yield change was as high as +70% for GaO^+ . But no ion yield change was observed with low energy (2.5 keV) bombardment. In Si, the changes of topography were seen from SEM micrographs. Figure 3.35 shows that an ion yield of $^{28}\text{Si}^+$ increased by 68% averaged over several measurements in the depth

range of 2.5-3.8 μm . Scanning Electron Microscope (SEM) micrographs show the topography changed from a smooth to a rippled surface with increasing critical depth. At a depth of 2.1 μm , a smooth surface was seen in the SEM, but as the sputter depth increased the ripple formation started to grow. The ridge lines of the ripples were perpendicular to the direction of the primary beam.

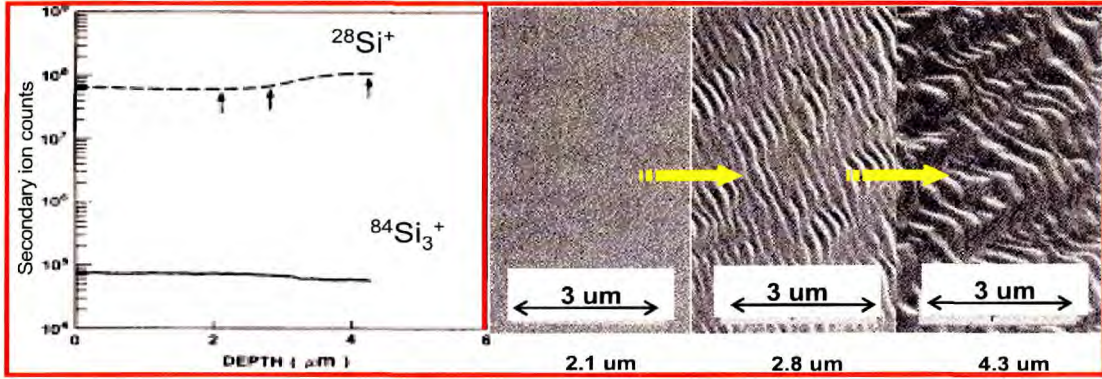


Figure 3.35 Shows a 6 keV O_2^+ sputter depth profile of Si(100). The arrows on the depth profile indicate depths at which SEM micrographs were taken. The incident angle was 41° [64].

Figure 3.36 shows SEM micrographs of SIMS crater bottoms in GaAs after O_2^+ bombardment at 5.5 keV and 2.5 keV. The angle of incidence used for 5.5 keV was 42° and, for 2.5 keV the angle was 57° . The surface topography was invariant for 2.5 keV to a depth of 1.94 μm , for 5.5 keV, the surface topography was observed to depth 0.91 μm . There was no change in ion yield or topography for Cs^+ bombardment [65].

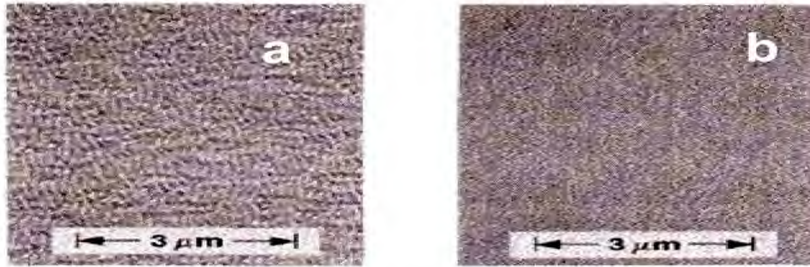


Figure 3.36 Scanning Electron Microscope micrographs of SIMS crater bottoms in GaAs after O_2^+ bombardment at a) 5.5 keV at 0.91 μm and b) 2.5 keV at 1.94 μm [65].

The incident angle of the primary beam is considered to be a more important factor than the primary beam energy in causing the change in topography and hence the change in ion yields. It appears that ripple formation occurs over a certain range of primary incident angles. It was reported that the bombardment of Si^- with a 17.5 keV Cs^+ beam at different angles showed that no ripples were formed from incident angles of 0° to 30° for sputtered depths of less than 4 μm [66]. Thus, the reason that Stevie *et al*

found no changes in ion yield for Cs^+ bombardment could be due to the incident angles (60°) used in their studies. Karen *et al* [67] used higher O_2^+ primary energies (5.5 to 13 keV) with different incident angles (30° - 40°) on the GaAs sample, and the As^+ ion yield were clearly seen to increase with increasing primary energy. This is because with larger slope angle of the ripples, the As^+ ion yield enhancement was bigger due to the higher oxygen concentration on the slope facing the ion beam closer to normal incidence. Wittmaack *et al* [8] studied the range of impact angles responsible for the formation of ripples. It was found that beam induced roughening is limited to rather narrow impact angles from about 32° to about 58° as shown in figure 3.37.

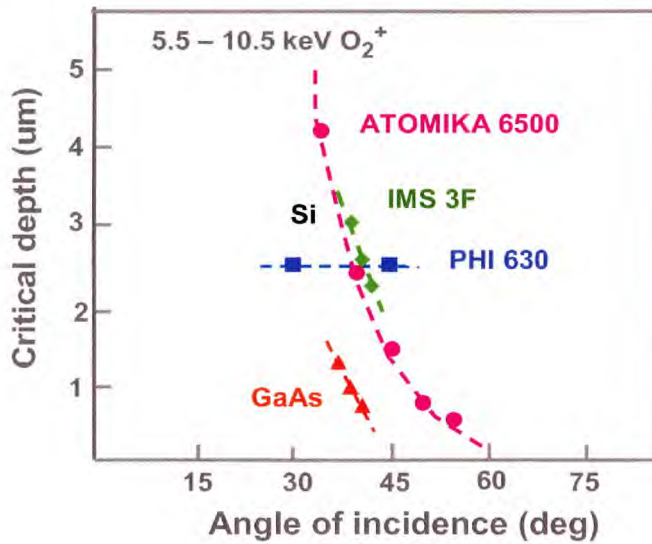


Figure 3.37 Surface roughening as a function of impact angle of oxygen ions. The primary ion beam energy ranges from 5.5 keV to 10.5 keV. Mass spectrometers used for analysis were: Atomika 6500, IMS 3F, and PHI 6300 [8].

As we have shown, the surface topography effect is caused by reactive ion bombardment. The ion yield can change significantly during the sputtering. However, with low energy bombardment, the variations in the ion yield can be avoided (e.g. 2.5 keV O_2^+ at 57°) regardless of what the beam angle is. In turn, the surface topography caused by the critical angles are limited to a narrow range ($32^\circ - 58^\circ$), even if a high beam energy is used (e.g. 17.5 keV Cs^+ at 60°). Sample rotation is another technique which is often used to eliminate ripple formation [68-70]. As a result of sample rotation no ripple formation was observed and so no ion yield variation was observed.

Cirlin *et al* [71] reported that rapid changes in the ion yield of AsO^+ occurred at a depth of ~ 200 nm under a 3 keV O_2^+ bombardment at an incident angle of 40° . The

change in the ion yield was due to the ripple formation. Figure 3.38 shows the effect of ripple formation on the ion yield. A bulk GaAs sample was bombarded with a 3 keV O_2^+ . As seen, without sample rotation, the secondary ion yield of AsO^+ increased with increasing sputter depth; this indicated ripple formation taking place (profile a). With sample rotation, the AsO^+ intensity stayed constant (profile b). Profile c shows that for the first 400 nm sputter depth, the sputtering was done without sample rotation, the AsO^+ intensity increased gradually. After 400 nm, the sample rotation was turned on, the ion yield returned to its original value and no ripple formation.

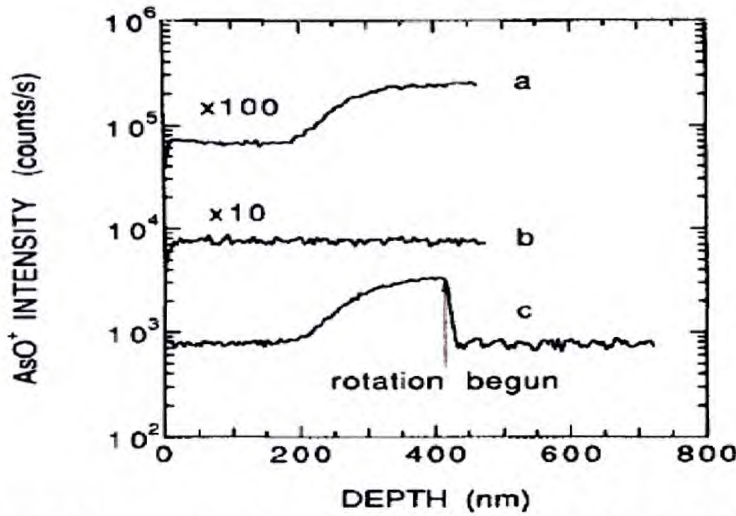


Figure 3.38 AsO^+ secondary ion profiles for GaAs obtained with 3 keV O_2^+ without (a) and with (b) sample rotation, (c) rotation was begun at ~400 nm. Rotation rate was 0.57 rpm [71].

3.7 Summary

In this section, we have shown the topography effect on the ion yield. The ripple formation during ion sputtering (e.g. oxygen and cesium) is mainly associated with the sputtering conditions. The two most important factors are the primary beam energy and the incidence angle; the growth of ripples is dependent on the sputtered depth. The range of impact angles responsible for the formation of ripples was reported to be limited to impact angles from 32° to 58° [8]. The sample rotation technique has also shown a promising way to eliminate the surface topography effect.

For this project, a specially grown test structure, AlGaAs/GaAs will be used to measure the ion mixing and roughness induced by the primary beam sputtering at different energy and angles. We will investigate the effectiveness of sample rotation to minimise the ion mixing and roughness.

3.8 Conclusions

In this chapter, we have shown some methods that have been used to enhance the ion yield in the literature. We have shown the primary ion source effect on the ion yield. Oxygen and cesium are the two most popular ion sources used for ion yield enhancement. Polyatomic ion source is often used in the ION-TOF system, but the question is that the increase in the signal intensity (or ion yield) is due to the higher sputtering efficiency or the increased ionisation probability. We have reported how the ion yield varied with the primary beam energy and the incident angle. The change in the ion yield was mainly due to be the surface concentration of the oxygen or cesium. The surface topography was induced during sputtering the reactive ion beam, the incident angle and beam energy again was thought to be the main factors of the ripple formation. However, the beam induced roughness can be avoided by using certain experimental conditions and techniques.

The question is now, what remains to be done? As far as this project is concerned, oxygen has been widely used but, low energy (particularly sub-keV) oxygen implantation has not been used so often ^[15, 72] to create the altered layer prior to SIMS analysis. It is worth investigating the ion yield enhancements of low energy oxygen pre-dosing. The benefit of using low energy oxygen implantation is to minimise the damage introduced into the sample during yield enhancement strategies. At a fixed energy, the degree of the ion yield enhancements is dependent on the implant dose, a systematic study of the ion yield enhancements using different doses thus has been carried out. Nitrogen has been commonly (especially in our SIMS lab) used to measure the oxygen depth profile, it would be interesting to use nitrogen ion yield enhancement studies and compare that with oxygen beam.

As mentioned, the ion yield can vary with different instruments, some methods used in the literature have been adapted to this project in order to see the outcome on the FIB SIMS located at Imperial College.

We have shown many examples of signal intensity enhancements in TOF SIMS using polyatomic ions. However, the methods of ion implantation (O₂, N₂) to improve the 'real' ion yield in TOF SIMS have not been reported in the literature. This project fills the gap. Furthermore, the results obtained from the two different techniques give us an opportunity to investigate the reliability and performance of ION-TOF IV and FIB SIMS. Oxygen flooding enhances the ion yield, but a direct comparison between

the ion implantation and oxygen flooding have not seen in the literature, this is also one of the aims of this project.

3.9 Reference

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Chapter Four

4. Experimental Techniques

4.1 The Atomika 6500

The Atomika 6500 used for this project is a quadrupole based SIMS instrument. The Atomika 6500 consists of three parts: a Floating Low Energy Ion Gun 5 (FLIG5), a main chamber and a secondary ion detection system.

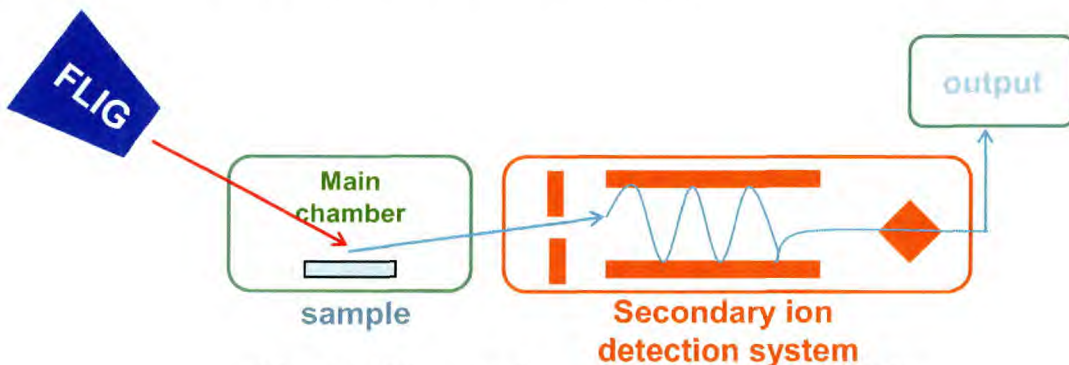


Figure 4.1 Shows a schematic view of the Atomika 6500.

4.1.1 The Floating Low Energy Ion Gun

For SIMS applications three types of ion sources are mostly used: gas phase sources, surface ionisation sources and liquid metal field emission ion sources (LMIS). A cold cathode duoplasmatron ion source is fitted on the primary FLIG column of the Atomika 6500. The source features a high brightness and ion intensity, a relatively narrow energy spread, long lifetime and is capable of operating with reactive (O_2^+) and inert (Ar^+) gases without a hot filament.

There are three different ion sources fitted in the Atomika 6500 at Imperial College SIMS lab, namely: $^{16/18}O_2^+$, $^{14}N_2^+$, $^{40}Ar^+$. The selection of an ion source depends on the specific application. For the purpose of this project, a good ion source should be of high intensity, high beam quality, high ionization efficiency, reliable and with a long source lifetime. The reactive ion sources such as oxygen provide high secondary ion yields and good sensitivity. Noble gas probes (i.e. argon) may also be used for profiling. But, the ion yield is much lower than with an oxygen source.

High energy ion bombardment results in a significantly broader atomic mixing layer in the surface region which imposes an absolute limit on depth resolution. At low energy bombardment (e.g. 250 eV), space charge effects and aberrations of the

wide beam seriously limit the final intensity of the probe and impair probe shape. A floating ion gun is designed to produce low energy ion beams with high beam currents. It has a floating column floated to a negative potential and transports primary ions at relatively high energy between the extraction region and the final lens. At the final lens, the beam is decelerated to the desired impact energy. Thus, it can deliver a probe of high current density at beam energies as low as 200 eV. The primary beam energies available on this machine range from 200 eV to 5 keV. There are six beam apertures; the beam diameter can be focused from 0.8 mm down to 0.1 mm. The beam current can be varied from 1 nA up to 10 μ A. This low energy performance makes the FLIG 5 a powerful tool for high resolution depth profiling, figure 4.2. The FLIG 5 also operates conventionally (non-floating) at higher energy ^[1].

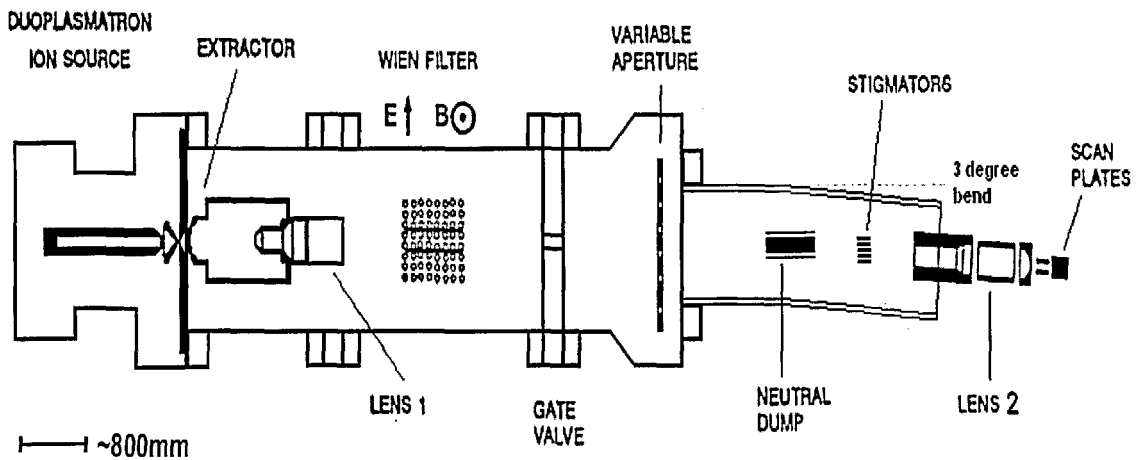


Figure 4.2 Schematic of the Floating Ion Gun ^[2].

The first part is the duoplasmatron source, where a magnetic field is applied to create a helical path to allow the emitted electrons from the cathode to pass through and reach the anode. Gas molecules are ionised in the anode. The gas pressure is maintained at 10^{-2} mbar. Those ions are then extracted from the source plasma through a narrow aperture (diameter ~ 0.5 mm) into the grounded acceleration electrode. The extractor and lens 1 are mounted at the opposite ends of the duoplasmatron ion source, and prior to the aperture is a Wien filter and the first alignment unit. Ions are extracted and accelerated at high energy between the anode of the ion source and extraction electrode. The beam is focused then by the extraction fields at lens 1. The Wien filter then removes any impurity masses by the application of a magnet and an electric field. A gate valve is positioned after the Wien filter to isolate the lower column from the extractor and source. This is essential for source

replacement or maintenance. The ion beam is now passing through an adjustable aperture mechanism with six apertures which is used to adjust the beam current and the beam spot size. The lower section of the gun is designed with a set of orthogonal electrostatic plates (neutral dump) which bends the ion beam around 3° . This eliminates any neutral particles from the beam. After the neutral dump is an octopole stigmator, designed to remove any beam astigmatism before passing through the final lens. Now, the ions are decelerated and focused onto the sample by a retarding immersion lens, Lens 2. Finally, the beam passes through a high precision scan unit, which maintains a uniform ion dose across the rastered area. The isolation valve allows isolation of the upper part of the column, allowing one to keep the vacuum in the main chamber during maintenance of the source ^[2].

4.1.2 The Main Chamber

The main chamber houses the sample manipulation stage, the sample carousel, and the electron gun. When insulating samples are analysed in the SIMS, the sample surfaces will build up electrical charge during analysis. This charge can have dramatic effects on the SIMS analysis, altering the energy distribution of the secondary ions and their collection efficiency. The electron gun allows electron flooding on the analysed surface with low energy electrons. The low energy electrons will overcome the surface charge build up with a self-adjusting compensation. The stage allows rotation of the carousel about the z direction, movement in the y direction and tilting about the y axis between 0° and 90° which corresponds to effective angles of incidence of -45° and 45° as the gun is mounted at 45° to the analyser chamber. The chamber is separated from the primary sources and the load lock by gate valves ^[3].

4.1.3 The Secondary Ion Detection System

Secondary ions that are emitted from the sample are extracted into the collection apertures of the Secondary Ion Optics (SIO) and accelerated into the energy filter, shown in figure 4.3. However, when an extremely small energy bandpass is needed (e.g. H) the acceleration voltage should be decreased. An additional potential (U_{foc1}) enables the collection of ions from all angles of emission. In a quadrupole mass spectrometer mass resolution mainly depends on the number of the RF cycles that an ion experiences. The kinetic energy and energy spread of the ions should be small to allow the ions to experience more cycles. The energy filter only allows secondary ions with a fixed energy and energy spread of 0.2 to 1 eV (band pass) to be transmitted to

the quadrupole axis. A second retarding lens slows the filtered ions down to ground potential before they reach the entry aperture of the mass spectrometer. This potential (potential bias) slows down the ions in order to apply more RF cycles. The potential is, therefore, one parameter which enhances the separation between two neighbouring mass peaks. It mainly affects the left tail (lower mass side) of the mass peak. If this potential is varied, all other secondary ion voltages have to be adjusted as well. This is because a variation that will directly affect the ion energy at the target is needed for the highest transmission. The width of a mass peak can be approximated by^[3]:

$$\text{Width} = \Delta M + (M * \text{resolution}) \quad (1)$$

This equation shows that the resolution parameter mainly affects the width at high masses, as ΔM controls the width at lower masses. In standard SIMS analysis, the width is usually adjusted to about 0.5 amu. The detector is operated in a pulse counting mode by converting secondary ion pulses into amplified electron pulses by the means of an electron multiplier.

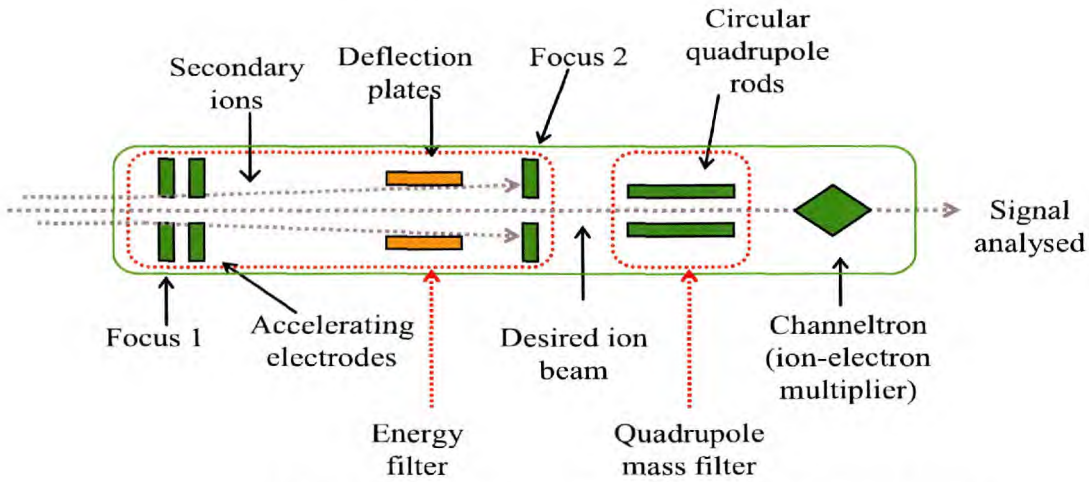


Figure 4.3 Shows a layout of secondary ion detection system.

4.1.4 Secondary Ion Optic Adjustment

The position parameter controls the directional component of the secondary ions from the plane. It deflects the parallel emission into the direction of the quadrupole axis. This parameter is set at zero. The U_{target} is a voltage that is applied at the sample to control the part of the kinetic energy distribution of secondary ions transmitted through the quadrupole (E_{filt}). When the secondary ions leave the sample surface it has a kinetic energy, E_{kin} . The relationship between E_{filt} and E_{kin} can be shown as:

$$E_{\text{filt}} = E_{\text{kin}} + e * U_{\text{target}} \quad (2)$$

Where, e is the electronic charge. As the equation shows, at a fixed E_{filt} , E_{kin} can be controlled by U_{target} . The maximum ion counts should usually be kept below 500k cps to minimise degradation of the detector. This is done by applying an offset (20 to 50 eV) from the maximum intensity in cases where an interference with molecular ions can occur. After this step, the transmission should again be improved by the position parameter and U_{foc1} (repelling voltage) to correct the position dependence of the energy filter. U_{foc1} is usually adjusted for maximum transmission. U_{foc2} is the focusing voltage used to inject the secondary ions in parallel to the quadrupole axis. U_{foc2} is set between 130 V and 170 V for optimum focusing. One should ensure that the shape of the mass peak is flat-topped and well resolved. All of the secondary ion optics parameters can be adjusted by the SIO software which is stored in the computer. The sequence and settings for optimum experimental conditions are given in the SIO default setting manual. After saving the optimised SIO conditions, a 'repeat until' loop is set to define how many cycles need to be run. This also involves defining the mass channels, frame time, polarity of secondary ion, scan type and gating mode. Signal intensity as a function of time is profiled on the computer screen.

4.1.5 Gating

In a depth profile, the total rastered area cannot be used for detection of secondary ions because of contributions from the crater walls. The probability of non-uniform bombardment of the analysis area increases as the analysis area increases. Also, the sputtering rate decreases if the primary ion density is held constant while the rastered area is increased. Therefore, depth profiles should be obtained using different rastered and detected areas until a relationship between the ion beam raster and detected area can be established to avoid crater sidewall effects^[4]. The Atomika 6500 operates in two scanning modes. In the raster scan mode, the ion beam scans in horizontal direction. The frame-time (i.e. time taken to complete a cycle) is typically of the order of a few seconds. In the spiral scan mode, the ion beam spirals into the centre of the crater and back out again. Both scan modes produce square crater. The secondary ions are only being counted from a certain area; ions from the crater edge will be eliminated. This is done by electronic gating. The most common use of gating is to reduce the crater edge effect. Figure 4.4 shows a primary ion beam is sputtered at the sample surface and the materials are being removed, whilst a flat crater bottom is being formed and the secondary ions are only collected from the analysed area.

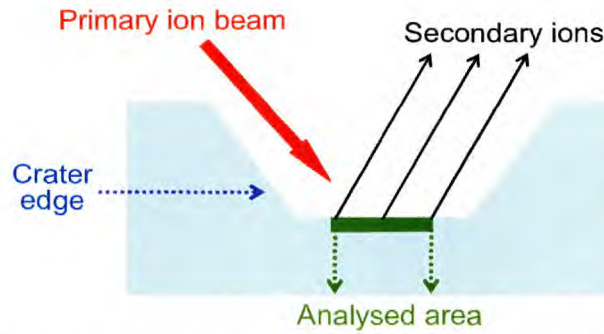


Figure 4.4a) A primary beam removes the sample materials to form a flat-bottomed crater. The secondary ions are only collected from the centre of the crater.

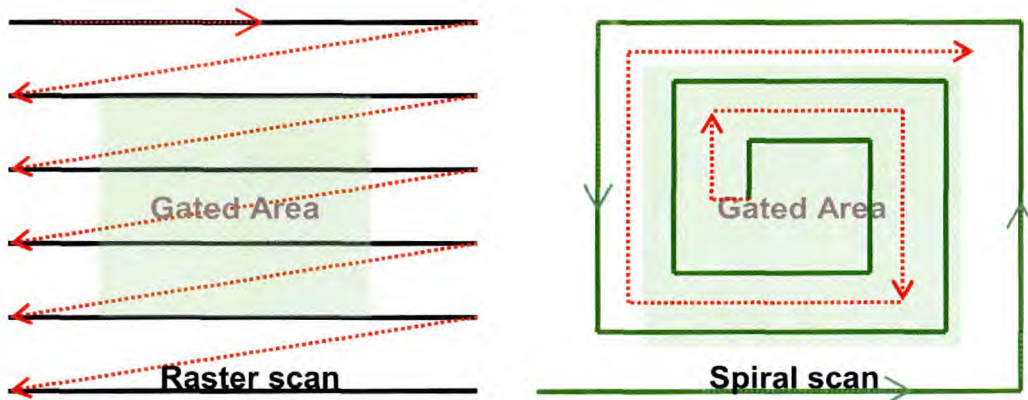


Figure 4.4b) Scan modes available on the Atomika 6500: the raster scan mode and spiral scan mode. The spiral scan mode in practice, is not suitable for high depth resolution and insulator work^[5]. The raster scan mode was used throughout this project.

There are two gating options available on the Atomika 6500: chequerboard gating with spiral scans and concentric gating with raster scans. In the chequerboard gating mode the central 25% of the raster area is divided into a square array of 16*16 sub-gates. In concentric gating mode the square area is sub-divided into eight square sub-gates.

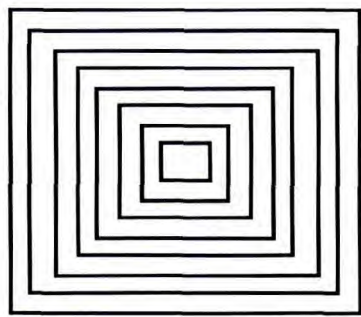


Figure 4.5a) Concentric

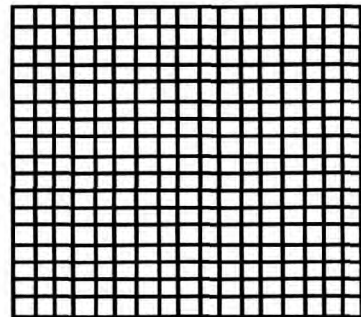


Figure 4.5b) Chequerboard

The main advantage of concentric gating is that the crater edge affects are minimised and the effects of crater base topography can be removed to some extent,

but it can not remove the effects of any topography that is located at the centre. With spiral scanning the linear gate sizes range from 10% to 80%. The main advantage of this system is that it allows large area selection, and the effect of small particles on the profile can be removed by de-selecting the sub-gates the particle is located on. The disadvantage is that the large quantity of data must be stored for each frame, this is time consuming.

4.2 ION-TOF IV

The ION-TOF IV is a Time Of Flight SIMS instrument. The TOF SIMS detects masses from sputtering events falling within the same time period. This increases the efficiency of the instrument with respect to the amount of material consumed if more than one mass is of interest. The high transmission of the TOF is a great advantage over other SIMS instrument. The TOF has parallel collection across 100s or 1000s of data, but its injection must be pulsed, typically with a width of a few nanoseconds and a repetition rate of microseconds. The short pulse length of the primary ion beam results in very precisely defined and short pulse lengths of the secondary ion pulses. The mass resolution is determined by the primary pulse length, especially at low and medium mass range. That is, the pulse length at the sample introduces variations of the starting time, long pulse length results imperfect compensation of the flight time dispersion due to the initial kinetic energy distribution of the secondary ions. When an insulator is being analysed, sample charging is most likely to occur, but with a pulsed electron beam directed onto the sample surface, the charging effect can be avoid. The ION-TOF IV consists of an analysis chamber, a TOF mass analyser, detectors and a computer.

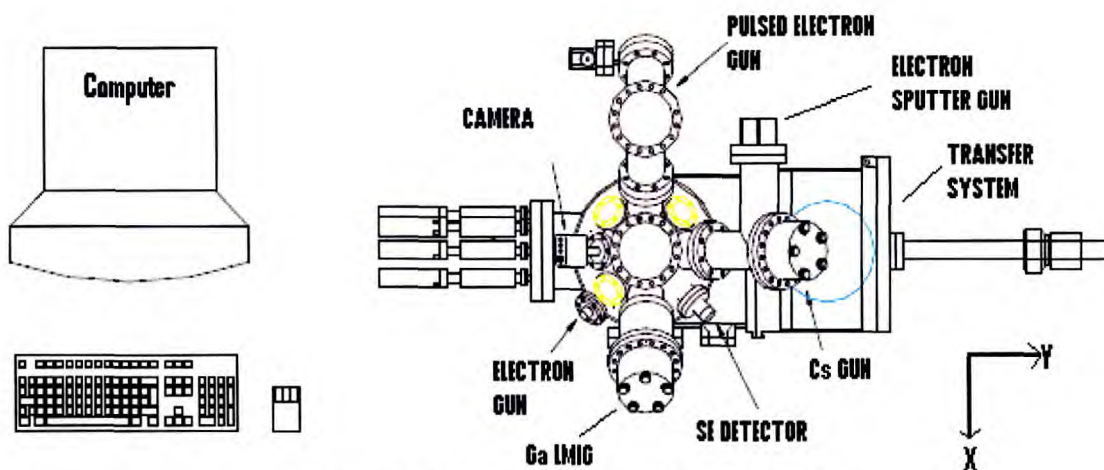


Figure 4.6 Schematic view of ION-TOF IV ^[6].

4.2.1 Analysis Chamber

The sample is at ground potential, the sample stage has 5 axis movements: X, Y, Z, Rotation and Tilt. The rotation is extremely useful for non-flat surface samples and allows the analysis of all the surface of a 100x80 mm² sample holder or the whole 200 mm diameter sample. The tilt option allows the sample to be tilted from -15° (toward rear of the instrument) to +45° (to come normal to the Gallium gun at front side, and grazing to sputter gun). The sample is transferred into the sample chamber through a transfer port. The sample chamber pressure will be pumped up to $\sim 1 \times 10^{-6}$ mbar for the sample to be able to transfer into the analysis chamber. The required Ar gas pressure for analysis is $\sim 2 \times 10^{-5}$ mbar. A secondary electron detector is also attached to the analysis chamber. There are two video cameras mounted to the analysis chamber. The first camera gives a macro view of the target region including ion optics and sample holder. The second camera is used for micro observation of the analysed area. The ION-TOF IV has a dual beam system which works in a such way that a sputtering beam with a high flux density and a long pulse length is interleaved with an analysis beam with a dose per cycle in the static SIMS range and a short pulse length [7]. The pulsed analysis Ga gun can be separated into four different units: liquid metal ion source (LMIS), blander/chopper, buncher and primary focusing unit. The schematic of the pulsed Ga primary ion gun (3-lens gun) is shown in figure 4.7.

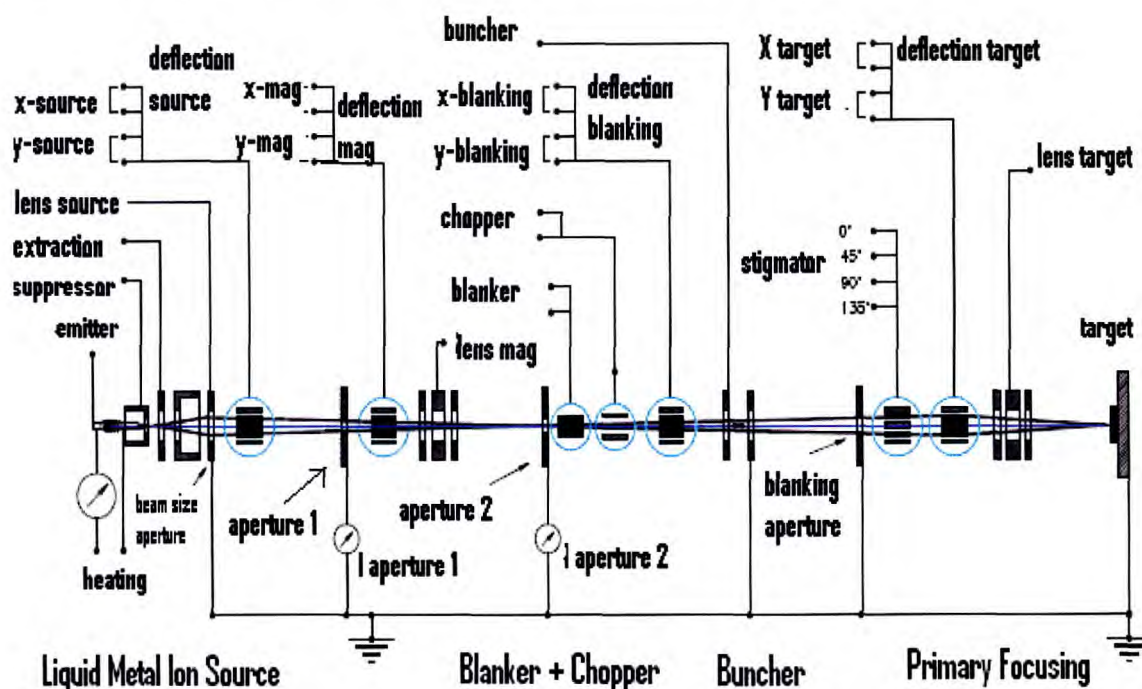


Figure 4.7 Schematic view of 3-lens gun [6].

The Ga LMIS used in this gun is isotopically enriched and consists nearly exclusively of the ^{69}Ga isotope. The potential of the emitter determines the total energy of the primary ions. The corresponding voltage which supplies the emitter is called 'ion energy' and can be varied between 0 and 25 keV (the energy used in the project was 25 keV throughout). For a stable operation of the LMIS, the LMIS must be operated under an ultra-high vacuum of 10^{-7} mbar or better. The emitter is also heated by feeding a well regulated current through the heating coil to maintain the cleanness of the emitter. The emitter is surrounded by a suppressor electrode which shields the Ga reservoir from the strong electric field. The voltage on the suppressor is used for a fine tuning of the emission current. The extraction electrode is located in front of the tip to produce an electric field at the tip. Once the extraction, that is the difference between the potential of the emitter and that of the extraction electrode, is achieved in the order of 10 keV the emission is started. The emission current is controlled by the extraction voltage, and a typical emission current used is between 1.5-2.5 pA. The extracted beam is focused by two lenses, the 'lens source' and the 'lens target'. The angular acceptance of the ion optical column is defined by the beam size aperture (aperture 1) located at the exit point of the 'lens source'. The beam is then centred on the middle of aperture 2 by rastering the 'x source' and 'y source' voltage. The Ga beam is pulsed by the Sinus blanker ('blanker') or 'chopper'. The length of the ion pulses can be adjusted from 1.5 to 20 ns with submicron spot sizes. The 'chopper' is used for the generation of long ion pulses from 20 ns to some 100 ns when the Sinus blanker is off. The electrodynamic bunching system (buncher) is used to compress the ion packets generated by the 'blanker' and 'chopper'. A set of deflection plates called 'x blanking' and 'y blanking' used to align the beam to the centre of the blanking aperture. These deflection plates are used to optimize the current on the target after the adjustment of deflection ion source. The position of the beam on the target is controlled by the raster plates 'x target' and 'y target'. Astigmatism of the ion beam (in a lens an entering beam is bent in proportion to its distance from the lens axis. Astigmatism occurs the component of the beam velocity in the direction of the magnetic field is not affected) can be corrected by a stigmator located between the blanking aperture and the 'lens target'. The setup of the low energy pulsed sputter gun (Ar, Cs and electron impact sputter gun) is very similar to the Ga analysis gun [6].

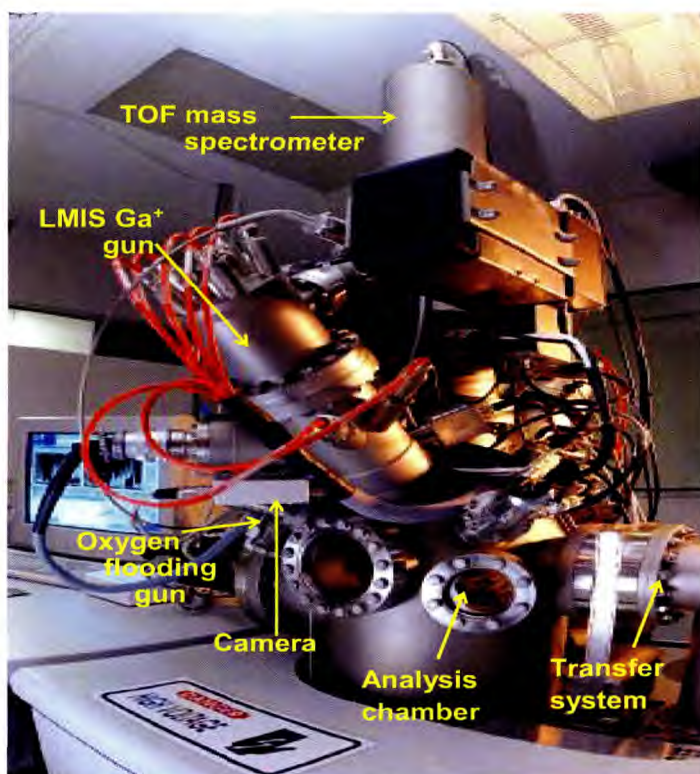


Figure 4.8 shows some of the main components of the ION-TOF IV.

4.2.2 TOF Analyser and Detector

The extractor generates an electric field to accelerate the secondary ions to a given potential. The potential of this electrode is called ‘energy’ since it determines the energy of the secondary ions. The travel time of ions to the detector will only depend on their masses. The kinetic energy, KE, of ion is $\frac{1}{2}mv^2$, the velocity v is inversely proportional to mass, the drift time t is L/v , where L is the drift tube length. The lighter ions reach the detector first. The lens (Einzel lens) focuses the beam onto the detector. The deflection analyser is used to align the beam. The ion mirror (reflector) acts as an energy analyser in the flight tube to compensate for the initial energy spread. As a result, all ions of the same mass will reach the detector at the same time. The post-acceleration optics improves the ion conversion probability by further accelerating the ions with the post-acceleration voltage. The secondary ions finally reach the detector. The detection system consists of a channelplate for ion to electron conversion, a scintillator for electron to photon conversion, and a photomultiplier outside the vacuum. Figure 4.9 shows the schematic of the mass analyser.

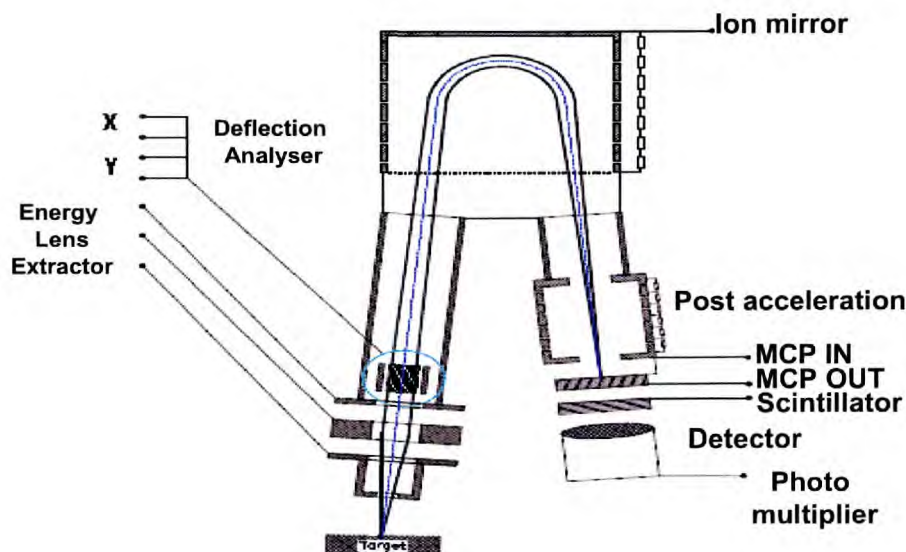


Figure 4.9 Schematic of the TOF analyser^[6].

TOF SIMS instruments are also equipped with a powerful computer and software system for system control and analysis. Digital gating is used in the ION-TOF IV system. The digital gating uses a scanned probe. Either the ion counting system is inhibited when the beam is scanning the crater walls or the whole scan is collected as an image and a depth profile reconstructed from those parts of the image corresponding to the bottom of the crater^[7]. Figure 4.10 shows one of the key features of the TOF SIMS software, the selection of areas of interest. Every molecule detected by the system can be stored by the computer as a function of the mass and its point of origin. This allows the user to obtain chemical maps or a reconstructed depth profile of specific regions not previously defined after the original data has been collected.

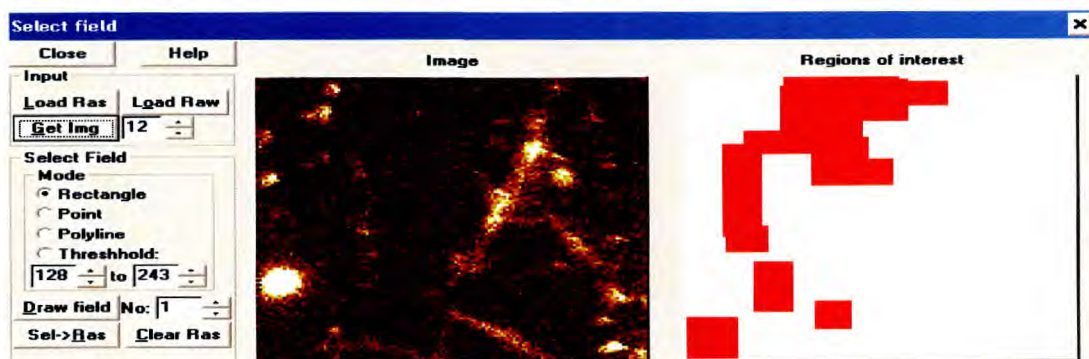


Figure 4.10 The select field window^[6].

There are three major operational modes of the pulsed Ga gun: the bunched mode, the burst mode and the collimated mode. The collimated mode probably offers the best spatial resolution by further narrowing the beam at the apertures, but this is at

a serious cost to the mass resolution. The burst mode offers high mass resolution and high lateral resolution. The general idea of burst mode is to use the time between the unit masses. When working at high mass resolution, the spectral lines, particularly in the lower mass range (<100 amu), are widely spaced, and up to ten repetitions of the primary pulse can be made during the analysis cycle without spectral interference. Figure 4.11 shows an example of how burst mode works.

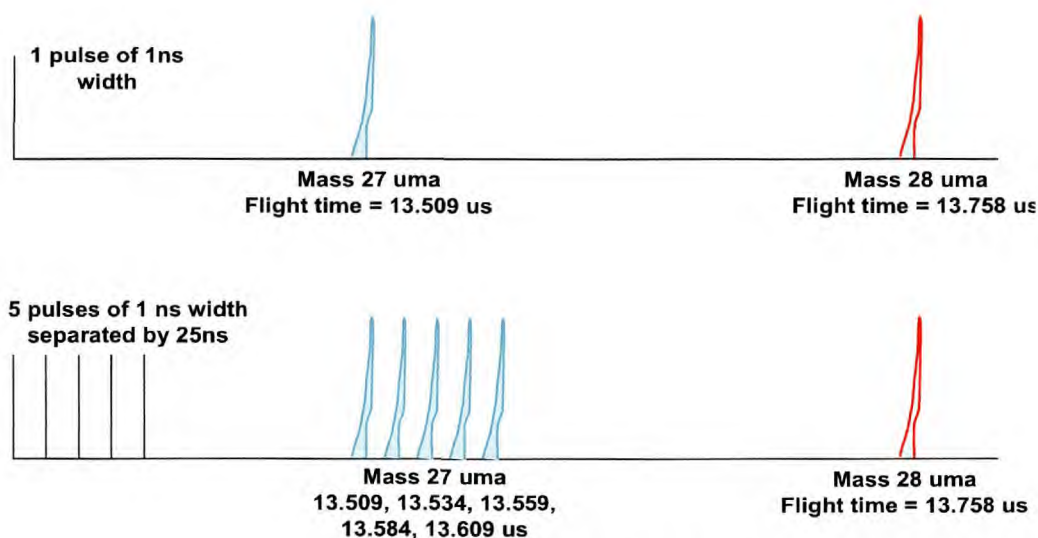


Figure 4.11 The basic idea of burst mode.

The basic principle of a bunching device is that the electrodynamic bunching creates compressed ion packets by accelerating the ions within the packets to different energies. With the correct amplitude of the HV pulse ('BUNCHER') the ions in the rear of the ion packet will catch up to the ones in the front at the moment the packet reaches the target. High mass resolution can be attained without concurrent loss of counts, but at a cost of spatial resolution. The benefit of retrospective analysis is also its curse. Every pixel of an image produced by TOF SIMS also contains a full mass spectrum for that point. Thus, it may take hours, days or weeks to fully analyze a single data set. Consequently, it is extremely important to have a very clear purpose in collecting TOF SIMS data, and to focus on analyzing and interpreting the data that are specifically related to the question at hand.

4.2.3 ION-TOF IV Settings

The sample wafer is shown in figure 4.12. There are 17 sample positions available on the sample wafer. Once the sample chamber pressure reaches 1×10^{-6} mbar, the sample is ready to be transferred in to the analysis chamber, the chamber pressure required to achieve optimum experimental condition is 2×10^{-5} mbar. The

coordinates show the position of the analysed area. To measure the current of the analysis gun (Ga^+) and the sputter gun (Ar^+), the beam is driven onto the letter 'C' (cup) of the sample wafer. The 'source emission' which is the total current of positive Ga ions extracted from the emitter, should be around $1.5 \mu\text{A}$ and the 'suppressor' and 'extractor' is at the middle of the bar, otherwise, the Ga reservoir needs to be heated at a current of 3.1 A for about 60 seconds. The 'I Gun' is the ion current measured on 'aperture 2' (close to zero). The 'I Target' can be selected by the list box, it should be between 10-20% of the selected current (1 pA of Ga current was used throughout this project). Other settings are normally already fixed and optimised.

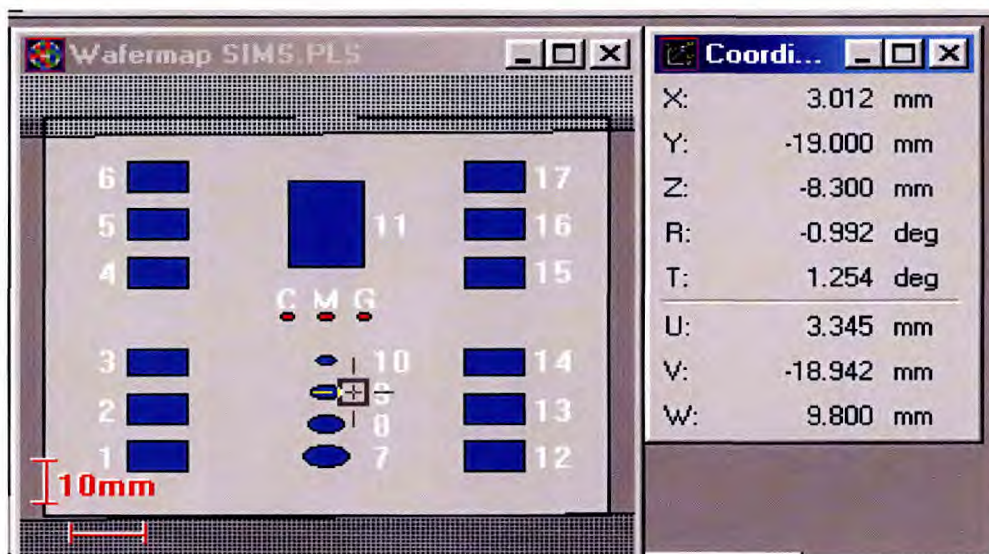


Figure 4.12 Schematic of sample holder (screen shot).

The third step is to align the beam to apertures, 'x source' is chosen as abscissa and I AP1 (figure 4.14) as ordinate, now, the 'x deflection' plates of the source are swepted, so that the beam is scanned over aperture 1. Adjust the parameters 'lens source' and 'y source' for maximum width of the profile and maximum slope of the flanks. Repeat the procedure with reversed roles for 'x source' and 'y source' for final adjustment. The 'lens mag', 'x mag' and 'y mag' also needs to be optimised. Figure 4.14 shows the oscilloscope for beam alignment on aperture 1 and 2 [6]. To focus the Ga beam, the beam is sputtering at static mode (i.e. continuous beam, chopper and blanker are off), use 'lens target' and 'lens target fine' to set the lens voltage for optimum focusing, 'x stigmator' and 'y stigmator' are used to compensate the astigmatism if astigmatism is observed in the secondary electron image. Figure 4.13 shows the hardcopy of the Ga gun dialog box of "Source" and "Gun".

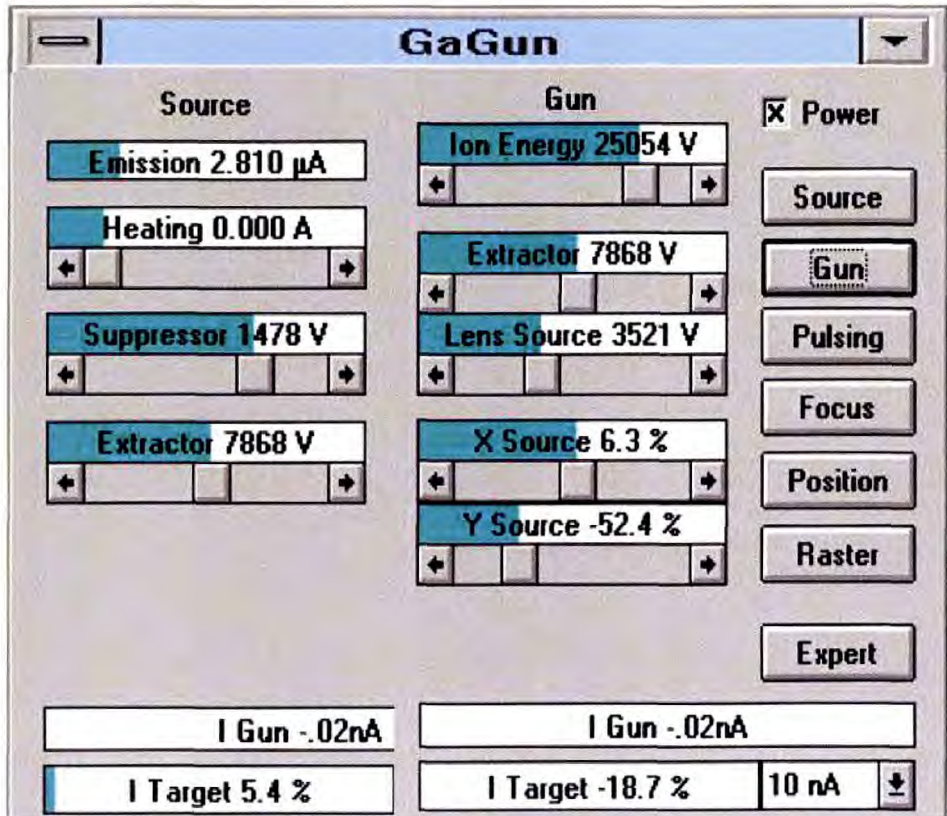


Figure 4.13 Screen shot of the Ga Gun control menu.

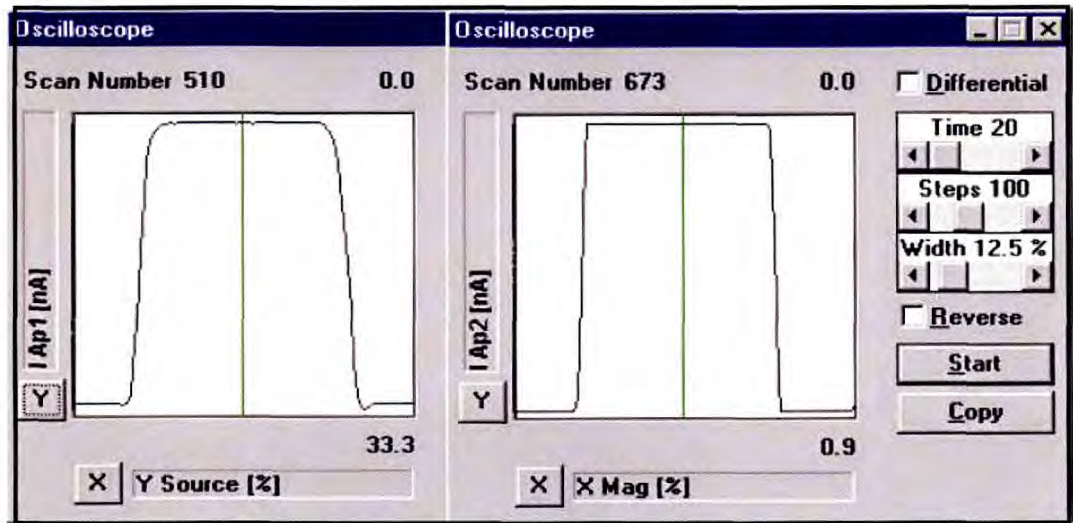


Figure 4.14 Using the oscilloscope for beam alignment on apertures. The scroll bars Time and Steps are used to adjust the time duration for a single sweep and the number of sample points included. The voltage range of the sweep is adjusted by the scroll bar Width.

The beam is now directed onto the letter 'G' (grid A) of the sample wafer. The joystick is used to move the Grid A in the centre of the macro/micro view window (camera 1/2). The sputter gun (or analysis gun) is now rastered on the sample and the secondary electron image SED (or secondary ion image) will appear. The 'x target'

and 'y target' (see figure 4.14) options allow users to centre the image. The eucentric height of the sample can be achieved by using the Z Adjust of the joystick. Figure 4.15 shows the secondary electron and ion image of grid A. As a result, the SED image should be identical to the image shown in micro view window.

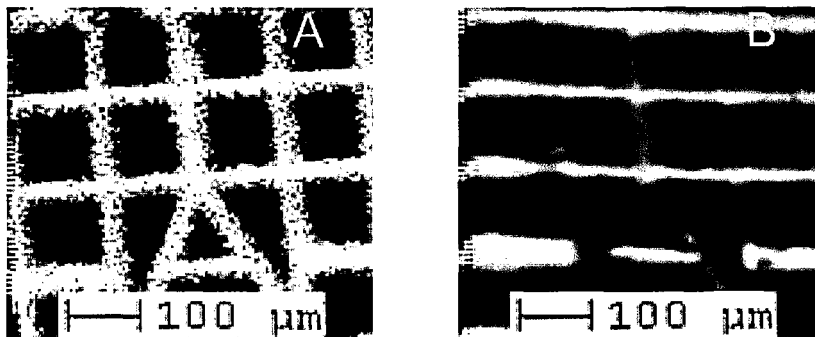


Figure 4.15 a) Secondary ion image, b) Secondary electron image.

A quick scan on the area of interest is required to obtain the mass spectrum for mass calibration. A peak list which includes the ions that need to be depth profiled or ion imaged will be added after the mass calibration. The total sputtered depth is measured by the Zygo, white light interferometer.

4.3 The FEI FIB 200 SIMS

A primary ion source of Ga^+ is used in this system. A potential on the electrode attracts secondary ions towards the detector. An attached quadrupole mass spectrometer allows SIMS analysis. The Continuous Dynode Electron Multiplier (CDEM or CDM) detector can detect both secondary electrons and ions which are emitted from the sample surface. The detector amplifies the individual ions into pulses of current that are then electronically counted by conventional counter electronics. The CDM-I mode is chosen for secondary ion detection and the CDM-E for collecting secondary electrons. A schematic view of the FIB 200 is shown in figure 4.16. The ion beam can be rastered at either 7 or 30 keV in the beam current range 1 pA – 20 nA. The beam spot size increases with increasing beam currents and can be estimated from an image of the erosion spots, shown in figure 4.17 ^[8]. As can be seen, the larger beam current creates larger damaged area. In the main chamber a 50x50 mm² stage (tilt eucentric) and holder for 8" wafers is available. The stage moves along the x, y and z-axis and the z-axis can tilt between 0 and 55°. Iodine and platinum are available for enhanced etch and deposition. A charge neutraliser is attached to reduce sample charging. A video camera is installed in the main chamber monitoring the sample.

One of the disadvantages of using Ga^+ is that its ionisation probabilities are low. Thus, the sensitivity is not as good as that found in conventional SIMS instruments. The optimisation of useful ions yields can improve the sensitivity of the FIB SIMS.

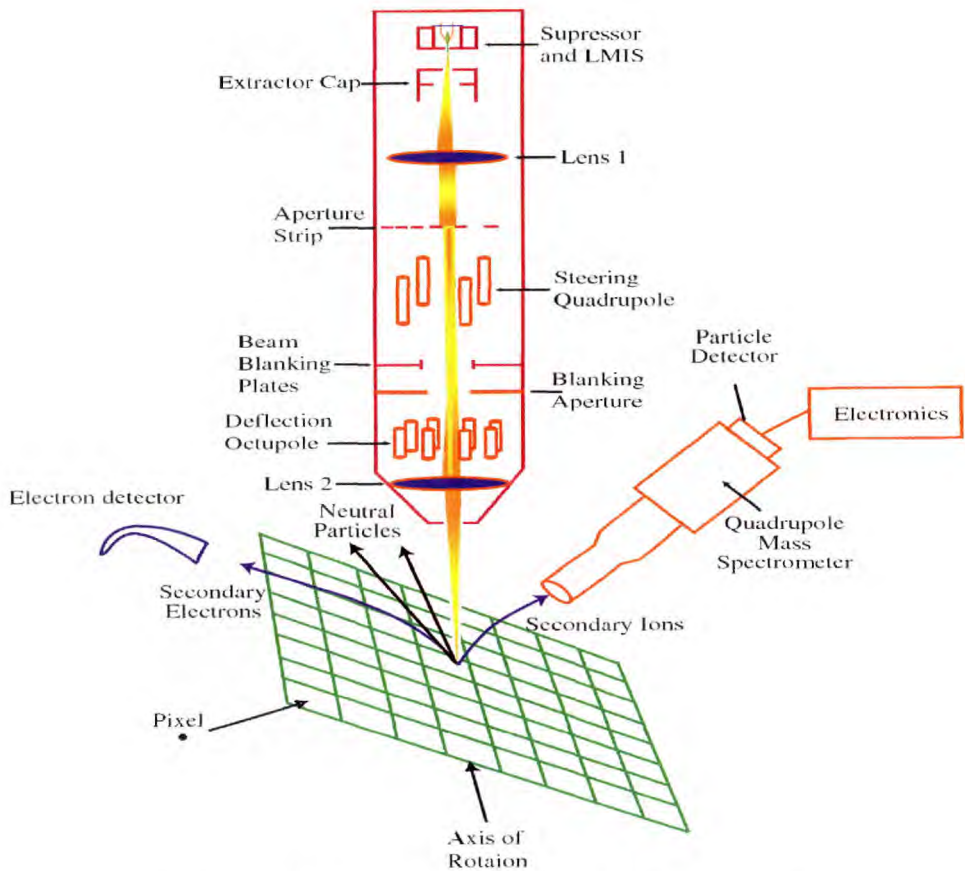


Figure 4.16 A schematic view of a FIB 200 system ^[9].

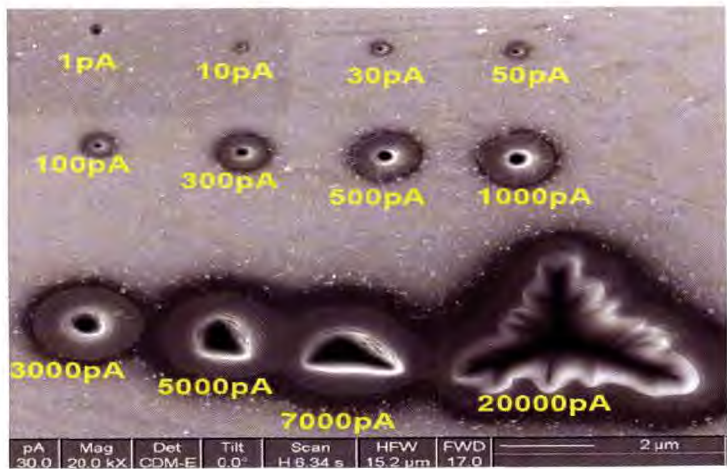


Figure 4.17 Shows the beam spot size with different beam current. The spot erosions take less than 10mins to achieve ^[10].

The LMIS Ga^+ beam is well known for its stability and long lifetime. During normal operation, the LMIS may require heating every 40-100 hours to re-supply the

Ga to the emitting region of the source. Improper heating results lead to poor performance and instability. A stable emission current is required to maintain the LMIS stability. The LMIS lifetime also partially depends on the emission current. This parameter is usually set at 2.2 μA . One should make sure that the ion column pressure of 10^{-7} mbar and chamber pressure of 10^{-6} mbar is achieved before starting the analysis. Once the system is pumped down to the required pressure, a detection mode is selected. In a CDM-E mode with the detector at a high positive potential only secondary electrons are detected. In a CDM-I mode the detector is maintained at a high negative potential to detect the secondary ions. In both cases, the contrast control needs to be adjusted to achieve an image of the surface for a range of values of the electrode potential ^[10]. To locate the feature of interest, the stage control can navigate with 5 axes: X, Y, Z, R (rotate) and T (tilt). Low beam current (1-1000 pA) should be used to find the features of interest to ensure less damage to the sample. Establishing the eucentric height (The height adjustment of the specimen) is an important part of setting up a sample for analysis. The eucentric point is where the beam focus, stage tilt axis, and the sample features of interest intersect. Therefore, when the eucentric point is achieved, no matter which direction the stage is tilted or rotated, the feature of interest remains focused and almost no image displacement occurs. Figure 4.18 shows the layout of the main chamber of the FIB 200. The Ga^+ LMIS gun is located right above the sample stage, the mass spectrometer is fitted at 45° with respect to the sample, the channeltron detector collects particles including secondary ion and electron in order to form image.

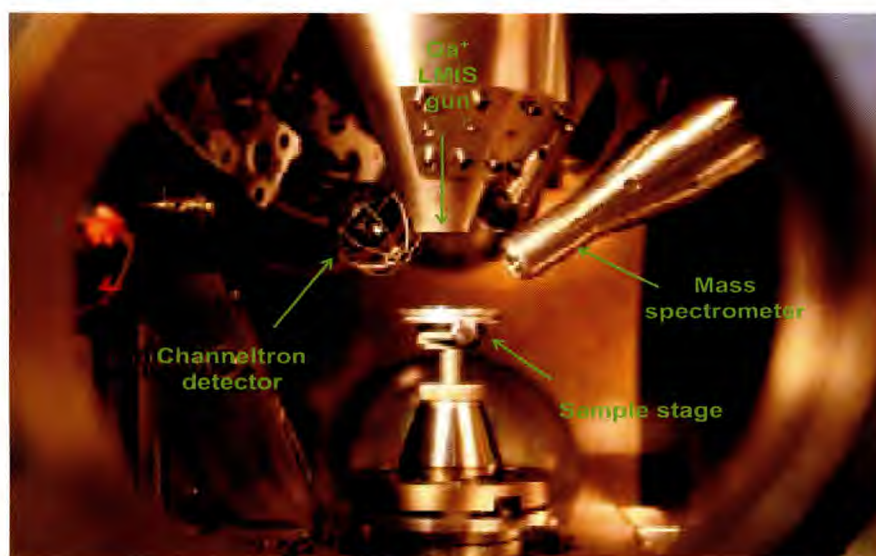


Figure 4.18 The main chamber of the FEI FIB 200.

For optimum FIB SIMS performance, it is critical that the CDEM grid bias voltage is adjusted for maximum secondary ion collection efficiency. Finally, a defined raster area is scanned with Ga^+ . Figure 4.19 shows the eucentric height adjustment process.

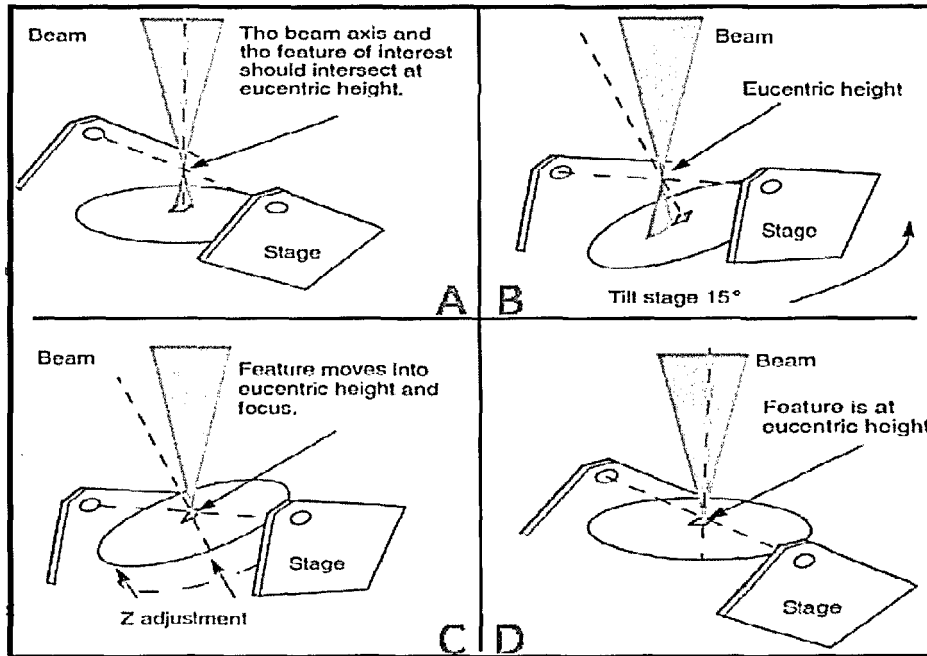


Figure 4.19 Shows a process to find the eucentric height, a) the sample is not at the eucentric height when it is below the eucentric point, b) the feature of interest is out of the beam when tilting the stage, i.e. 15° , c) adjusting the z-axis when the stage is tilted moves the feature of interest back into the field of view. It normally brings the feature into focus, provided that the beam is focused at the eucentric point, d) at the eucentric point, the feature of interest stays at the focal point of the beam^[11].

4.4 The Zygo

The Zygo is a 3D imaging surface structure analyser, i.e. a non-contact means of determining detailed surface information and accurate measurement of characteristics such as roughness using filtered white light interferometry^[12]. A schematic view of the Zygo is shown in figure 4.20. The instrument comprises two main parts. The first part is the microscope which combines optical microscopy with interferometry to provide the raw data for topological characterisation. Three objective lenses available are: 2.5X, 10X and 50X. The computer controls the measurement process and uses the raw data to form the surface maps and profiles. Scanning the measured surface by vertically moving the objective with a piezoelectric transducer, the video system detects the intensity of the phase modulated signal at each pixel of the camera. The

surface characterisation is three-dimensional. Vertical measurements along the Z-axis direction are performed using interferometry whereas lateral measurements are calculated using the pixel size for the objective being used and its associated field of view. The system has a maximum vertical resolution of 2-3 nm. The lateral resolution is objective lens dependent and ranges from 11.8 μm to 0.5 μm [13].

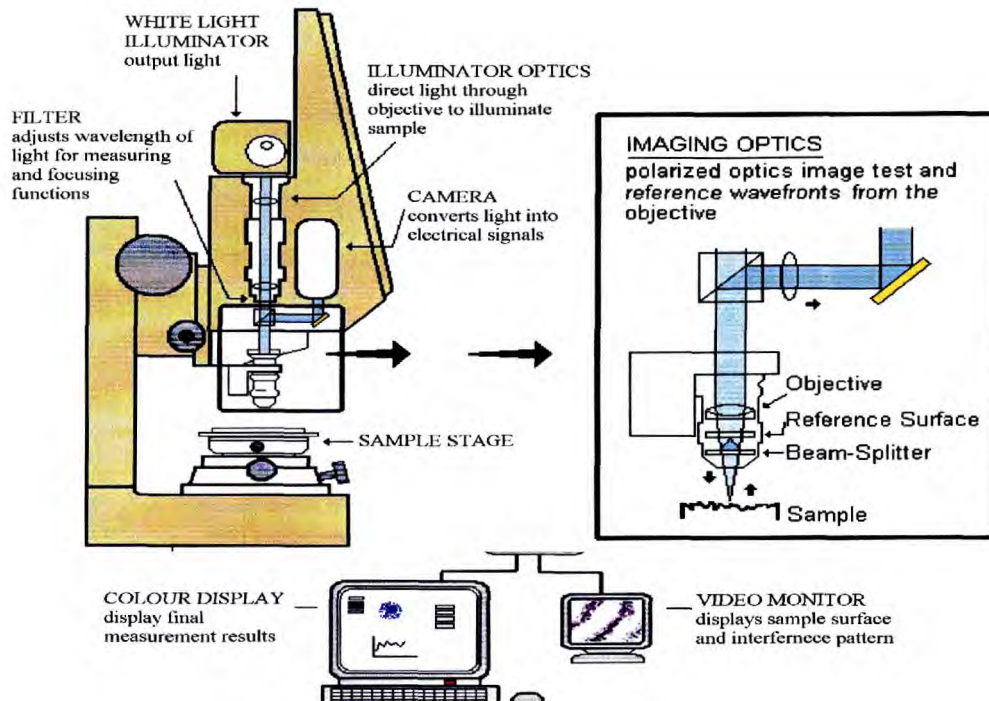


Figure 4.20 Schematic view of the Zygo [12].

For a 2.5X objective lens the field of view is about $3 \times 2 \text{ mm}^2$, for a 10X objective lens, the field of view is about $0.5 \times 0.7 \text{ mm}^2$ [12]. Figure 4.21 shows the depth measurement of a crater.

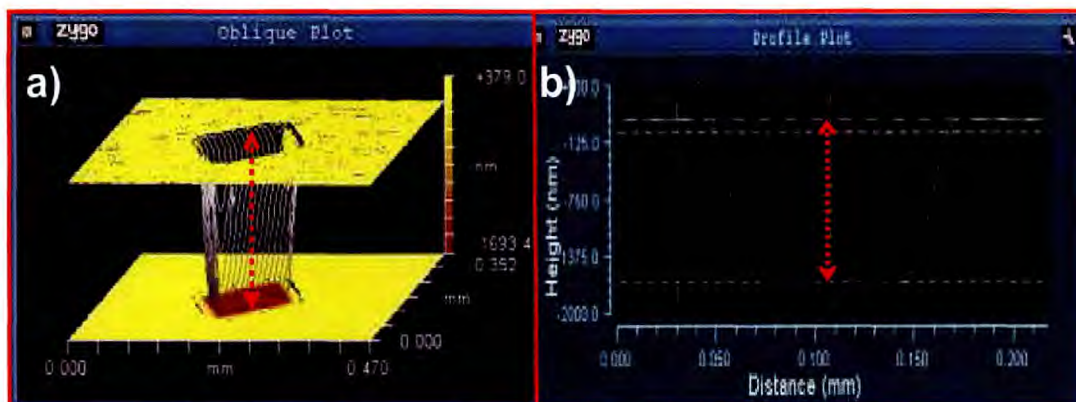


Figure 4.21a) Oblique view of the measured crater, b) the distance between the bottom of the crater and the top of the crater is measured as the total sputtered depth, shown as the red vertical line.

The Zygo has three major errors: instrumental, environmental and geometric. When an insulating sample with a gold coating is being measured the refractive index of a SIMS crater base changes and the reflected wavelength will therefore be different from the crater base of the original surface. One solution is to coat the sample with gold layer again, this will reduce the variations in the refractive index. The previous result from this lab has shown that the Zygo has a $\pm 6\%$ error ^[1].

4.5 Transmission Electron Microscopy (TEM)

TEM is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through it. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen, a fluorescent screen in most TEMs, plus a monitor, or on a layer of photographic film, or to be detected by a sensor such as a CCD camera ^[14]. To obtain a TEM image, the objective aperture is inserted in the back focal plane of the objective lens. The primary undiffracted beam passes through the aperture, creating an enlarged image of the sample in the image plane of the objective lens and the intermediate and projector lenses (the beam is focused and centred to the intermediate and projector lens), and a TEM image appears on the viewing screen, as shown in figure 4.22.

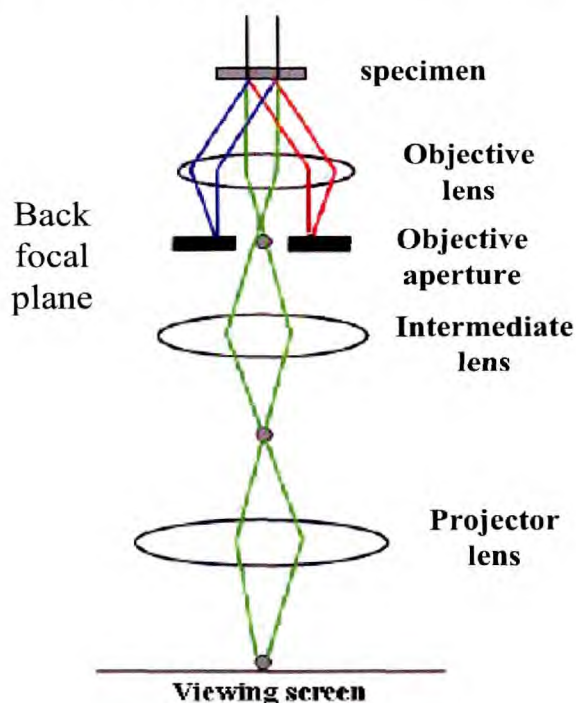


Figure 4.22 TEM image formation. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and display on the screen.

The major drawback of TEM is the extensive sample preparation needs to produce a sample thin enough to be electron transparent, which makes TEM analysis a relatively time consuming process with a low throughput of samples. The structure of the sample may also be changed during the preparation process. The Jeol 2000FX and high resolution Jeol 2010FX TEM imaging instrument was used in this project.

4.6 Experimental Procedure

Silicon wafers were cleaved into small pieces and assigned labels so that pieces could be identified during analysis. A ‘three-stage’ chemical cleaning was required to remove contaminants on the sample surface in order to obtain good experiment results. This involves submerging the sample in acetone (5 mins), ethanol (5mins) and finally isopropanol (2mins), followed by a de-ionised (DI) water rinse to wash off the isopropanol leaving the surface “extremely” clean. A nitrogen gun was used to dry the sample. For insulating samples used in the experiments (i.e. Silica), thin gold layers were coated on the sample surface to make it conductive. This was done by sputter coating in an argon process gas environment coater. The Lacomit varnish was firstly used to cover half of the sample to avoid gold coating, shown in figure 4.23. A three minutes pump hold time was used to achieve a more uniform gold layer. The final thickness of the gold layer was about 20 nm.

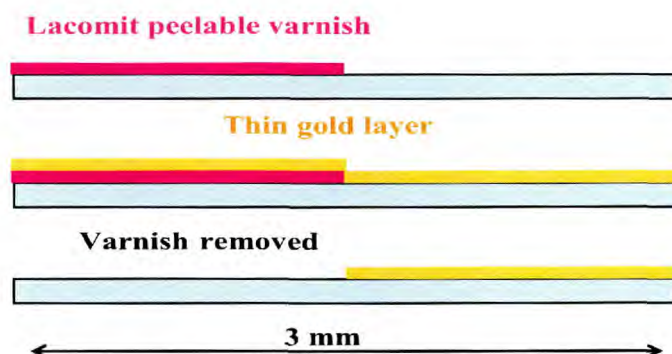


Figure 4.23 Lacomit varnish was used to cover half of the sample surface followed by a thin gold layer coating, finally the varnish was peeled off from the sample surface.

Once the samples were mounted on the sample carousel, they were placed on the transfer port in a load lock transit chamber to be transferred to the analysis chamber. The load lock’s vacuum was isolated from the analysis chamber via a gate valve and thus can be brought to atmospheric pressure without affecting the pressure in the analysis chamber. The operational pressure in the analysis should be maintained below 2.6×10^{-8} mbar. There are six beam energies available on the FLIG5, 250 eV to

5 keV. The beam was then directed onto the screw hole on the sample carousel. A series of objective apertures can be chosen from to set the desired beam current. Small adjustments of the beam current can be made by adjusting the values of Extractor, X-align and Wien filter. After setting up the beam current, it was necessary to focus the ion beam. This was done by directing the ion beam onto one of the copper grids on the sample carousel, figure 4.24. A number of secondary ion optic (SIO) parameters need to be detected by means of the control software to gain sufficient ion counts.

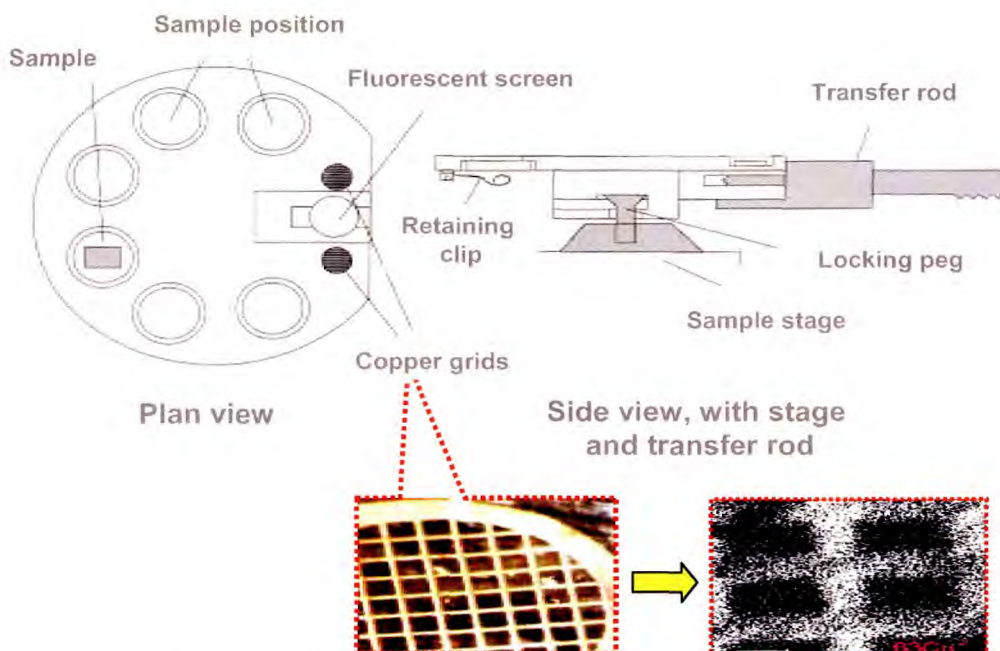


Figure 4.24 Shows a plan view of a sample carousel and a well-focused ion beam image of a copper grid generated in Atomika 6500. The sample holder is capable of holding up to six samples up to 9 mm^2 , the size of the sample carousel is about 12 cm^2 , and the copper grid spacing $\sim 200 \mu\text{m} - 500 \mu\text{m}$).

Figure 4.25 shows the experimental set-up for ion implantation in the Atomika 6500 and the analysis in the FIB SIMS and ION TOF.

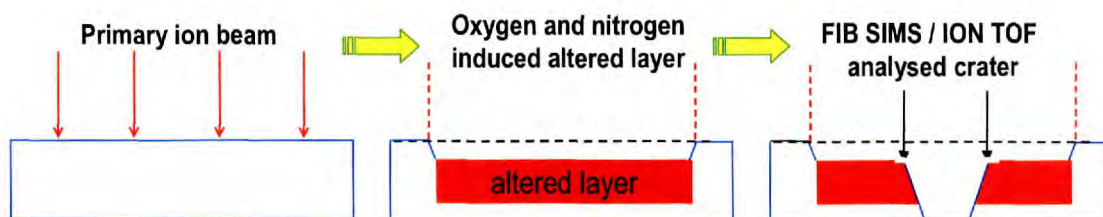


Figure 4.25 Experimental set-up. $^{16}\text{O}_2^+$ or $^{14}\text{N}_2^+$ ions were implanted into the silicon sample at various energies at normal incidence. The ion induced altered layers were then depth profiled with the FIB 200 and the ION-TOF IV.

Germanium doped silicon samples ($\text{SiGe}_{.45}$, (100)) were used for the implantation of $^{16}\text{O}_2^+$ and $^{14}\text{N}_2^+$ at various energies and doses to form altered layers and for oxygen flooding. The implantations were done at normal incidence. The SIMS analysis of the ion beam induced altered layers were performed with a FIB 200 and ION-TOF IV. The ion implantation was performed using a quadrupole based Atomika 6500 instrument with a FLIG5 gun^[1].

4.7 Reference

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Chapter Five

5. Results and Discussion - Secondary Ion Yield Enhancements

5.1 Summary

The aim of this part of the work was to systematically study ion yield enhancements in silicon dosing the silicon sample using nitrogen and oxygen beams. The ion yield enhancements were measured with a gallium primary beam on the FIB SIMS and ION-TOF IV as a function of implant energy and dose of the nitrogen and oxygen. Nitrogen has very similar properties to oxygen and is often used to measure oxygen depth profiles. However, the use of nitrogen for the positive secondary ion yield enhancements studies is little studied. So it is very interesting to know the nitrogen yield enhancement, in this context. From a scientific point of view it is interesting to compare and contrast the yield enhancement produced by two adjacent elements in the periodic table.

We used low energy oxygen and nitrogen implantation to create the altered layer prior to SIMS analysis. In particular, a sub-keV beam energy which has not been reported so often for FIB SIMS yield enhancement studies in the literature. The ion yield enhancements observed from different bombarding energy formed altered layer were compared. The ion yield and the thickness of the altered layer of oxygen and nitrogen were also compared. At a fixed energy, different oxygen and nitrogen dose was used to investigate how the ion yield enhancement varies with the implant dose.

The oxygen and nitrogen induced altered layers were also analysed in TOF SIMS. A lot of work has been done on improving the ion yield in TOF SIMS using polyatomic ions. However, the methods of prior ion implantation ($^{16}\text{O}_2$, $^{14}\text{N}_2$) for this purpose have not been reported elsewhere. It is also interesting to compare the yield enhancement on the two different techniques as both use high energy gallium beams for analysis. There are however, important experimental differences since the ION-TOF uses an inert gas ion beam for sputtering. This allowed us to study the cause of the ion yield variations from the point view of instrumental aspects.

Finally, the oxygen flooding was used to enhance the ion yield, the dependence of the ion yield enhancement on oxygen pressure was studied. A direct comparison of the ion yield enhancement was made between ion implantation and oxygen flooding.

5.2 Energy Dependence with $^{14}\text{N}_2^+$ Irradiation

$^{14}\text{N}_2^+$ ions were implanted into the silicon sample at energies of 0.5, 0.625, 2.5, 5 keV at normal incidence until steady state in Atomika 6500. The ion induced altered layers were then analysed with the FIB 200 and ION-TOF IV to compare the ion yield enhancement of different nitrogen beam energies.

The FIB 200 sputtering conditions used were: 30 keV Ga^+ energy at normal incidence, the raster area of $50 \times 50 \mu\text{m}^2$ was set within the altered layer, 300 pA beam current. The ION-TOF IV sputtering conditions were: 1 keV Ar^+ sputter beam with a raster area of $500 \times 500 \mu\text{m}^2$, 11 nA beam current, 25 keV Ga^+ analysis beam with a raster area of $400 \times 400 \mu\text{m}^2$ set within the Ar^+ sputtered area, 1.2 pA beam current. The crater depth was measured with a 3D imaging surface structure analyzer, the Zygo. The experimental conditions are tabulated in table 5.1.

Altered layer formation - Energy dependence				
Beam	Energy (keV)	Area (μm^2)	Current (nA)	Angle ($^\circ$)
Nitrogen	0.5 - 5	500×500	50	0
Layer characterisation				
FIB 200	Ga 30keV	50×50	300pA	0
ION TOF IV	Ga 25keV	400×400	1.2pA	45
	Ar 1keV	500×500	11	45

Table 5.1 Experimental conditions used for nitrogen induced altered layer formation in Atomika 6500 and layer characterisation in the FIB 200 and the ION-TOF IV.

5.2.1 Layer Characterisation with FIB SIMS

The depth profile of $^{28}\text{Si}^+$ was stopped when the steady state substrate was reached. It was found that the nitride was removed about 1.6 times slower than the silicon substrate by Ga^+ beam. The depth scale of the profiles was subsequently corrected by shifting the nitride region from the surface to the 50% drop-off point at the interface towards the surface by a factor of 1.6. Figure 5.1 shows that the $^{28}\text{Si}^+$ signals remained steady and flat before dropping off suggesting that silicon nitride layers were fully formed at all the nitrogen implant energies used. Thus, the ion yield enhancements remained constant throughout the altered layer. The peak intensity of each profile was almost the same. Native oxide layer (no $^{14}\text{N}_2^+$ implant) produced a much shallower depth profile with a lower intensity level than those with prior nitrogen implantation. The ion mixing effect was clearly demonstrated in the native

oxide layer depth profile as the signal intensity decreased slowly from a sputter depth of 5 nm to 20 nm. The thickness of the altered layers increased with increasing primary beam energy. The interface between the nitride surface layer and the silicon substrate was assigned to the 50% drop-off point in the $^{28}\text{Si}^+$ intensity, and the depth from the surface to this point was also estimated as the thickness of the altered layer. The thickness of beam induced altered layer was also defined as the ion yield enhancement depth.

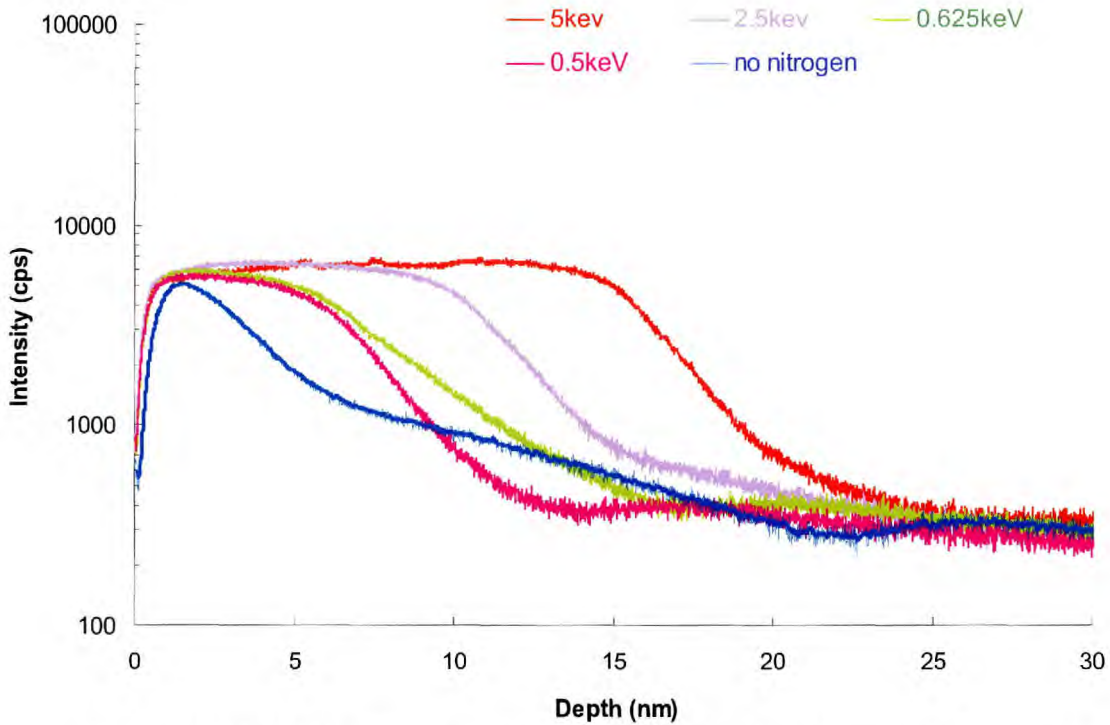


Figure 5.1 FIB SIMS depth profiles of $^{28}\text{Si}^+$ in the altered layers produced with a normal incidence $^{14}\text{N}_2^+$ beam at different energies.

During the sputtering process, the total path length of an ion traveling vertically into a horizontal silicon surface is called the range, and is composed of a mixture of vertical and lateral motion. The average depth of the implanted ion is called the projected range R_p . The statistical fluctuations in the projected range are called the projected straggle ΔR_p . The projected range plus projected straggle is defined as the total ion range. The projected range and total ion range determined by TRIM2008 ^[1] and the altered layer thickness determined by the TEM technique and FIB SIMS for different $^{14}\text{N}_2^+$ energy bombardment of silicon was compared in figure 5.2.

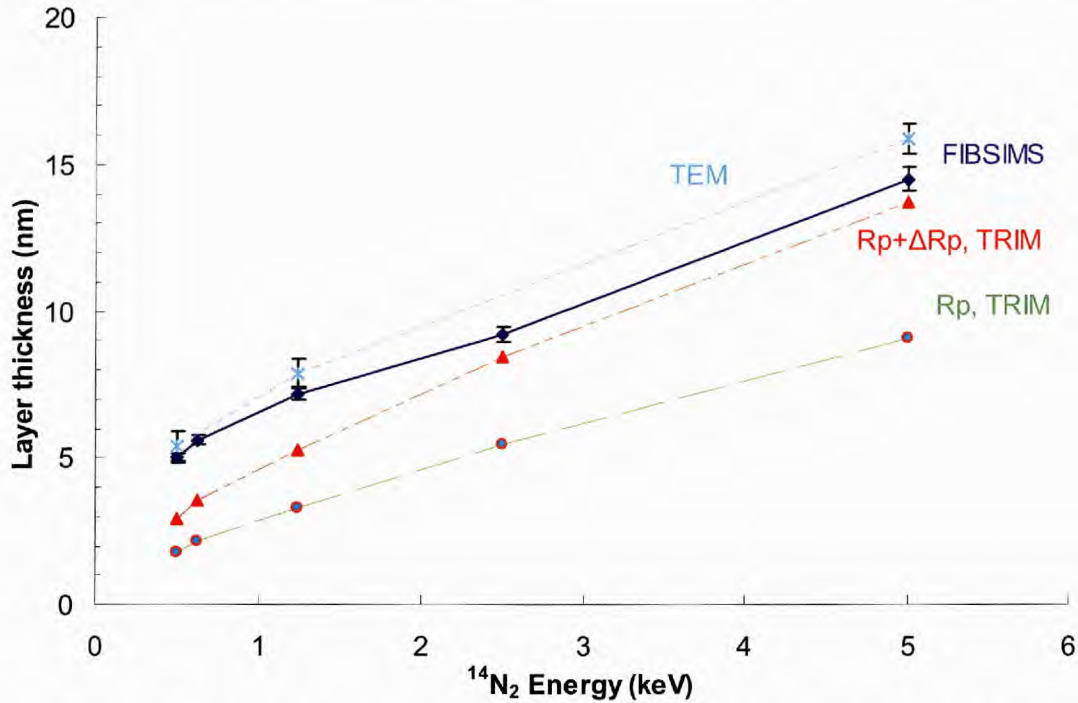


Figure 5.2 Altered layer thicknesses as a function of $^{14}\text{N}_2^+$ implant energies (diamonds) produced by normal incidence $^{14}\text{N}_2^+$ bombardment. The figure also shows the projected range R_p (blue circles) and the projected range plus straggle (full triangles) $R_p + \Delta R_p$ as determined by TRIM2008 for $^{14}\text{N}_2^+$ bombardment of silicon.

The trend of the total range is the same as the trend of the layer thickness. With energies from 0.5 keV to 5 keV, the thickness of the layer is always larger than the total projected range of nitrogen in silicon. This is due to the diffusion of nitrogen into the interface. In the sub-keV region, the thickness of the altered layer increases at a faster rate for every small increase in primary energy. At a low energy of implantation, the low sputter rate of the nitrogen beam leads to high growth of the altered layer rather than sputtering the material, so the steady state is reached much quicker.

The thickness of the altered layers obtained from the TEM are also included in the figure (TEM experimental procedure is discussed in chapter 6). A linear relationship between the thickness of the altered layers was shown. The thickness of the altered layer increased with increasing beam energy although there were not many data points to support this observation in the TEM profile. This effect was also seen in oxygen beam synthesised oxide layer thickness measurement [2, 3]. The thickness of the altered layers obtained with SIMS was smaller than that found in the TEM. SIMS has problems when it comes to depth calibration that could affect the layer thickness estimation. The factors which could affect the thickness measurement from the two

techniques are described as follow. Firstly, the method used to obtain the layer thickness from the SIMS depth profiles was taken rather arbitrarily, i.e. 50% of the maximum signal intensity. On top of this, unstable primary beam currents can lead to minor changes in the sputter rate. The sputter rate also changes in the Ga^+ FIB 200 depending on whether the matrices are silicon nitride or silicon, the depth profiles were corrected by applying a factor of 1.6 (the nitrogen beam sputters 1.6 times faster in the silicon nitride layer than it does in the silicon), but the unknown sputter rate in the transient regions shifted everything closer to the surface. The transient region is much bigger at high primary energy causing greater errors in layer thickness measurements. Thirdly, the ion mixing effect and crater bottom roughness are common problems in the layer thickness measurement. Finally, the Zygo itself has a 6% instrumental error in depth measurements. The overall difference in layer thickness measurements is within 5%. In the TEM image, the thickness of the altered layers are measured based on the contrast of the image. A change in contrast might not fully reflect the true thickness of the altered layer. Furthermore, the TEM used for the nitrogen induced altered layers, the JEOL 2000FX TEM, was not high resolution. The edge of the altered layers was not well resolved, so over or underestimate of the layer thickness was possible. Each layer was measured five times at different places, and the average value was used. Figure 5.3 and 5.4 shows the TEM images of cross sections of the altered layers produced with normal incidence nitrogen ions at 1.25 keV (see Appendix 2 for 0.5 keV and 5 keV).

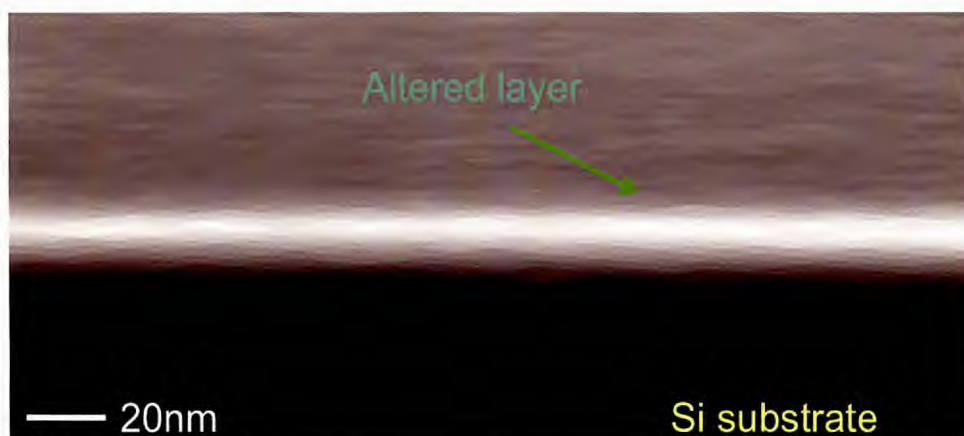


Figure 5.3 TEM image of cross section of the altered layer formed at $^{14}\text{N}_2^+$ using 1.25 keV. The procedure to prepare the TEM specimen is described in chapter 6.

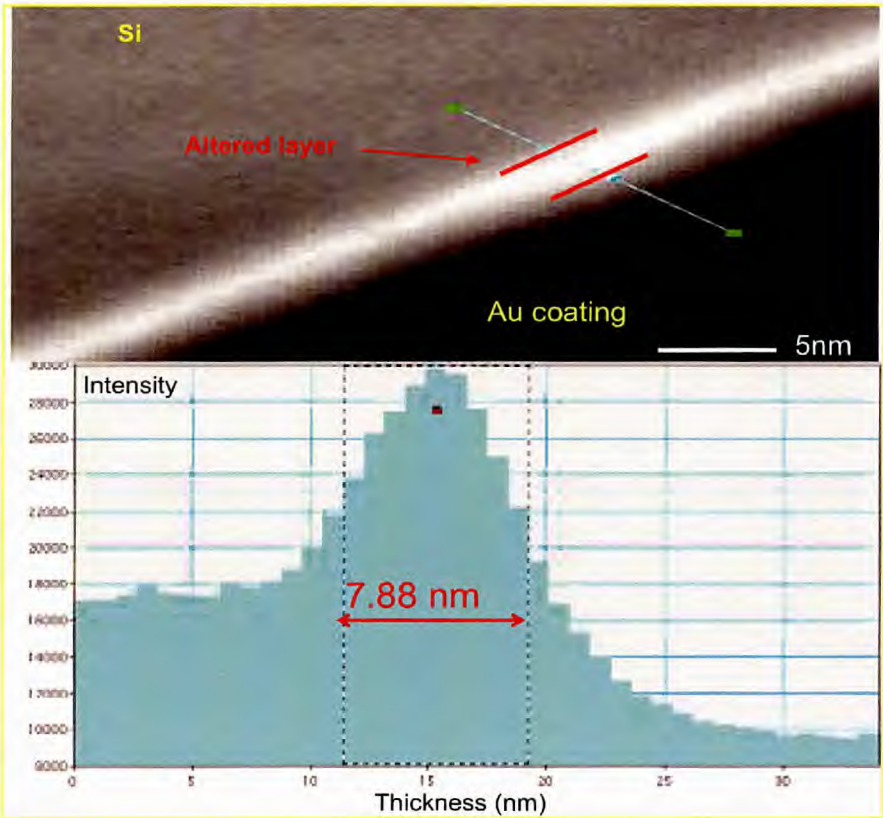


Figure 5.4 The thickness of the nitrogen induced altered layers was measured in Gatan DigitalMicrograph® software.

The ion yield enhancement ratio was defined as the maximum signal intensity, I_{max} , divided by the background signal intensity, $I_{\text{background}}$. The ion yield enhancement depth was defined as the sputter depth at the half maximum signal intensity, figure 5.5. The ion yield enhancement ratio and depth are plotted in figure 5.6.

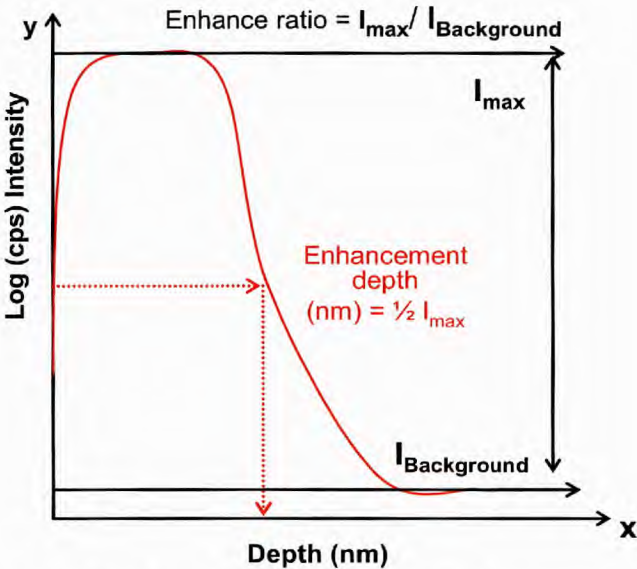


Figure 5.5 The method used to calculate the ion yield enhancement ratio and depth.

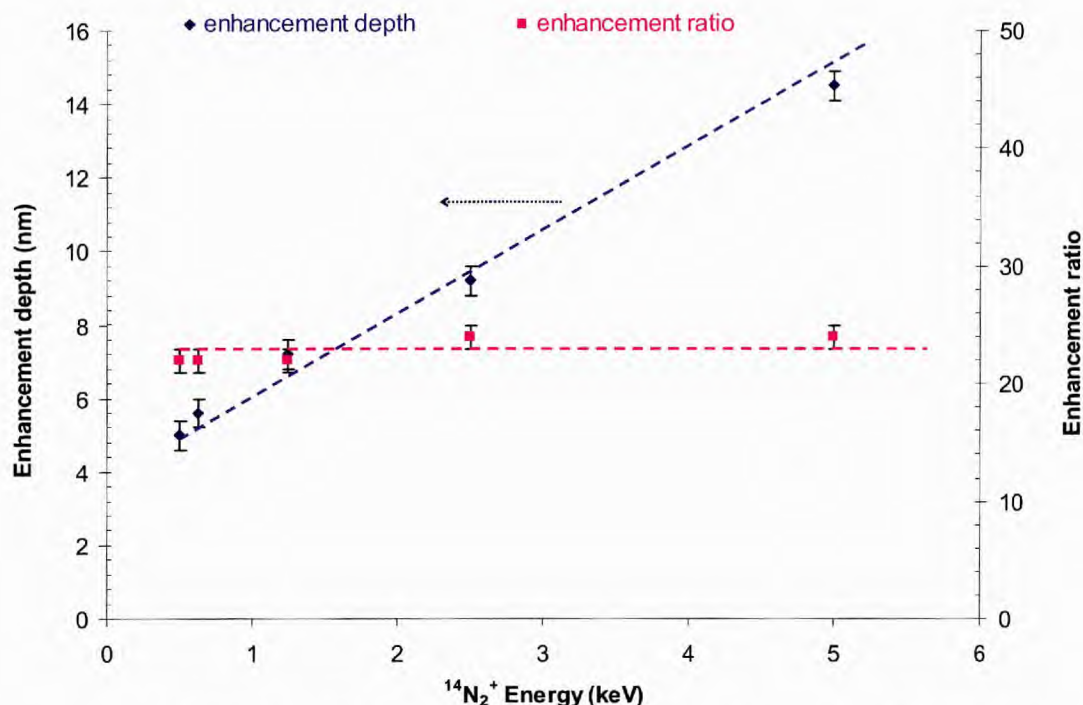


Figure 5.6 Ion yield enhancement depth and ratio observed in the FIB 200 as a function of $^{14}\text{N}_2^+$ energy.

The ion yield enhancement depth increased with increasing primary energy. The maximum enhancement depth was gained at an energy of 5 keV. The ion yield enhancement ratio was almost the same for all implant energies. The small differences could be the transmission or current density variation of the FIB 200. However, at lower nitrogen implant energy, the thickness of the altered layer was very thin. The long projected range of a 30 keV Ga^+ primary beam allowed Ga^+ to mix through the thin altered layer much quicker. The concentration of the primary ions decreased, as a result, ion yield decreased quicker at lower implantation energies.

5.2.2 Layer Characterisation with ION-TOF IV

In this section, the nitrogen formed altered layers were characterised with the ION-TOF IV. The experimental conditions are shown in table 5.1. The $^{28}\text{Si}^+$ profile can be divided into three regions. Region A is the native oxide layer, the thickness is about 1.8 nm, the intensity is higher than region B. Region B is the nitrogen induced layer, and the intensity in this region stays almost constant. Region C is where the altered layer comes to the end reaching the steady state. As figure 5.7 shows, the thickness of the altered layer decreased with decreasing energy and the gradient increased much quicker at shallower layers (i.e. 0.5 keV), the beam goes through the thin layer quicker than it goes through the thicker ones under the same sputtering

conditions. The depth profile of the native oxide layer was the shallowest. Figure 5.7 demonstrates the energy effect, at an energy of 5 keV the intensity of the $^{28}\text{Si}^+$ decreased slowly in region B (almost constant) but dropped quickly in region C, where there was not much altered layer left, and finally reached the steady state. The three regions A, B and C are only found at high energy implantation. It must be noted that the primary current of the sputtering Ar^+ gun is 11 nA and the sputtering angle is fixed at 45° , therefore, the very thin altered layers formed by low implant energy will be degraded much quicker. The smallest altered layer was formed at 0.5 keV. The difference in background intensity between depth profiles was thought to be mainly due to the variation of the emission current of the beam during beam sputtering.

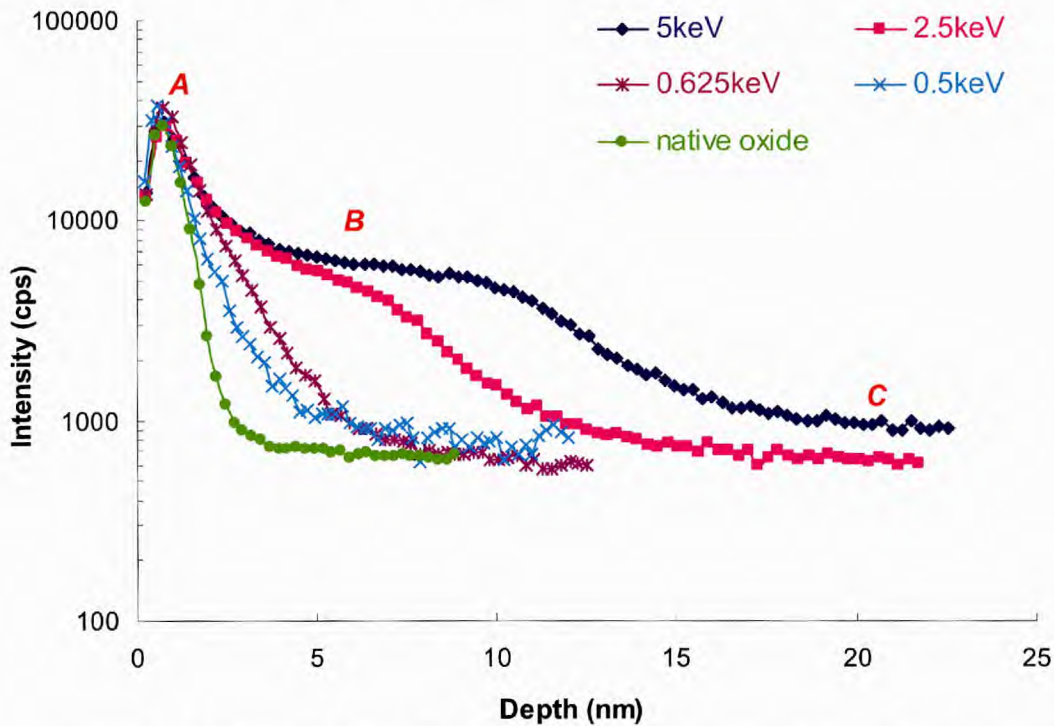


Figure 5.7 Depth profiles of $^{28}\text{Si}^+$ in the altered layers with a normal incidence $^{14}\text{N}_2^+$ beam at different energies. The sample was depth profiled with the ION-TOF IV. The experimental conditions were tabulated in table 5.1.

Figure 5.8 shows the depth profile of the altered layer formed by a 5 keV nitrogen beam. A big spike due to native oxide on the sample surface was seen at the beginning of all depth profiles. The thickness of this native oxide layer was estimated to be about 1.8 nm from the $^{16}\text{O}^+$ profile (pink line). All the profiles dropped after the native oxide layer, particularly the $^{44}\text{SiO}^+$ signal. The $^{44}\text{SiO}^+$ signal was much higher than $^{42}\text{Si}^+$ in the beginning of the profile and then dropped below the $^{42}\text{Si}^+$ signal. All profiles except $^{44}\text{SiO}^+$ stayed almost constant to 11 nm after the native oxide layer.

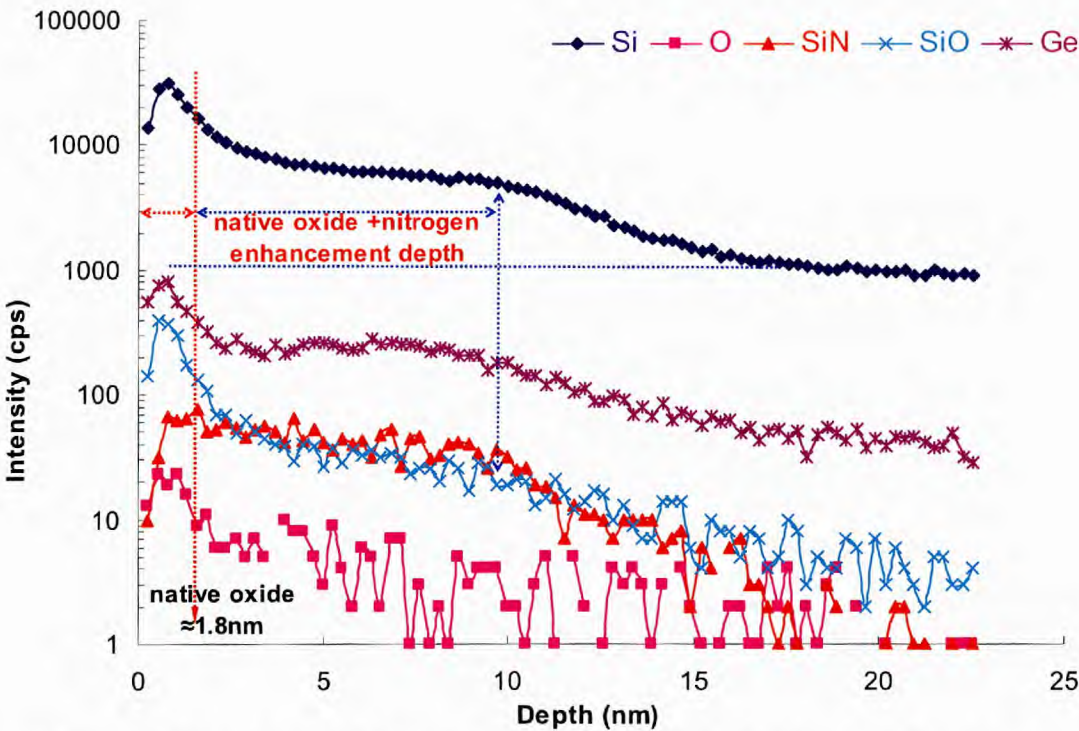


Figure 5.8 Depth profile of the altered layer formed by a 5 keV nitrogen beam.

To work out the ion yield enhancement ratio, the average intensity of the B region was divided by the average intensity of the C region. The ion yield enhancement depth was defined as the distance from surface to the end of B region, which equals the sum of region A (native oxide) and region B. The definition for ion yield enhancement ratio and depth is shown in figure 5.9.

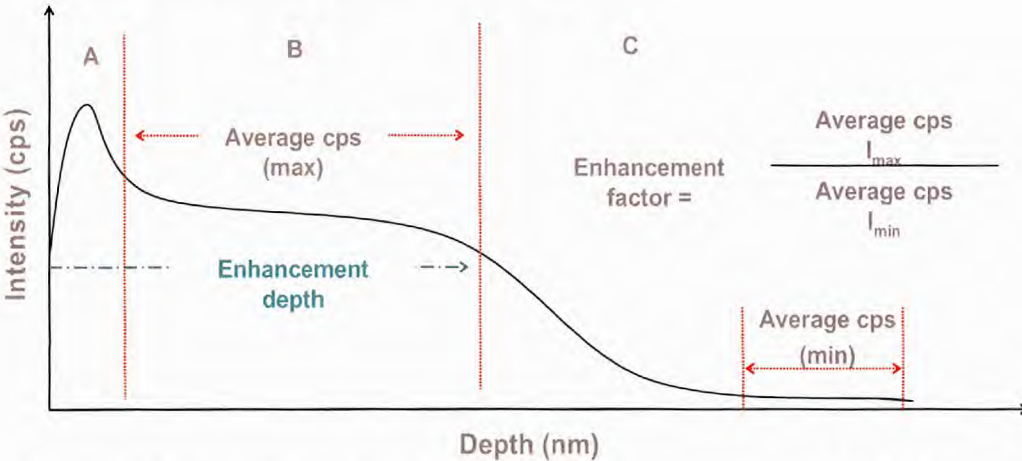


Figure 5.9 The method used to calculate the enhancement ratio and depth observed in ION-TOF IV.

Figure 5.10 shows the ion yield enhancement ratio and depth as a function of nitrogen implantation energy obtained with ION-TOF IV. The trend is very similar to that obtained with the FIB 200. The ion yield enhancement depth increased with

increasing beam energy, the largest enhancement depth was achieved at a beam energy of 5 keV. The enhancement ratio varied little with beam energies. The largest enhancement depth was about 11 nm, and the enhancement ratio was about one order of magnitude. Comparison with FIB SIMS is discussed later.

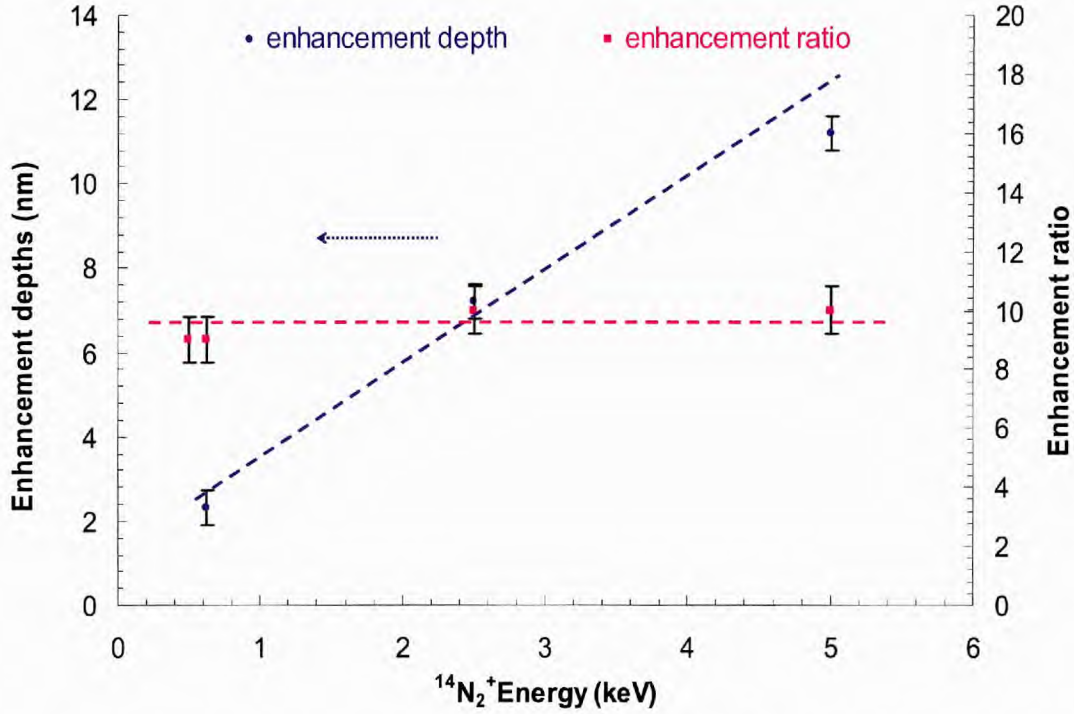


Figure 5.10 Ion yield enhancement depth and ratio of $^{28}\text{Si}^+$ signal obtained with the ION-TOF IV as a function of nitrogen implant energy.

5.3 Dose Dependence with $^{14}\text{N}_2^+$ Irradiation

The degree of yield enhancements increases with increasing primary ion doses until the critical dose is reached ^[4]. The implantation dose of nitrogen D_{Dose} (ions/cm²), is determined by the beam current, I_B , raster area, A , and implantation time, t .

$$D_{\text{dose}} = \left(\frac{I_B \times t}{e \times A} \right) \times 2 \quad (1)$$

In this set of experiments, the investigation of dose effect on the secondary ion yield was carried out. The $^{14}\text{N}_2^+$ ions were implanted into the silicon samples at a beam energy of 1.25 keV with various doses by changing the irradiation time in a cycle in the Atomika 6500. The doses used for FIB SIMS analysis were: 1×10^{16} , 2×10^{16} , and 3×10^{16} N/cm². The FIB 200 sputtering conditions used were: 30 keV Ga^+ energy at normal incidence, the raster area of $50 \times 50 \mu\text{m}^2$ was set within the altered layer, 300 pA beam current. The ION-TOF IV sputtering conditions were: 1 keV Ar^+

sputter beam with a raster area of 500x500 μm^2 , 11 nA beam current, 25 keV Ga^+ analysis beam with a raster area of 400x400 μm^2 , 1.2 pA beam current. The depth was calibrated by measuring the crater depth and the ratio of the sputter rates in silicon nitride and silicon (ratio $\approx$ 0.724). The experimental conditions are shown in table 5.2

Altered layer formation - Dose dependence				
Beam	Energy (keV)	Area (μm^2)	Current (nA)	Angle ($^\circ$)
Nitrogen	1.25	500x500	40	0
Layer characterisation				
FIB 200	Ga 30keV	50x50	300pA	0
ION TOF IV	Ga 25keV	400x400	1.2pA	45
	Ar 1keV	500x500	11	45

Table 5.2 Experimental conditions used for nitrogen induced altered layer formation in Atomika 6500 and layer characterisation in the FIB 200 and the ION-TOF IV.

The depth profile of different nitrogen dose implanted altered layers are shown in figure 5.11. The $^{28}\text{Si}^+$ signal intensity was normalised for simplicity.

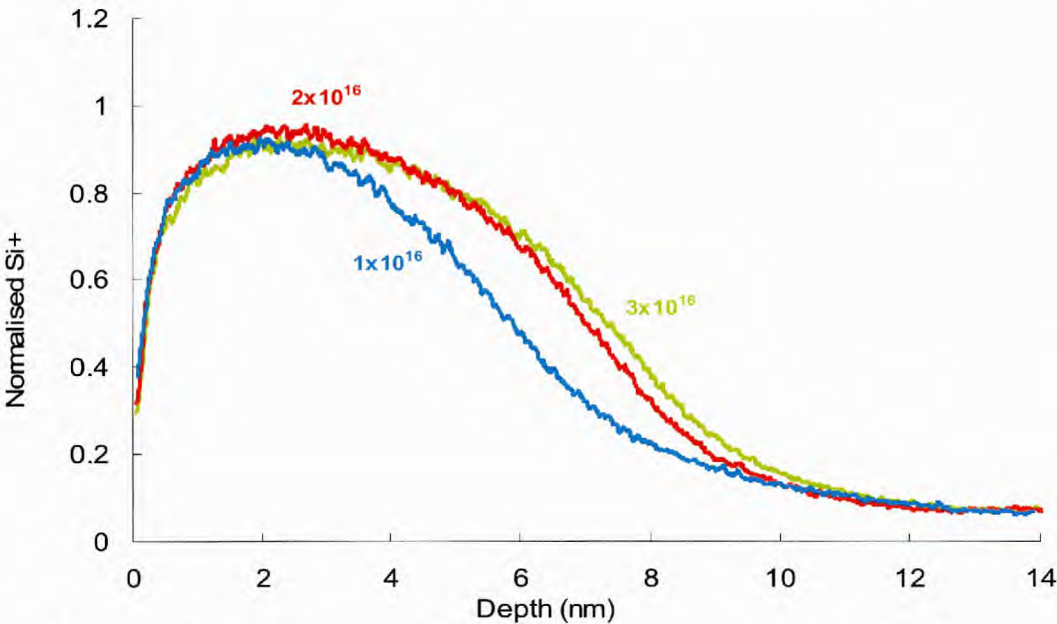


Figure 5.11 Depth profiles of $^{28}\text{Si}^+$ the altered layers produced using a $^{14}\text{N}_2^+$ beam at different doses. The altered layers were depth profiled with the FIB 200.

The depth profile of $1 \times 10^{16} \text{ N/cm}^2$ was the shallowest, 2×10^{16} and $3 \times 10^{16} \text{ N/cm}^2$ were almost identical with very small difference, the enhancement depth was very similar between the two different doses. The small difference could be due to the experimental error (e.g. crater depth measurement). The enhancement depth increased

with increasing dose and then became constant at a primary dose of $2 \times 10^{16} \text{ N/cm}^2$. Hence, the critical dose required to reach a constant nitrogen concentration at the near-surface region at an implant energy of 1.25 keV was $2 \times 10^{16} \text{ N/cm}^2$.

The same experiments were repeated with the ION-TOF IV to confirm the critical dose obtained with the FIB 200 was correct. The doses used for analysis were: 1×10^{16} , 1.5×10^{16} , 2×10^{16} , 2.5×10^{16} and $3 \times 10^{16} \text{ N/cm}^2$. The ion yield enhancement ratio obtained with the ION-TOF IV as a function of primary dose is plotted in figure 5.12.

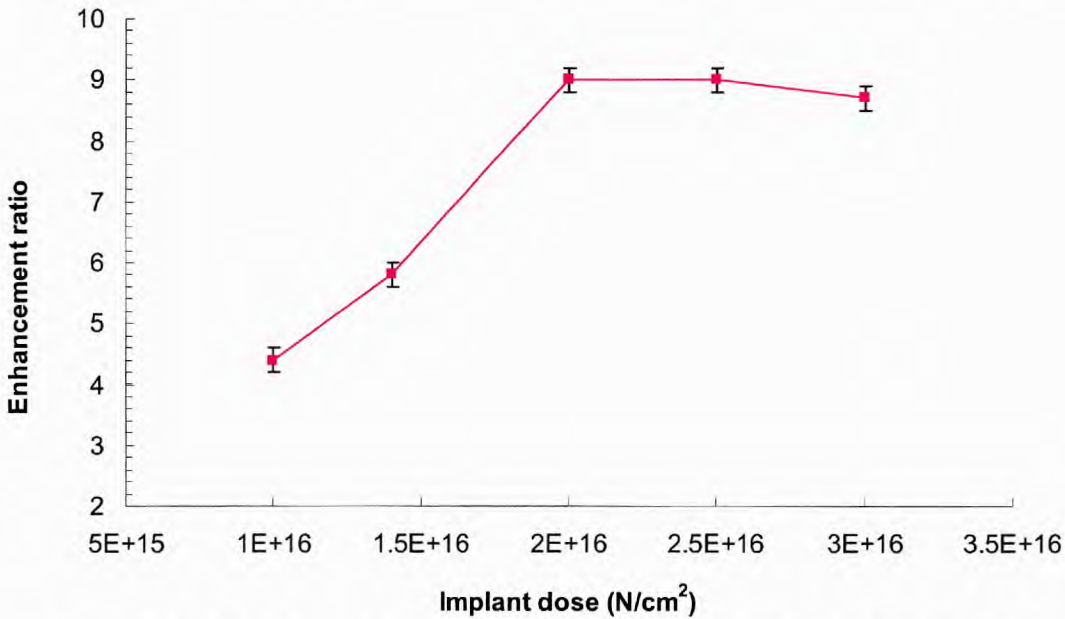


Figure 5.12 The ion yield enhancement ratio obtained with the ION-TOF IV as a function of nitrogen dose.

Again, the enhancement ratio showed that it increased with increasing dose up to a dose of $2 \times 10^{16} \text{ N/cm}^2$ and then became constant. The results from these two techniques confirmed that the ion yield enhancement varied with primary dose until the critical dose was achieved. This can be checked with the “steady state time”, i.e. the total time used when the nitrogen induced altered layer is completed. The $^{28}\text{Si}^+$ signal was monitored during the nitrogen sputtering and the beam was stopped when the observed secondary ion signal ($^{28}\text{Si}^+$) levelled out. It took about 72s to reach the steady state using an implant energy of 1.25 keV at a beam current of 50 nA, the implanted dose was calculated as $1.8 \times 10^{16} \text{ N/cm}^2$. The critical dose gained from the nitrogen sputtering had a good agreement with the figure shown above. The small difference could be due to small variations in the primary beam current or miscalculation of the steady state time.

5.4 Comparison of FIB SIMS and TOF SIMS

The ion yield enhancement due to nitrogen implantation was shown in both techniques. The enhancement ratio was not dependent on the implant energy of $^{14}\text{N}_2^+$. It showed that the enhancement ratios of different energies were very similar. In other words, the energies used in this experiment were efficient enough to provide maximum ion yield enhancements. The three regions observed with the ION-TOF IV analysis were not shown in the FIB 200. The high primary beam energy of the Ga^+ FIB 200 allows quick passage through the native layer to reach the altered layer. The ion yield enhancement depth gained in the FIB 200 was much larger than that found with the ION-TOF IV. The ion mixing effect occurred during ion sputtering, especially if the primary ion energy was 30 keV Ga^+ FIB. This high energy shifted the whole profile away from the surface and caused an overestimation of the layer thickness. The crater bottom roughness was relatively large which could affect the layer thickness estimation. Moreover, in the dual beam mode of the ION-TOF IV, the sputter gun (Ar^+) and the analysis gun (Ga^+) work quasi-simultaneously; the sputtering gun erodes a high quantity of sample while the analysis gun is only analysing a small amount of the sample.

In conclusion, the FIB 200 and the ION-TOF IV have shown that the secondary ion yield was enhanced by the implantation of nitrogen. The low nitrogen implant energy was efficient enough to provide maximum ion yield enhancements. The flat topped signal of $^{28}\text{Si}^+$ obtained in the FIB 200 suggested that the altered layers were fully formed. The ion yield enhancement depth increased with increasing energy. A comparison of the FIB SIMS and the TOF SIMS data is made in figure 5.13b. The enhancement depth observed with the FIB 200 was larger. The enhancement ratio was also found to be greater than that found with the ION-TOF IV. However, with oxygen implantation, the enhancement ratio in ION-TOF IV was greater than that in FIB SIMS (shown in section 5.5). It is not certain why the enhancement ratio showed different trend. One possibility is that the transmission of the FIB SIMS is not fully optimised. Looking at the FIB SIMS depth profiles of oxygen induced altered layers, the maximum $^{28}\text{Si}^+$ intensity was only 1000 counts higher than that of nitrogen induced altered layers. However, in ION-TOF IV the difference in the $^{28}\text{Si}^+$ was much larger. The background intensity of $^{28}\text{Si}^+$ of the two techniques stayed unchanged regardless of the beam source. Thus, the enhancement ratio in FIB SIMS due to

different beam implantation varied less than that of ION-TOF IV. This effect leads to a future work, that is, the optimisation of the transmission factor of FIB SIMS. A direct comparison between the two sets of data was made in figure 5.13a.

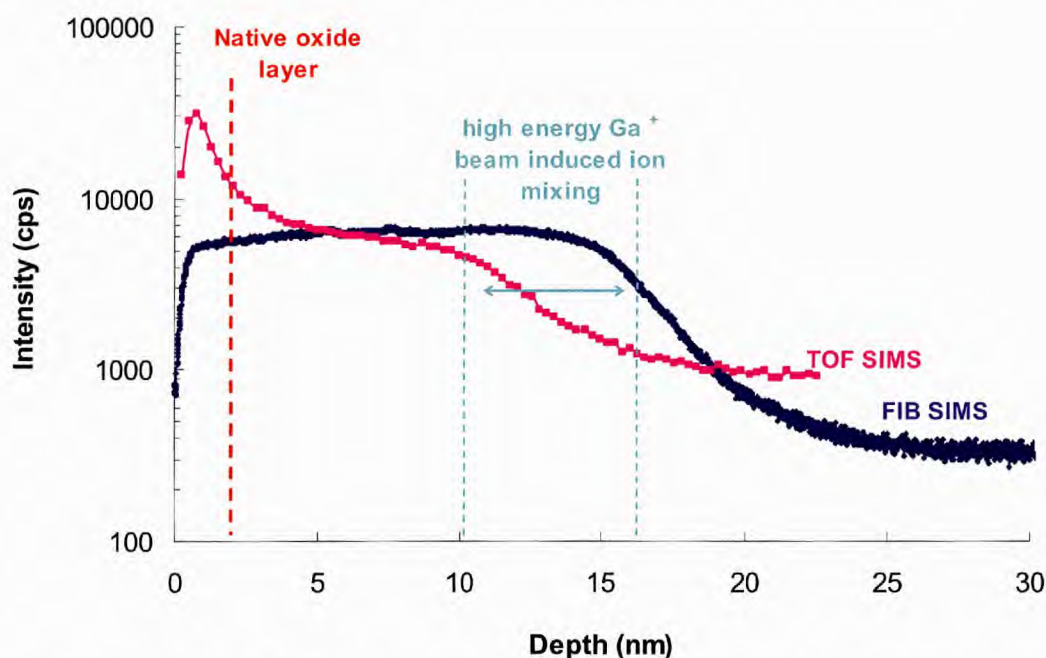


Figure 5.13a) The $^{28}\text{Si}^+$ depth profile of a 5 keV nitrogen beam induced altered layer obtained on the ION-TOF IV and the FIB 200.

As the figure shows, the TOF SIMS depth profile has a big spike at the surface which is due to the native oxide layer. This effect is not seen in the FIB SIMS depth profile, the high energy of Ga^+ beam smashed through the native oxide and pushed the whole profile away from the surface resulted in a much larger altered layer. The difference in the altered layer thickness due to different primary ion energy used in the two techniques was seen in the figure. The intensity of the $^{28}\text{Si}^+$ in the nitrogen induced altered layer obtained from both techniques were about the same, but the TOF SIMS depth profile dropped much quicker. The background intensity of the two techniques stayed constant. However, the background intensity of the TOF SIMS is much higher than that of the FIB SIMS. The reason is thought to be due to the crater edge effect. The sputter area used in the TOF SIMS analysis is $500 \times 500 \mu\text{m}^2$ and the analysis area is $400 \times 400 \mu\text{m}^2$, this could result in a high background intensity. Thus, this could also be one of the reasons that the ion yield found in the TOF SIMS was lower than that found in the FIB SIMS since the maximum intensity due to the nitrogen implantation was about the same in the two techniques.

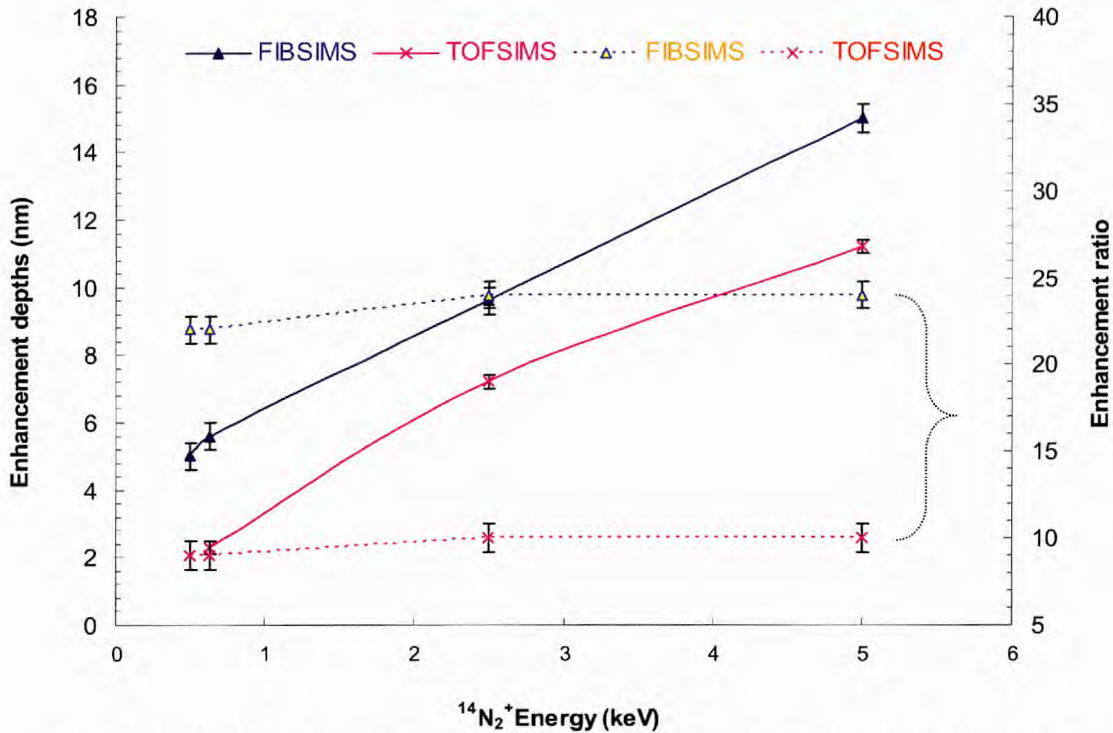


Figure 5.13b) Ion yield enhancement depth and ratio of obtained with the FIB 200 and the ION-TOF IV as a function of nitrogen implant energy.

Comparing the two beam spot sizes, that of Ga^+ FIB (50 nm) is much smaller than the size of TOF SIMS Ga^+ beam (250 nm). The advantage of having a much smaller beam size is not just a much better lateral resolution but also the possibility of a smaller crater size. The thickness measurements of the native oxide were successfully obtained in the ION-TOF IV but failed with the FIB 200. Hence, the use of TOF SIMS can provide better accuracy of altered thickness measurement.

5.5 Energy Dependence with $^{16}\text{O}_2^+$ Irradiation

$^{16}\text{O}_2^+$ ions were implanted into the sample at energies of 0.5, 0.625, 2.5, 5 keV at normal incidence. The beam was rastered with a raster area of $500 \times 500 \mu\text{m}^2$ at a current of 50 nA until the steady state was reached. The SIMS analysis of the oxygen induced altered layers were performed with a FEI FIB 200 attached with a quadrupole mass spectrometer and ION-TOF IV.

The FIB 200 sputtering conditions used were: 30 keV Ga^+ energy at normal incidence, the raster area of $50 \times 50 \mu\text{m}^2$ was set within the altered layer, 300 pA beam current. The ION-TOF IV sputtering conditions were: 1 keV Ar^+ sputter beam with a raster area of $500 \times 500 \mu\text{m}^2$, 11 nA beam current, 25 keV Ga^+ analysis beam with a raster area of $400 \times 400 \mu\text{m}^2$, 1.2 pA beam current. The crater depth was measured with

a 3D imaging surface structure analyzer, the Zygo white light interferometer. The experimental conditions are tabulated in table 5.3

Altered layer formation - Energy dependence				
Beam	Energy (keV)	Area (μm ²)	Current (nA)	Angle (°)
Oxygen	0.5 - 5	500x500	50	0
Layer characterisation				
FIB 200	Ga 30keV	50x50	300pA	0
ION-TOF IV	Ga 25keV	400x400	1.2pA	45
	Ar 1keV	500x500	11	45

Table 5.3 Experimental conditions used for oxygen induced altered layer formation in Atomika 6500 and layer characterisation in the FIB 200 and the ION-TOF IV.

5.5.1 Layer Characterisation With ION-TOF IV

The oxygen induced altered layers were characterised with the ION-TOF IV. The depth profiles are shown in figure 5.14a.

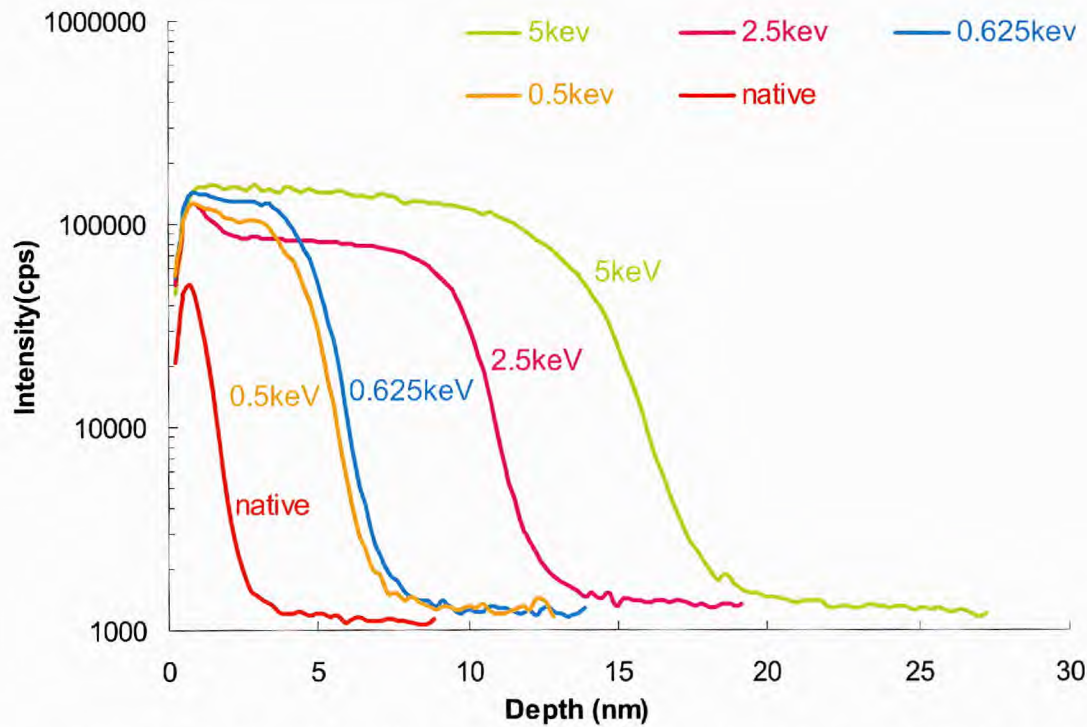


Figure 5.14a) Depth profiles of $^{28}\text{Si}^+$ in the altered layers produced by the normal incidence bombardment of silicon using a $^{16}\text{O}_2^+$ beam at different energies. The sample was depth profiled with the ION-TOF IV. The experimental conditions were tabulated in table 5.3.

The $^{28}\text{Si}^+$ signals of the oxygen ion beam formed layers stayed flat topped before they reached steady state. This suggested that the altered layers formed by various

oxygen energies were fully oxidised. The native oxide depth profile (red line) in figure 5.14a was much shallower and the intensity level was lower than that of the altered layers. The three regions (region A, B and C) found in the SiN altered layer depth profiles were not seen here. Hence, the ion yield enhancements due to oxygen implantation were clearly demonstrated. The largest oxide thickness was observed at an oxygen implantation energy of 5 keV. The 0.5 keV and 0.625 keV profiles have almost the same oxide thickness. It must be pointed out that the 2.5 keV profile (pink) has a spike at the beginning of the profile. This observation was thought to be due to the large amount of surface contaminants that exist in the altered layer, figure 5.14b.

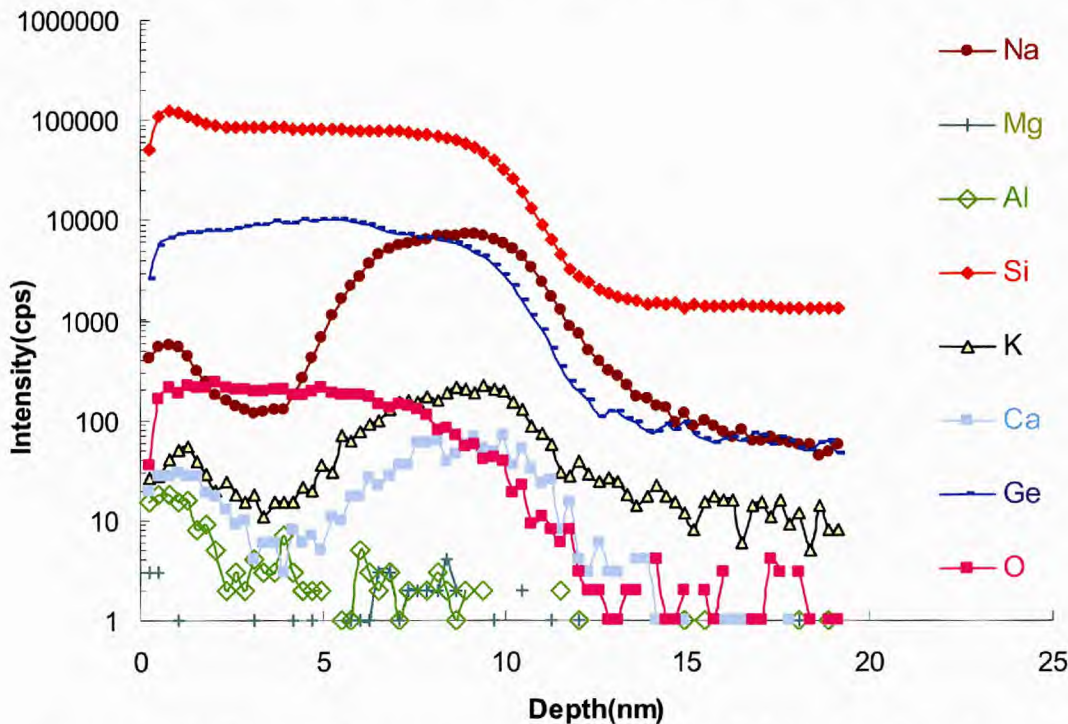


Figure 5.14b) Shows surface contaminants $^{23}\text{Na}^+$, $^{39}\text{K}^+$, $^{40}\text{Ca}^+$ that have been detected in the crater formed by an oxygen beam energy of 2.5 keV. The $^{28}\text{Si}^+$, $^{73}\text{Ge}^+$, $^{16}\text{O}^+$ distributions were also shown.

During the oxygen implantation process, some surface contaminates segregate away from the surface to a depth (depends on primary energy and dose) underneath the sample surface. The intensity of $^{23}\text{Na}^+$ was relatively low in the first few nanometres and then rose to almost 10000 cps. $^{39}\text{K}^+$, $^{40}\text{Ca}^+$ were also seen in deep sample surface, $^{27}\text{Al}^+$ was found only in the top few layers. The intensity level of those contaminants in the 2.5 keV formed altered layer was much higher (especially $^{23}\text{Na}^+$) than others (Appendix 1). The ion yield enhancement ratio and oxide thickness were summarised in table 5.4. The ion yield enhancement depth was also defined as

the oxide thickness here. The oxide thickness obtained in this project was compared with the previous result from this lab and plotted in figure 5.15.

Energy (keV)	Enhancement ratio	Oxide thickness (nm)	Literature ^[5] (nm)
5	111	13.89±0.3	13.9
2.5	86	9.17±0.3	9.3
0.625	105	4.4±0.3	4.6
0.5	100	4.2±0.3	4.2

Table 5.4 Ion yield enhancement ratio and depth as a function of primary energy.

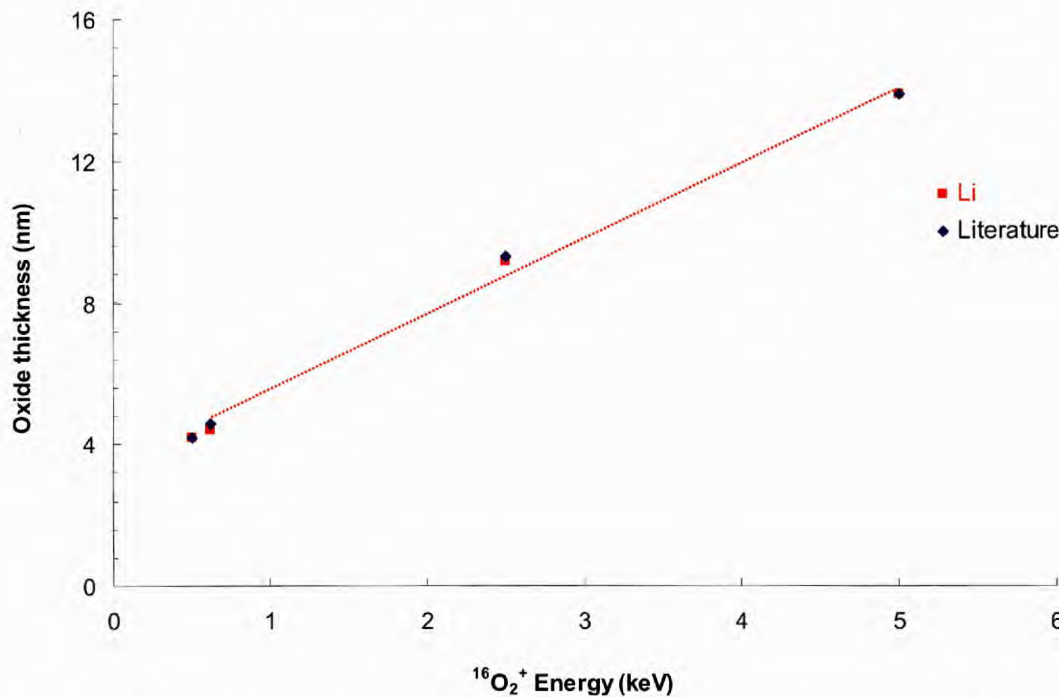


Figure 5.15 The oxide thickness versus implant oxygen energies. Literature data was from Christofi^[1].

As the figure show, the oxide thicknesses observed from this project were very similar to the literature data. The oxide thickness increased with the oxygen implant energy. The ion yield enhancements were about two orders of magnitude which was much larger than that found with nitrogen implantation. *It should be pointed out that the ion yield enhancement was not studied by the author who is referenced here.*

5.5.2 Layer Characterisation with FIB SIMS

The ion yield enhancements produced by oxygen implantation were observed. Figure 5.16 shows the depth profiles of $^{28}\text{Si}^+$ in the altered layer produced by oxygen beam at different energies.

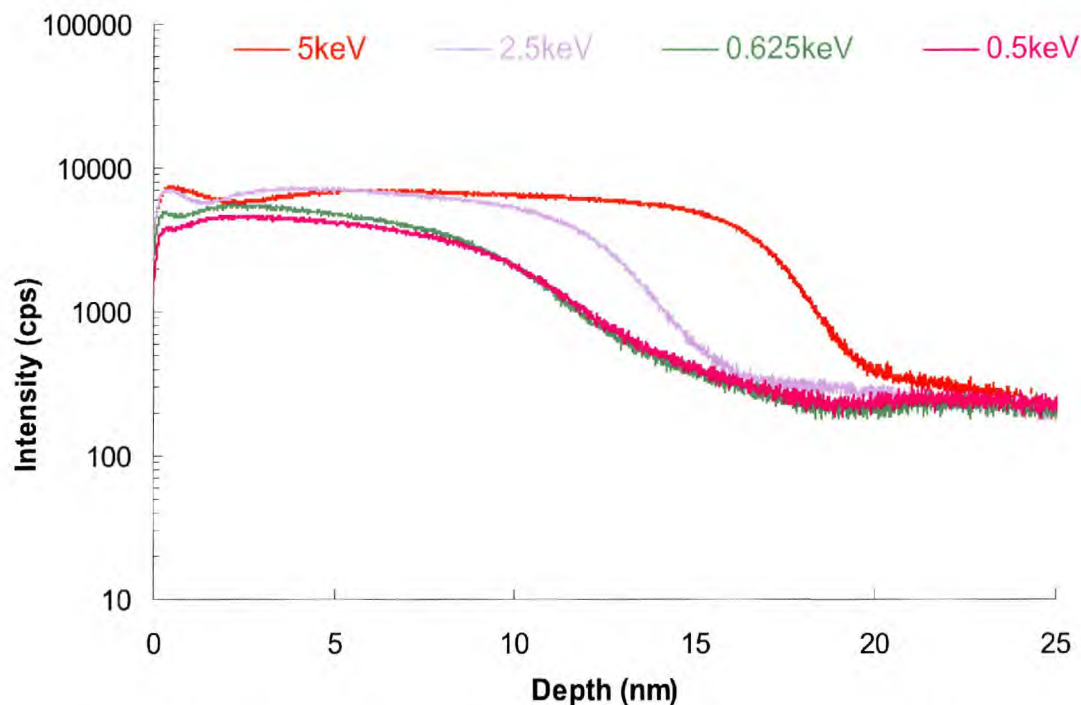


Figure 5.16 Depth profiles of $^{28}\text{Si}^+$ in the altered layers produced by the normal incidence bombardment of silicon using a $^{16}\text{O}_2^+$ beam at different energies. The sample was profiled by the FIB 200.

The profiles stayed constant before dropping off suggesting that fully oxidised layers were formed by all $^{16}\text{O}_2^+$ implant energies. The oxide layer thickness increased with increasing oxygen energy. Compared with the oxide thickness observed with the ION-TOF IV, the oxide thickness was much higher here, especially for the low oxygen energy implant. The ion mixing effect took place during the sputtering process and the high Ga^+ implant energy broadens the depth profiles greatly. Hence, the oxide thickness obtained from the ION-TOF IV was much more reliable.

The ion yield enhancement depth and ratio as a function of primary $^{16}\text{O}_2^+$ implant energy are plotted in figure 5.17. The ion yield enhancement ratio was not dependent on implant energy, the energies used in this experiment were sufficient to provide maximum ion yield enhancement as shown in the depth profiles of nitrogen implanted altered layer in the previous section. The small difference in ion yield enhancement ratio between the implant energies were very small and were thought to be due to transmission or current density variations in the FIB 200.

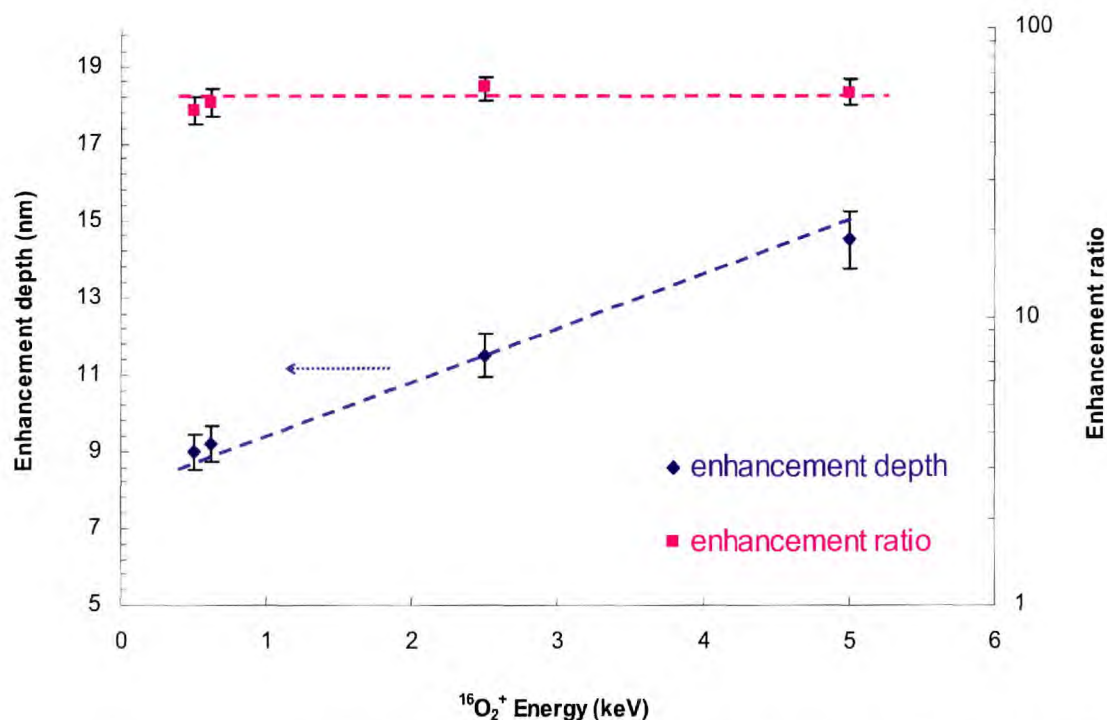


Figure 5.17 The enhancement ratio and depth obtained with the FIB 200 as a function of primary $^{16}\text{O}_2^+$ implant energy.

Compared with the ION-TOF IV, the ion yield enhancements ratio was lower, and the oxide thickness was higher. Again, the larger oxide thickness obtained in the FIB 200 was due to the ion mixing of high beam energy of Ga^+ primary ion beam which shifted the whole depth profile away from the surface. The lower ion yield enhancement ratio was because the transmission of the FIB SIMS is not as good as that of the ION-TOF, the optimisation of the FIB SIMS transmission is required. The thickness obtained with the low ION-TOF IV beam energy was much more accurate.

5.6 Dose Dependence with $^{16}\text{O}_2^+$ Irradiation

The dose was varied by changing the irradiation time in a cycle in the Atomika 6500. An $^{16}\text{O}_2^+$ beam was implanted into the sample over an area of $500 \times 500 \mu\text{m}^2$ at 1.25 keV at normal incidence. The oxygen doses used for FIB SIMS analysis were: 1.5×10^{16} , 2.5×10^{16} and 3×10^{16} O/cm^2 and for TOF SIMS analysis were: 1×10^{16} , 1.5×10^{16} , 2×10^{16} , 2.5×10^{16} and 3.75×10^{16} O/cm^2 . The FIB 200 and ION-TOF IV analysis area was set within the altered layer. The experimental conditions are tabulated in table 5.5.

Altered layer formation - Dose dependence				
Beam	Energy (keV)	Area (μm^2)	Current (nA)	Angle ($^\circ$)
Oxygen	1.25	500x500	40	0
Layer characterisation				
FIB 200	Ga 30keV	50x50	300pA	0
ION TOF IV	Ga 25keV	400x400	1.2pA	45
	Ar 1keV	500x500	11	45

Table 5.5 Experimental conditions used for oxygen induced altered layer formation in Atomika 6500 and layer characterisation in the FIB 200 and the ION-TOF IV.

Figure 5.18 shows the depth profiles obtained with the ION-TOF IV.

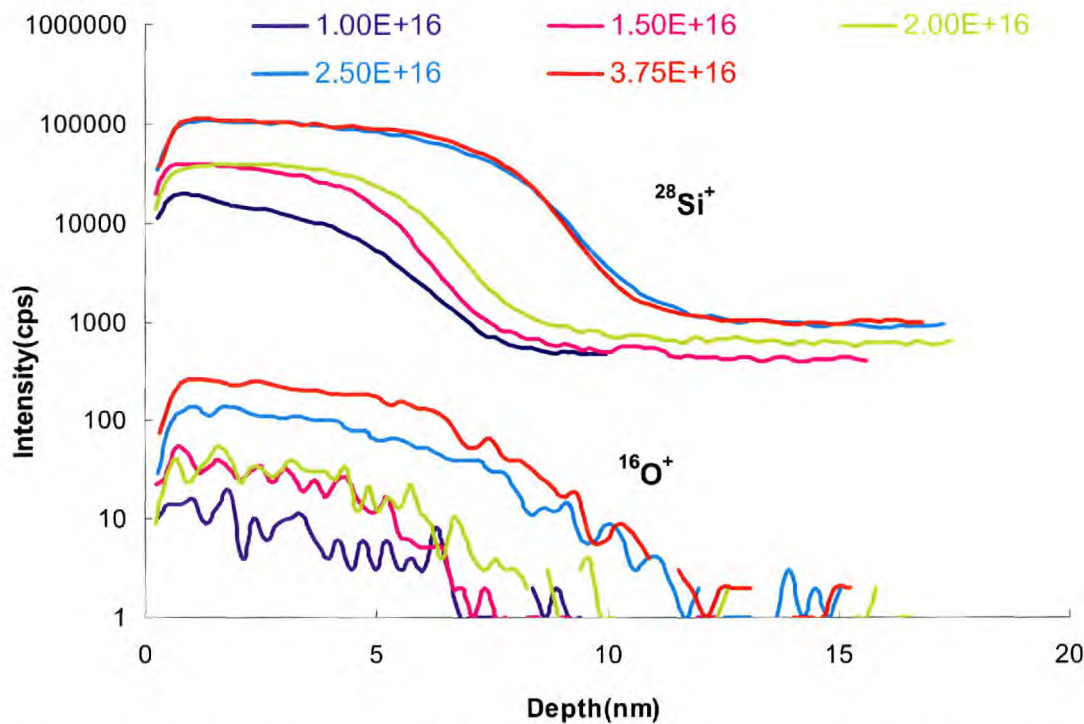


Figure 5.18 Depth profiles of $^{28}\text{Si}^+$ and $^{16}\text{O}_2^+$ in the altered layers produced by the normal incidence bombardment using a $^{16}\text{O}^+$ beam at different doses.

The shape of all the profiles was very similar, and the oxide layer thickness increased with increasing oxygen dose. The $^{28}\text{Si}^+$ signals stayed constant before dropping off. The oxide layer formed by a dose of $1 \times 10^{16} \text{ O/cm}^2$ was the thinnest and the $^{28}\text{Si}^+$ intensity decreased quicker in this thin layer. The oxide thicknesses formed by implant dose of $2.5 \times 10^{16} \text{ O/cm}^2$ and $3 \times 10^{16} \text{ O/cm}^2$ were the same suggesting that the critical dose required to form a continuous oxide layer at an oxygen implant energy of 1.25 keV was achieved at a dose of $2.5 \times 10^{16} \text{ O/cm}^2 \pm <1\%$ experimental error. The $^{16}\text{O}^+$ signals showed that with increasing oxygen implant dose more oxygen

was being implanted into the layer. But the thickness of the oxide layer stopped growing at a dose of 2.5×10^{16} O/cm². The ion yield enhancement due to oxygen implantation was obvious. The critical dose required to form a continuous oxide layer at a fixed energy can be checked with Li's formula ^[6]:

$$\Phi_c = 2.5 \times N_o^{SiO_2} \times \Delta Rp \quad (1)$$

Where, Φ_c is the critical dose, $N_o^{SiO_2}$ is the number of oxygen atoms in silica (4.48×10^{22} O/cm³) and ΔRp is the straggle. The straggle of $^{16}\text{O}^+$ at an energy of 1.25 keV is about 2.4 nm (TRIM2008). According to Li's formula the critical dose for a 1.25 keV $^{16}\text{O}^+$ beam is about 2.67×10^{16} O/cm². This is fairly similar to the value gained in this experiment.

The oxide thickness and yield enhancement ratio were summarised in table 5.6.

Implant dose (O/cm ²)	Enhancement ratio	Oxide thickness (nm)
3.75×10^{16}	94	7.2 ± 0.2
2.5×10^{16}	99	7 ± 0.2
2×10^{16}	85	5.3 ± 0.2
1.5×10^{16}	76	3.6 ± 0.2
1×10^{16}	31	3.6 ± 0.2

Table.5.6 Ion yield enhancements ratio and oxide thickness of different oxygen doses.

The ion yield enhancements were observed with all the oxygen doses used. The oxide layer formed by the lower oxygen implant dose was not very thin and degraded quickly in the sputtering process. The ion yield enhancement ratio increased with increasing oxygen implant dose up to dose 2.5×10^{16} O/cm². The difference in the ion yield enhancement ratio between the 3.75×10^{16} and 2.5×10^{16} O/cm² layers could be small variations in the transmission of the ION-TOF IV, and can be disregarded. The small difference in the oxide thickness between the maximum dose and the critical dose was thought to be the error in depth calibration.

Another effective way to check the critical dose required is by monitoring the $^{23}\text{Na}^+$ signal intensity. Using oxygen or oxygen flooding leads to strong chemical gradients near the sample surface, as the Na^+ ions tend to segregate away from the surface. This tendency of segregation in an oxygen gradient can be correlated with the heat of formation of the oxide of that element relative to that of the matrix. *The*

standard enthalpy of formation of a compound is the change of enthalpy that accompanies the formation of 1 mole of a substance in its standard state from its constituent elements in their standard states, e.g. $\text{Si} + \text{O}_2 = \text{SiO}_2$. The heat of formation of SiO_2 is very high (-911 kJ/mol) during flooding or implantation and Na^+ segregates away from the surface. Also, because the oxide layer is an insulator, surface charge occurs and electron migration causes diffusion of some species, particularly of alkali elements and elements with low solubility in oxide segregate to the subsurface SiO_2/Si interface^[7]. Figure 5.19 shows the depth profile of $^{23}\text{Na}^+$ in the altered layer. The implantation depth of $^{23}\text{Na}^+$ varies with oxygen implant dose. For implant doses of 1×10^{16} , 1.5×10^{16} and 2×10^{16} O/cm^2 , the implant depth of $^{23}\text{Na}^+$ was relatively shallower and only existed in the top layers. As the oxygen dose increased, the $^{23}\text{Na}^+$ moved much deeper and Gaussian shaped distributions were formed. This indicates that the critical dose required to form a continuous buried stoichiometric oxide layer was achieved.

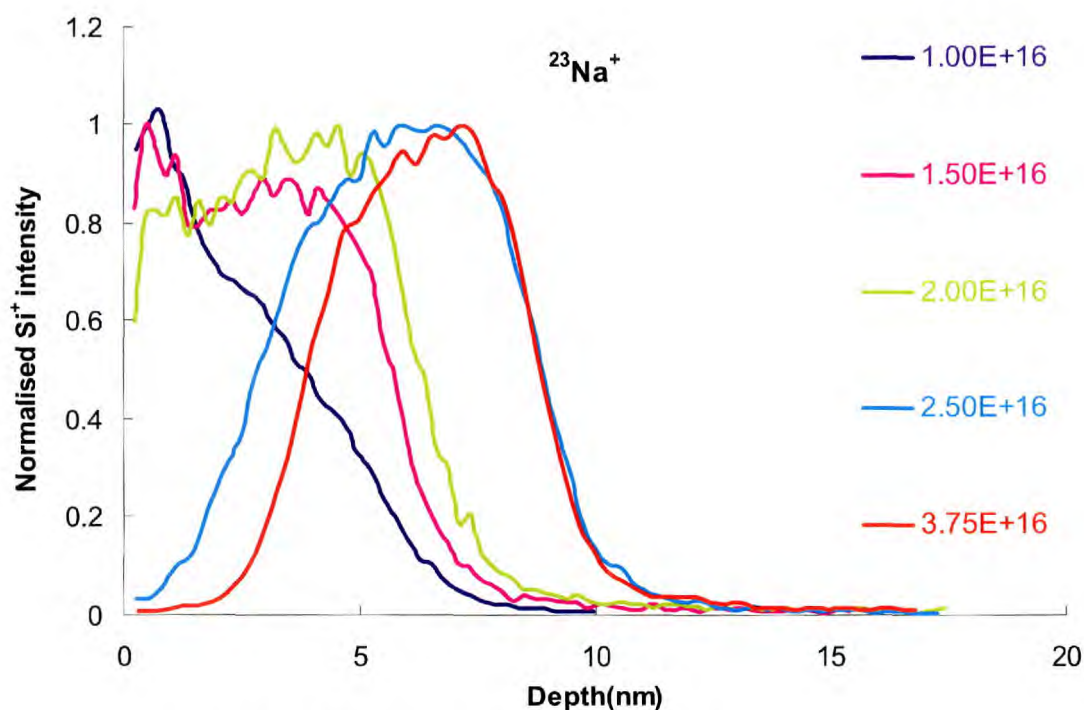


Figure 5.19 $^{23}\text{Na}^+$ distributions in the altered layers.

The ION-TOF IV analysis showed that the critical dose required for 1.25 keV oxygen implant was 2.5×10^{16} O/cm^2 . The same experiments were performed with the FIB 200, and three oxygen doses of 1.5×10^{16} , 2.5×10^{16} and 3×10^{16} O/cm^2 were used. Figure 5.20 clearly shows that the critical dose was 2.5×10^{16} O/cm^2 . The oxide layer thickness and the $^{28}\text{Si}^+$ intensity at a dose of 1.5×10^{16} O/cm^2 were smaller than the

other two profiles. When the primary ion dose increased to $2.5 \times 10^{16} \text{ O/cm}^2$, the altered layer was fully formed. The thickness of the oxide layer was not changed with a further increase of the oxygen dose ($3 \times 10^{16} \text{ O/cm}^2$).

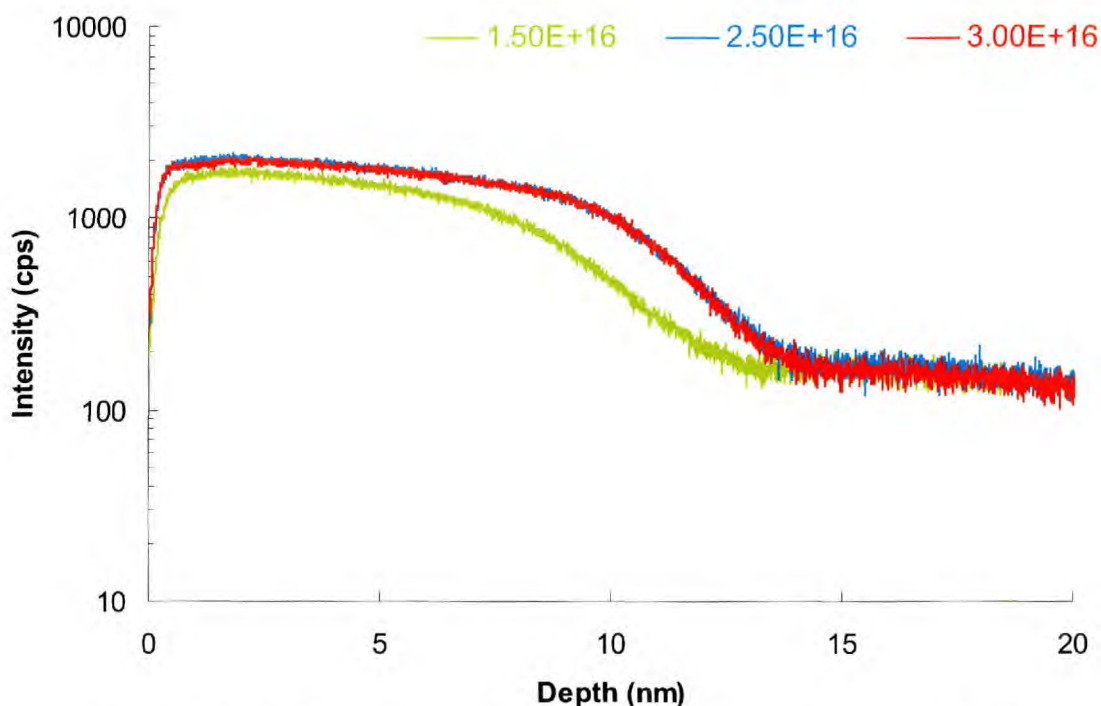


Figure 5.20 Depth profiles of $^{28}\text{Si}^+$ in the altered layers produced by the normal incidence bombardment using a $^{16}\text{O}^+$ beam at different doses.

5.7 Comparison of FIB SIMS and TOF SIMS

The ion yield enhancements were achieved with both techniques. At an oxygen energy of 1.25 keV, different oxygen doses were implanted into the silicon sample, and those beam induced altered layers were analysed with the FIB 200 and ION-TOF IV. The depth profiles of both techniques showed similar trends, i.e. the oxide thickness increased with increasing oxygen implant dose. When the oxygen dose reached $2.5 \times 10^{16} \text{ O/cm}^2$, the thickness stopped increasing and became constant. In other words, the critical dose was reached at a dose of $2.5 \times 10^{16} \text{ O/cm}^2$. However, the thickness of the oxide layers obtained from the FIB 200 was much larger due to an ion mixing effect. The high FIB 200 primary beam energy pushed ions further into the layer. The oxide thickness was much larger than the true thickness.

Figure 5.21 compares the ion yield enhancement depth and ratio obtained with the FIB 200 and the ION-TOF IV. The ion yield enhancement ratio was not dependent on the oxygen implant energy, and the enhancement ratio of different energies was

very similar. Thus, the oxygen energies used in the experiment were efficient enough to provide maximum ion yield enhancements. The maximum ion yield enhancement ratio was about two orders of magnitude with the ION-TOF IV analysis. The enhancement ratio observed with the ION-TOF IV was higher than that found with the FIB 200.

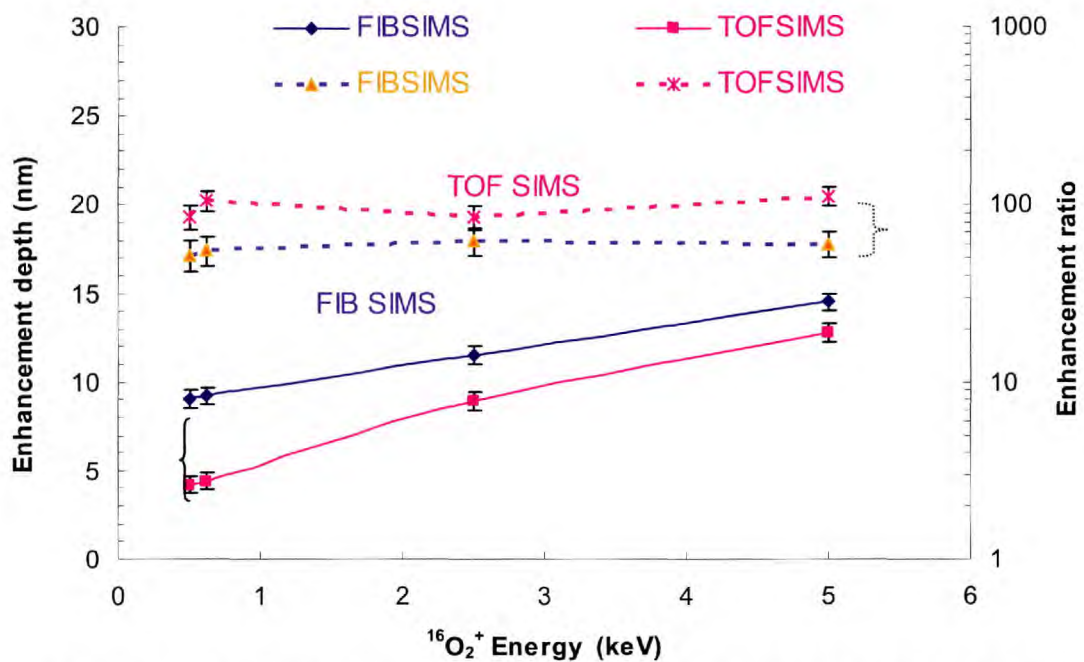


Figure 5.21 Ion yield enhancement depth and ratio obtained in the FIB 200 and the ION-TOF IV as a function of oxygen implant energy.

One possible explanation is that, if we look at the absolute $^{28}\text{Si}^+$ intensity from the depth profile of oxygen and nitrogen induced altered layers, tabulated in table 5.7, the maximum Si^+ intensity gained in the FIB SIMS increased much less dramatically with the beam source compared to that in the ION-TOF IV.

Maximum Signal Intensities $^{28}\text{Si}^+$		
FIBSIMS	Oxygen	~ 7,200
FIBSIMS	Nitrogen	~ 6,000
ION TOF IV	Oxygen	~ 120,000
ION TOF IV	Nitrogen	~ 7,000

Table 5.7 Maximum $^{28}\text{Si}^+$ intensity from oxygen and nitrogen induced altered layers.

It can be said that the transmission of the FIB SIMS is not optimised and needs to be developed. The oxide thickness gained with the FIB 200 was much larger than that found with the ION-TOF IV because of the larger projected range of a 30 keV Ga⁺ beam, the same reason as we observed in the previous sections. The oxide thickness increased with increasing oxygen implant energies.

Finally, we compared the ion yield enhancements observed with the two different primary sources, ¹⁴N₂⁺ and ¹⁶O₂⁺. Figure 5.22 shows the ion yield enhancement ratio in the FIB 200 and ION-TOF IV as a function of oxygen and nitrogen beam energy. As can be seen, the enhancement ratio due to oxygen implantation was about 60 which was three times more than that of nitrogen implantation (x20). The primary beam effect is demonstrated. The high electron affinity of oxygen favours electron capture and the ionisation probability of the sputtered atoms is greatly enhanced by the oxygen resulting in a much higher ion yield. However, with nitrogen implantation, the ionisation probability is less enhanced resulting in a smaller ion yield.

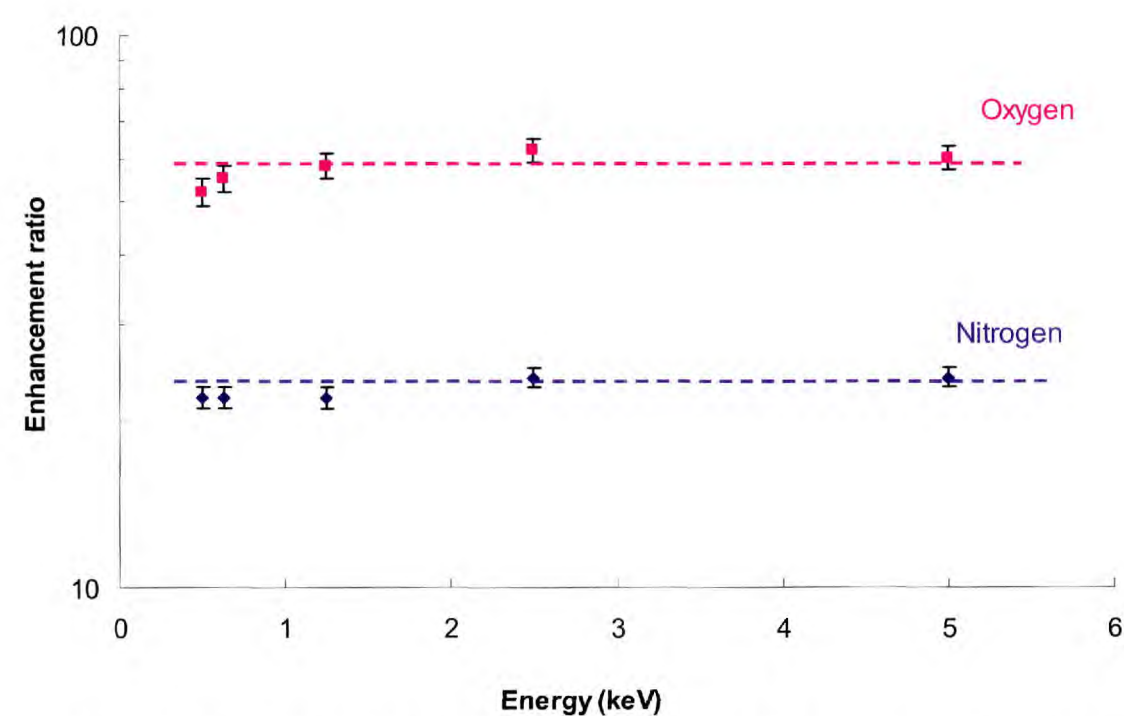


Figure 5.22a) The ion yield enhancement ratio of oxygen and nitrogen implantation as a function of beam energy, FIB SIMS.

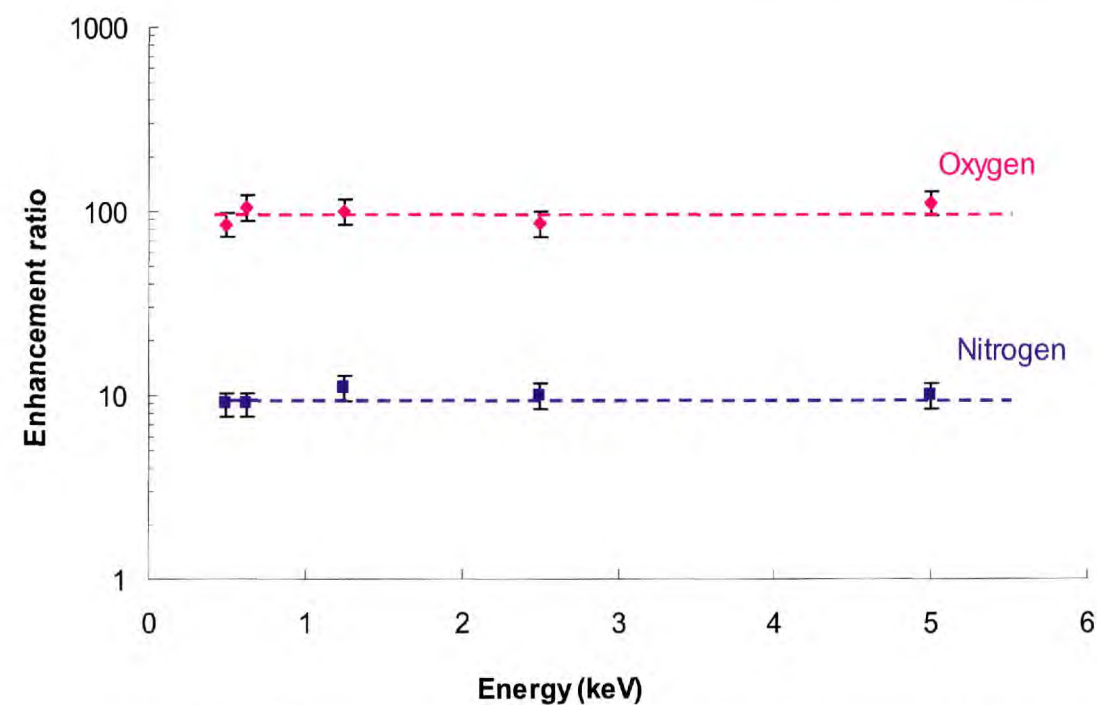


Figure 5.22b) The ion yield enhancement ratio of oxygen and nitrogen implantation as a function of beam energy, ION-TOF IV.

Figure 5.22c shows the enhancement ratio as a function of implantation dose.

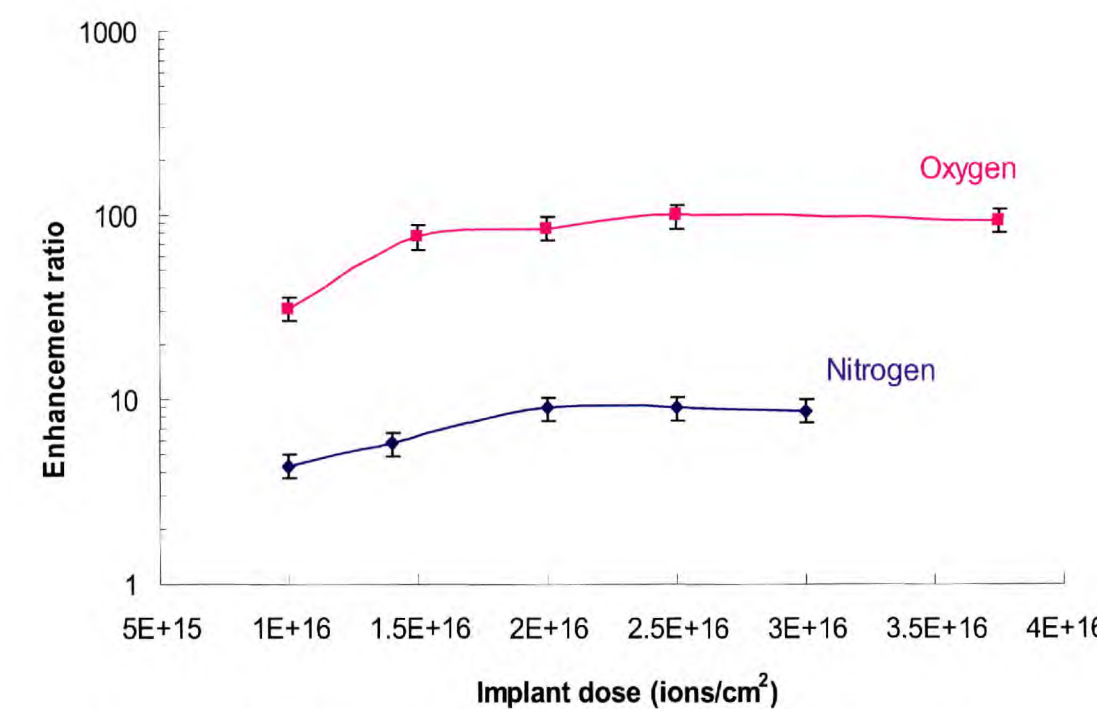


Figure 5.22c) The ion yield enhancement ratio of oxygen and nitrogen implantation as a function of beam dose, the implantation was done at an energy of 1.25 keV in the Atomika 6500. The depth profiles were done in the ION-TOF IV and shown in figure 5.11 and 5.18.

The trend of the enhancement ratio of oxygen and nitrogen was similar, i.e. the ion yield enhancement stopped increasing at the critical dose of 2×10^{16} N/cm² and 2.5×10^{16} O/cm². Again, the ion yield enhancement ratio of oxygen was much higher than that of nitrogen at all ion doses due to the high ionisation probability of oxygen. The enhancement ratio of $^{16}\text{O}_2^+$ implantation was about two orders of magnitude, however, for $^{14}\text{N}_2^+$ implantation, the enhancement ratio was one order of magnitude.

5.8 Oxygen Flooding Effect

Under oxygen flooding, the degree of ion yield enhancements largely depends on the oxygen pressure [8]. In this set of experiments, the oxygen/nitrogen induced altered layers were analysed with the ION-TOF IV with oxygen flooding at different pressures. Oxygen was implanted at 1.25 and 5 keV at normal incidence to form $500 \times 500 \mu\text{m}^2$ oxide layer. The nitrogen implanted altered layers were formed at two different primary energies 2.5 keV and 1.25 keV at normal incidence over an area of $500 \times 500 \mu\text{m}^2$. The implantation of O_2^+ and N_2^+ were carried out in the Atomika 6500. The experimental set-up is shown in figure 5.23.

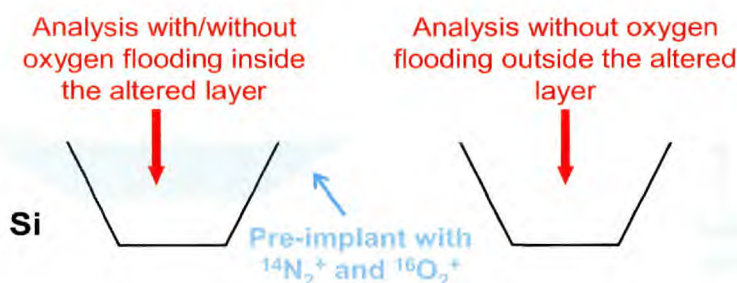


Figure 5.23 Experimental set-up of altered layer formation in Atomika 6500 and oxygen flooding in ION-TOF IV.

5.8.1 Oxide Layer Analysis

The experimental conditions used for oxygen pre-implantation and the ION-TOF IV analysis are tabulated in table 5.8. The oxygen flooding pressures used were 1×10^{-5} , 1.2×10^{-6} and 3×10^{-8} mbar. One depth profile was gained outside the altered layer without oxygen flooding, named as “native oxide layer” in figure 5.25.

Altered layer formation – Atomika 6500				
Beam	Energy (keV)	Area (μm^2)	Current (nA)	Angle ($^\circ$)
Oxygen	1.25 and 5	500×500	50	0
Oxygen flooding ION TOF IV				
Ar	1	200×200	13	45
Ga	25	150×150	1pA	45
Oxygen flooding pressure		1×10^{-5} , 1.2×10^{-6} and 3×10^{-8} mbar		

Table 5.8 The oxygen implantation conditions in Atomika 6500 and the oxygen flooding conditions in ION-TOF IV.

The method used to calculate the ion yield enhancement ratio and depth produced by the oxygen flooding is shown in figure 5.24. $Y_{(\text{max})}$ is the max intensity of

$^{28}\text{Si}^+$ with oxygen flooding, the ion yield enhancement depth was defined as the position where the max intensity of $^{28}\text{Si}^+$ reached to its half. A is the background intensity under oxygen pressure 1.2×10^{-6} mbar, B is the background intensity under oxygen pressure 3×10^{-8} mbar.

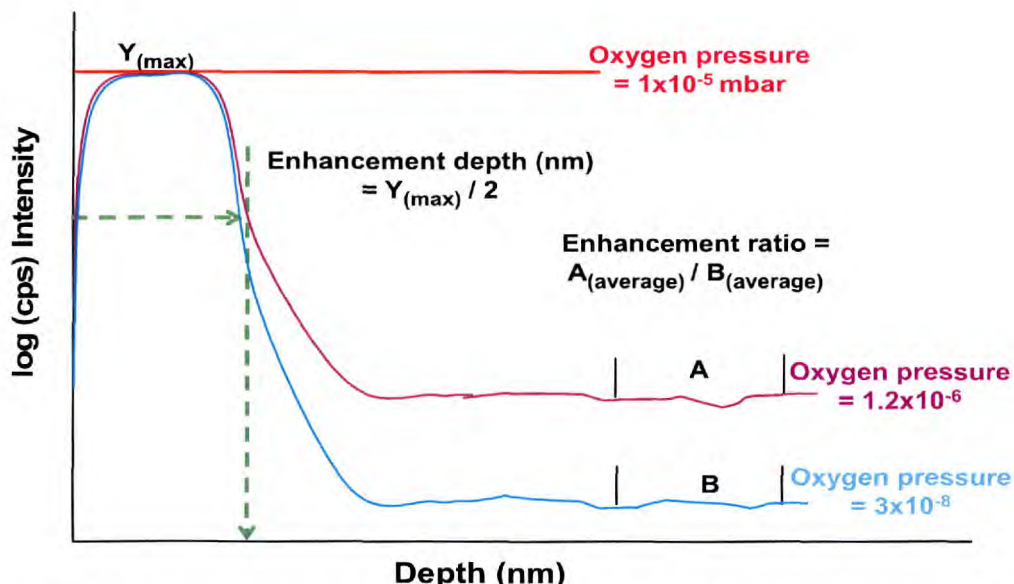


Figure 5.24 The method used to calculate the ion yield enhancement ratio and depth.

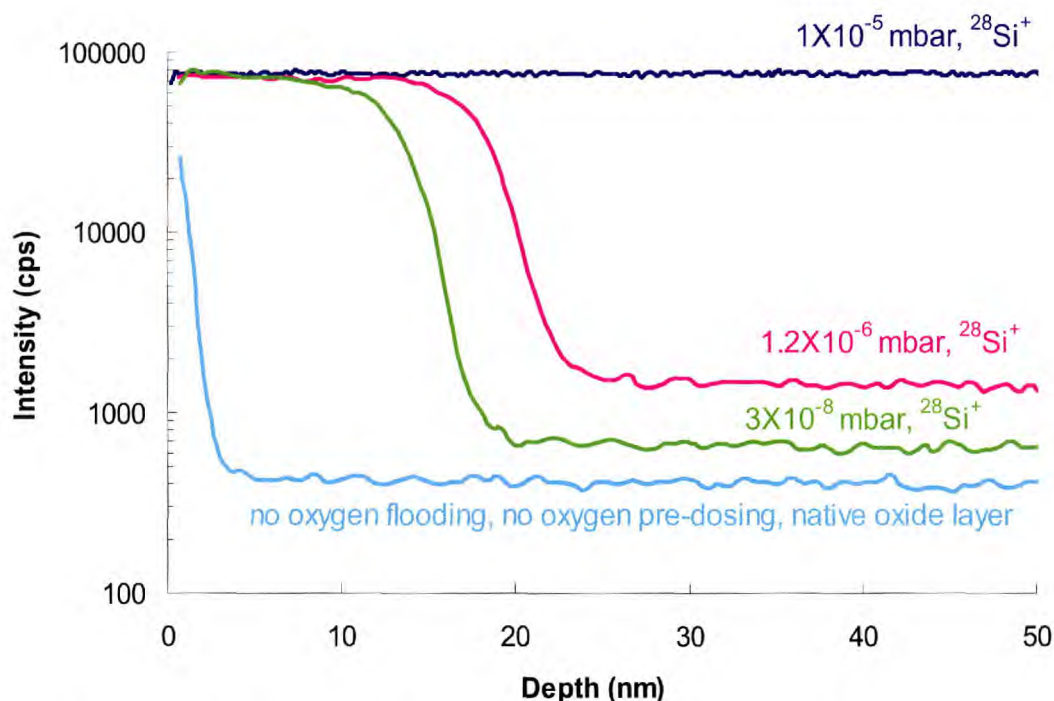


Figure 5.25a) The intensity of $^{28}\text{Si}^+$ as a function of oxygen flooding pressure. The analysis area was set in the $500 \mu\text{m}^2$ oxygen area; the oxygen was implanted at an energy of 5 keV in Atomika 6500. The analysis was done with the ION-TOF IV. One depth profile was done outside the oxygen area (blue line).

Figure 5.25 shows the depth profiles of $^{28}\text{Si}^+$, $^{73}\text{Ge}^+$, $^{44}\text{SiO}^+$, $^{16}\text{O}^+$, $^{23}\text{Na}^+$, $^{40}\text{Ca}^+$ and $^{39}\text{K}^+$ gained within the 5 keV oxygen induced altered layers under different oxygen pressures. In figure 5.25a the $^{28}\text{Si}^+$ signal stayed constant throughout the analysis under an oxygen flooding pressure of 1×10^{-5} mbar. When the flooding pressure was changed to 3×10^{-8} mbar (very little oxygen), the $^{28}\text{Si}^+$ signal stayed flat for a period of time, then dropped almost to background level. The flat topped signal was due to the prior implantation of oxygen. The key finding here is that both oxygen flooding and ion implantation give the same yield enhancement. However, when the analysis beam exceeded the depth of oxygen implantation (altered layer), the signal quickly dropped. A depth profile was gained from outside the oxygen raster area (blue line). The intensity was much lower and sharper than the ones gained inside the altered layer and it soon dropped down to the background level after a few seconds of primary beam sputtering. At an oxygen flooding pressure of 1.2×10^{-6} mbar, the profile showed a similar trend. But the ion yield enhancement depth was larger than that of 3×10^{-8} mbar. This demonstrated that some of the oxygen introduced into the analysis chamber reacted with the sample surface. The background intensities under the two oxygen pressures were different (1.2×10^{-6} and 3×10^{-8}) and higher than that without oxygen flooding. The difference could be a result of crater bottom roughness as this effect was not seen either with the highest oxygen pressure 1×10^{-5} mbar or without oxygen pressure [9]. Moreover, variations in the beam shape and current and crater edge effect could also affect the background intensity as well. The $^{44}\text{SiO}^+$ and $^{16}\text{O}^+$ intensities under the three different pressures are plotted in figure 5.25b. At a flooding pressure of 1×10^{-5} mbar, the signal intensities of $^{44}\text{SiO}^+$ and $^{16}\text{O}^+$ were stable. At a flooding pressure of 1.2×10^{-6} mbar, the $^{16}\text{O}^+$ signal was almost flat at the beginning of the profile; this is the result of pre-dosing of oxygen and oxygen flooding. When the analysis was being carried out with little oxygen flooding or no flooding (3×10^{-8} and native oxide layer), the intensity of $^{44}\text{SiO}^+$ and $^{16}\text{O}^+$ dropped to almost zero (≤ 1 cps) after the oxygen implant depth or native oxide layer. The $^{44}\text{SiO}^+$ and $^{16}\text{O}^+$ signal of the native oxide layer were the shallowest and the lowest.

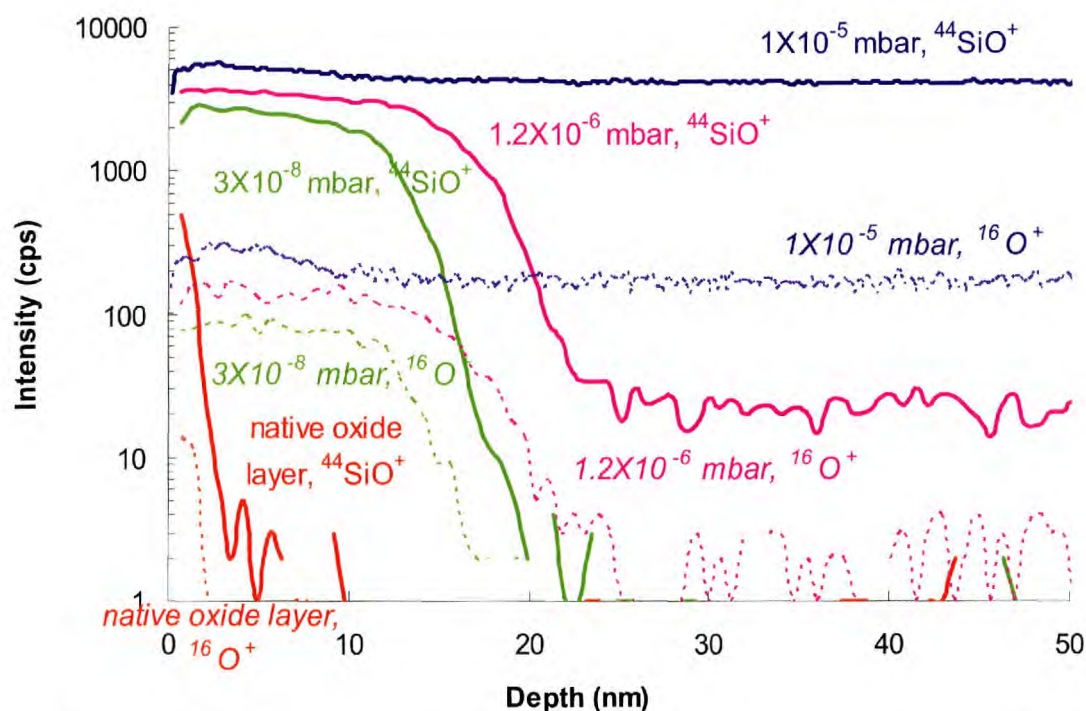


Figure 5.25b) The intensity of $^{44}\text{SiO}^+$ and $^{16}\text{O}^+$ as a function of oxygen flooding pressure. The analysis area was set in the $500 \times 500 \mu\text{m}^2$ oxygen area. One profile was done outside the altered layer (red line). Depth profiled with ION-TOF IV.

Some common surface contaminants were also monitored during the analysis, and the Na, Ca and K are plotted in figure 5.25c. This allowed us to locate the SiO_2/Si interface which could be used for the altered layer thickness estimation. That is, the surface contaminants (e.g. sodium) adsorbed on the sample surface from the ambient, were relocated during the oxygen implantation, until they reach the SiO_2/Si interface. Those contaminants were the perfect marker for the localization of the interface ^[10]. Under an oxygen pressure of 3×10^{-8} mbar, the peak of the $^{23}\text{Na}^+$, $^{39}\text{K}^+$ and $^{40}\text{Ca}^+$ profiles were at roughly around 13~14 nm which was almost the same as the altered layer thickness observed from the $^{28}\text{Si}^+$ depth profiles (see table 5.4). Under an oxygen pressure of 1×10^{-5} mbar more oxygen was introduced into the analysis chamber, thus, much less time was required for the profiles to reach the steady state due to the suppressed transient region and sputtering yield.

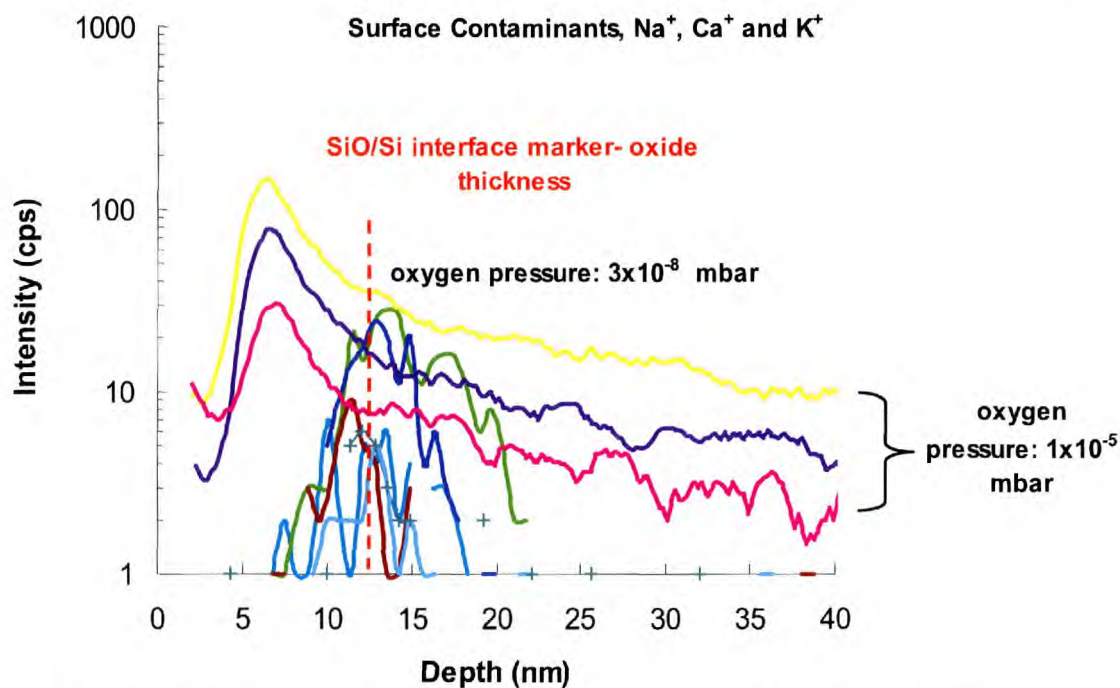


Figure 5.25c) Depth profiles of surface contaminants $^{23}\text{Na}^+$, $^{39}\text{K}^+$ and $^{40}\text{Ca}^+$, depth profiled with the ION-TOF IV.

The ion images of selected ions at different oxygen pressures of 1×10^{-5} , 1.2×10^{-6} and 3×10^{-8} mbar are shown in figure 5.26. The images were taken inside the 5 keV oxygen induced altered layer by the ION-TOF IV. The contrast of each individual ion image of the monitored ion is a function of ion intensity. The higher the ion intensity, the brighter the image is. The total intensity count of the monitored ion is also displayed under its ion image. As we can from the O ion image in figure 5.26a, the intensity count for O ion is 6873, as the oxygen flooding pressure changed from 10^{-8} mbar to 10^{-6} mbar to 10^{-5} mbar, the intensity count increased dramatically and the brightness of the image increased. Figure 5.26a the ion image was done inside the 5 keV oxygen formed layer with very little oxygen flowing into the analysis chamber (3×10^{-8} mbar), the secondary ion yields of all monitored ions were enhanced by the prior oxygen implantation, (b) sputtered at an oxygen flooding pressure of 1.2×10^{-6} mbar, larger ion yield enhancements were clearly observed, more oxygen was introduced into the analysis chamber, and ion images appeared brighter compared with (a), (c) more oxygen was leaked into the chamber at a flooding pressure of 1×10^{-5} mbar, a huge amount of oxygen flooded onto the sample surface as seen in the $^{16}\text{O}^+$ image, the $^{28}\text{Si}^+$ image appeared almost white. The big spot in the ion image was associated with the surface contaminants. This area was avoided when the depth profiles were reconstructed. The ion images showed a good agreement with the depth

profiles shown in figure 5.25. As the oxygen flooding pressure changed the secondary ion yield changed.

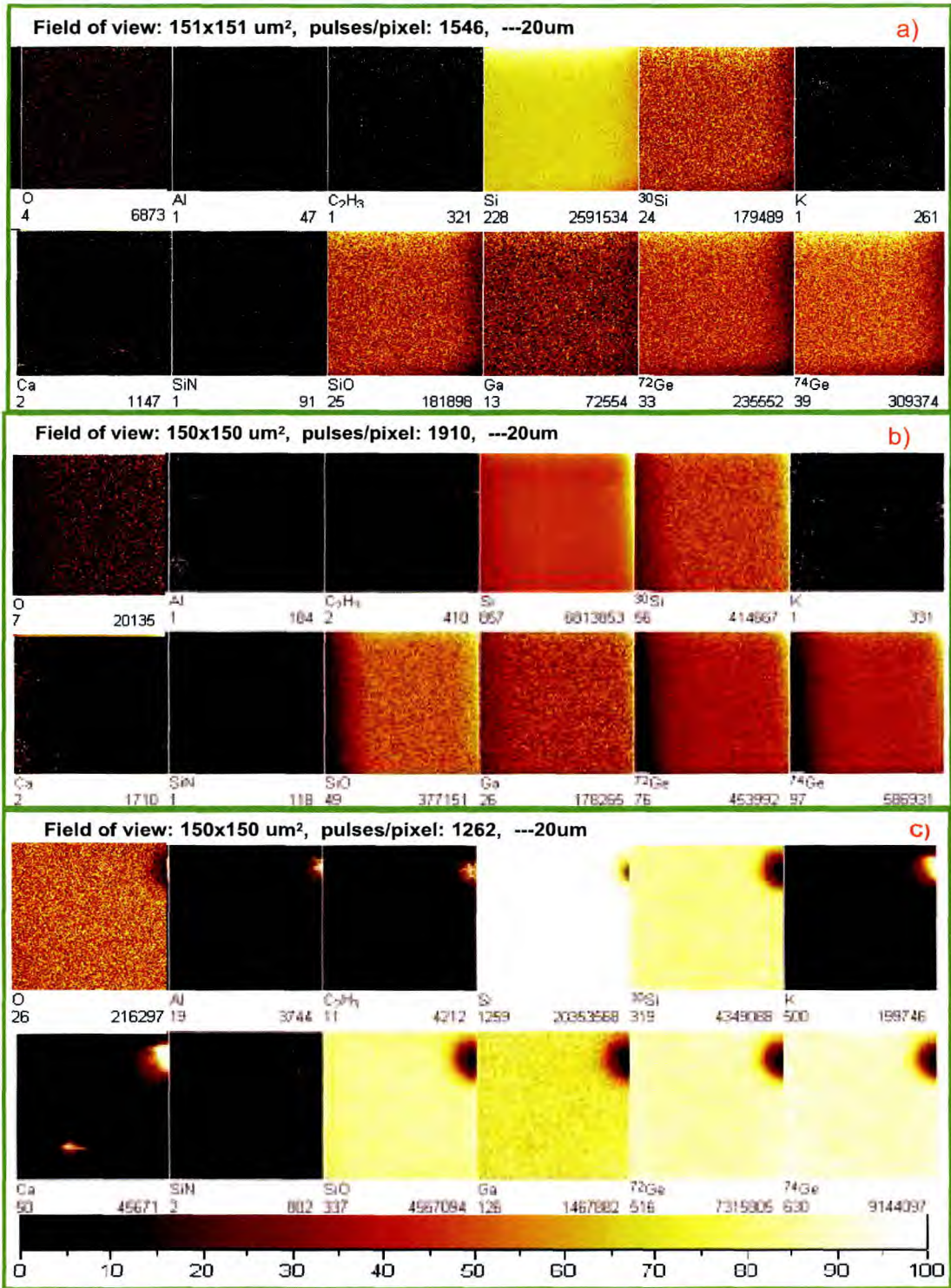


Figure 5.26 Ion images of selected ions under different conditions of oxygen flooding pressure: a) 3×10^{-8} , b) 1.2×10^{-6} and c) 1×10^{-5} mbar. Images were taken on the ION-TOF IV.

The ion yield enhancement ratios and depths are summarised in table 5.9. The maximum yield enhancement ratio was obtained under an oxygen flooding pressure of

1×10^{-5} mbar, the minimum was under an oxygen pressure of 3×10^{-8} mbar. The ion yield enhancement depth increased with oxygen pressure. At an oxygen pressure of 3×10^{-8} mbar, the ion yield enhancement depth was about 13.54 nm, but it increased to 18.35 nm when the oxygen pressure was increased to 1.2×10^{-6} mbar. The surface chemistry was changed when oxygen was introduced into the analysis chamber.

Oxygen pressure (mbar)	Enhancement ratio	Enhancement depth (nm)
1×10^{-5}	114	-
1.2×10^{-6}	3	18.35
3×10^{-8}	-	13.54

Table 5.9 Ion yield enhancements ratio and depth of different oxygen pressures.

The experiments were repeated with a 1.25 keV oxygen induced altered layer. The purpose is to (1) confirm the interpretation obtained above; (2) to investigate how the ion yield may change with different oxygen implantation energy during oxygen flooding. The oxygen induced altered layers were formed using an energy of 1.25 keV oxygen beam in the Atomika 6500. The oxygen flooding and depth profiling was carried out in the ION-TOF IV, and the sputtering conditions were the same as the experiments done above. The altered layers were analysed with oxygen flooding at a pressure of 1×10^{-5} mbar and without oxygen flooding. The experimental set-up is shown in figure 5.27 and the depth profiles are shown in figure 5.28.

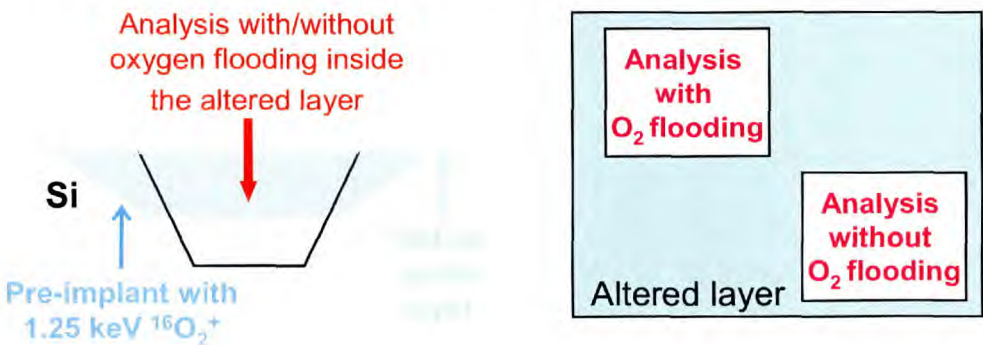


Figure 5.27 Experimental set-up for ION-TOF IV analysis with and without oxygen flooding inside the 1.25 keV oxygen beam formed altered layer.

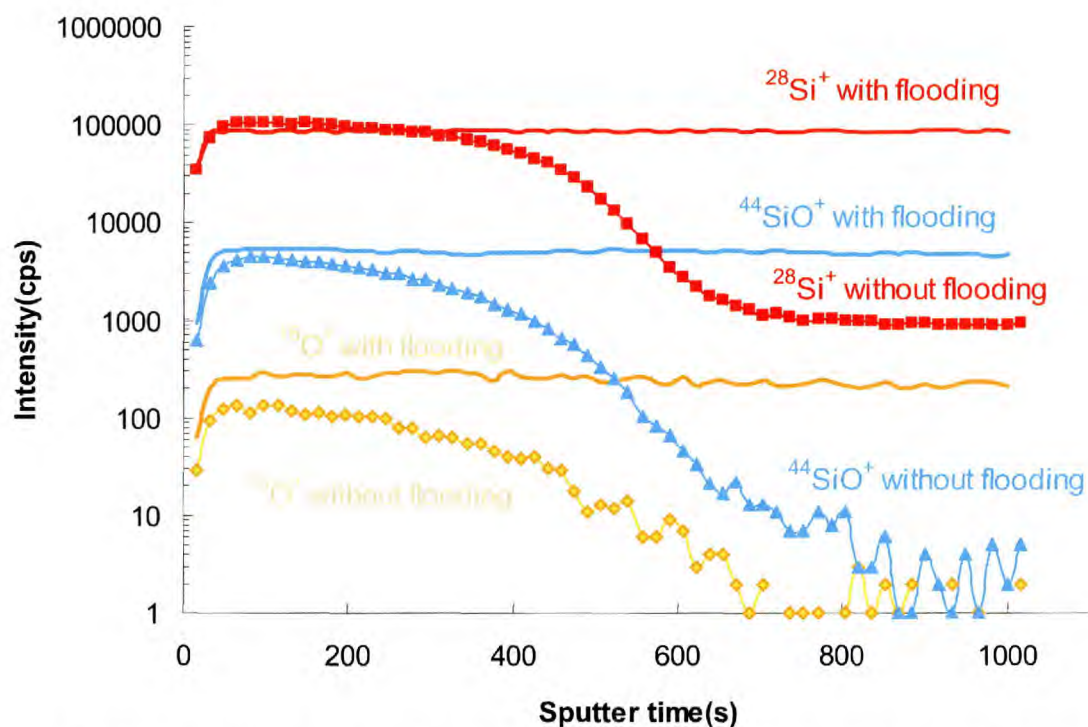


Figure 5.28 ION-TOF IV depth profiles obtained with/without oxygen flooding inside the altered layer formed by 1.25 keV oxygen beam in the Atomika 6500.

The $^{28}\text{Si}^+$, $^{44}\text{SiO}^+$ and $^{16}\text{O}^+$ signals stayed constant (straight line) with oxygen flooding. When the crater was analysed without oxygen flooding the intensities stayed almost constant only up to the oxygen implanted depth (7 ± 0.2 nm). Beyond this enhancement depth, the intensities dropped quickly and soon reached the steady state. Again, the intensity level of the monitored secondary ions with and without oxygen flooding was very similar, and the maximum ion yield enhancement was achieved. However, oxygen flooding provides an unlimited enhancement depth. For oxygen implantation, the enhancement depth can only be up to a certain depth depending on the oxygen implant energy and dose. The results have a good agreement with the studies shown above.

The ION-TOF IV ion images in figure 5.29 clearly showed that oxygen pre-dosing gave an obvious increase in contrast and brightness of monitored ions. In other words, the ion yield was much enhanced with oxygen implantation (e.g. $^{28}\text{Si}^+$, $^{44}\text{SiO}^+$). Some surface contaminants were also monitored.

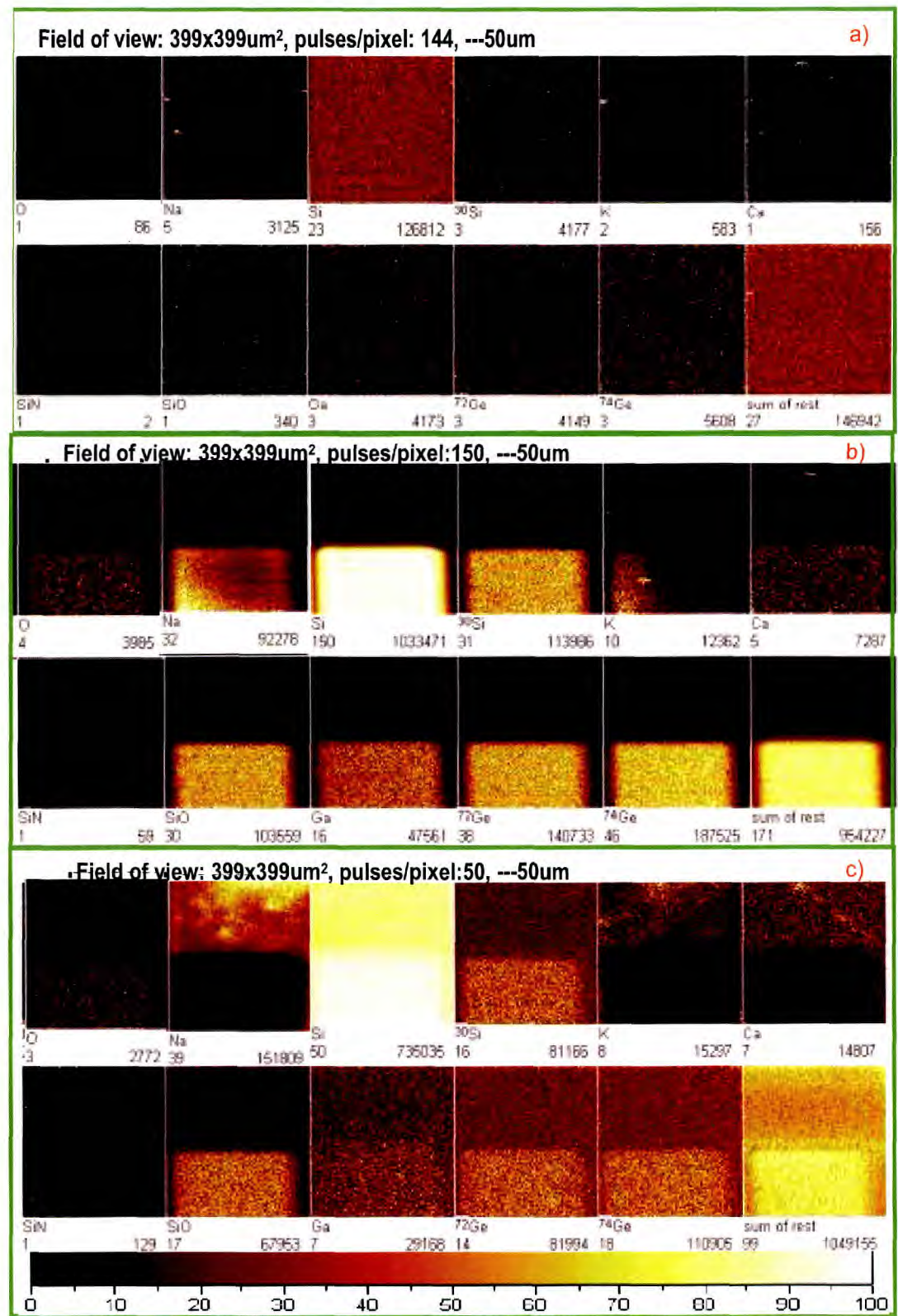


Figure 5.29 Ion images of selected ions of a) imaged with no oxygen flooding or prior implantation, b) imaged in the 1.25 keV pre-implanted oxygen crater, c) imaged in the 1.25 keV pre-implanted oxygen crater at an oxygen flooding pressure of 1×10^{-5} mbar. Images were taken on the ION-TOF IV.

Figure 5.29a the ion image was done with no prior oxygen implantation or flooding, (b) ion image of oxygen formed crater, and the ion intensity inside the crater was much higher than the one outside. As the figure shows, Si^+ , SiO^+ , Ge^+ were enhanced by the implantation of oxygen, so were some surface contaminants (e.g. $^{23}\text{Na}^+$, $^{39}\text{K}^+$ and $^{40}\text{Ca}^+$). If one compares (a) and (b), the total ion observed in (b) is much larger than that of (a), (c) the ion image was done inside the same crater as used in (b) but with oxygen flooding at pressure 1×10^{-5} mbar. The ion yield enhancements due to oxygen implantation and oxygen flooding were seen. The contrast of the ion image decreased compared with (b), this means the ions outside the oxygen crater were enhanced by the oxygen flooding. This illustrates one of the main limitations of oxygen flooding namely that one cannot control the area of the material that is chemically altered as precisely as with an ion beam. To compare oxygen flooding and oxygen implantation, the $^{28}\text{Si}^+$ image can be used. The Si^+ intensity inside the crater was slightly higher than that outside the crater, the sum of the rest (total ion) showed the same result. However, some surface contaminant ion images showed a different story. For instance, for $^{23}\text{Na}^+$, $^{39}\text{K}^+$ and $^{40}\text{Ca}^+$, the intensities inside the crater were lower than those outside the crater. The previous results (figure 5.24c) showed that the surface contaminants could be implanted deep into the layer, this might be the reason that the contaminants on the surface has a higher intensity than the ones that have been implanted into the layer.

5.8.2 Nitride Layer Analysis

So far, we have compared the ion yield enhancement produced by the oxygen and nitrogen implantation, and oxygen flooding. This showed that the oxygen was better than the nitrogen in improving the ion yield, and the oxygen implantation and flooding had the same yield enhancement ratio, and the $^{44}\text{SiO}^+$ was also influenced by the oxygen pressure in terms of thickness. It would be interesting to compare the ion yield enhancements produced by the nitrogen implantation and oxygen flooding. More importantly, to investigate how the $^{42}\text{SiN}^+$ intensity will vary with the pressure and the correlations between the $^{42}\text{SiN}^+$ and $^{44}\text{SiO}^+$. The experimental conditions are tabulated in table 5.10, the experimental set-up is shown in figure 5.30 and the ION-TOF IV depth profiles are shown in figure 5.31. The x-axis was not converted due to the shallow sputter depth and the rough crater bottom.

Altered layer formation – Atomika 6500				
Beam	Energy (keV)	Area (μm^2)	Current (nA)	Angle ($^\circ$)
Nitrogen	1.25 and 2.5	500x500	50	0
Oxygen flooding ION TOF IV				
Ar	1	300x300	13	45
Ga	25	200x200	1pA	45
Oxygen flooding pressure		1×10^{-5} , 4×10^{-6} and 3×10^{-7} mbar		

Table 5.10 The nitrogen implantation conditions in Atomika 6500 and the oxygen flooding conditions in ION-TOF IV.

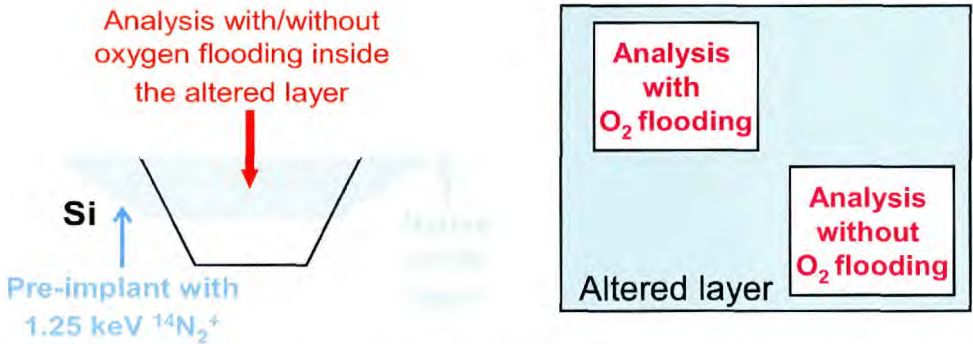


Figure 5.30 Experimental set-up for ION-TOF IV analysis with and without oxygen flooding inside the 1.25 keV nitrogen beam formed altered layer.

To compare the ion yield enhancement produced by the nitrogen implantation and oxygen flooding, the 1.25 keV nitrogen formed altered layer was analysed with (1×10^{-5} mbar) and without oxygen flooding, shown in figure 5.31. Without oxygen flooding the ion intensities soon reached background level after a short period of sputtering time. For example, the intensity of $^{44}\text{SiO}^+$ reached the background soon after the beam went through the native oxide layer. With oxygen flooding the $^{44}\text{SiO}^+$ and $^{16}\text{O}^+$ intensity signal stayed flat throughout the analysis. The three regions (region A, B and C) were seen in the $^{28}\text{Si}^+$ depth profiles and the ion yield enhancements due to the nitrogen implantation were easily seen without the flooding. The ion yield enhancement produced by oxygen flooding over nitrogen produced was X1 divided by X2. The ion yield enhancement due to oxygen flooding was X1 divided by Xb. It was found that the ion yield enhancement due to oxygen flooding was about 90 fold which was 9 times greater than that created by the nitrogen implantation.

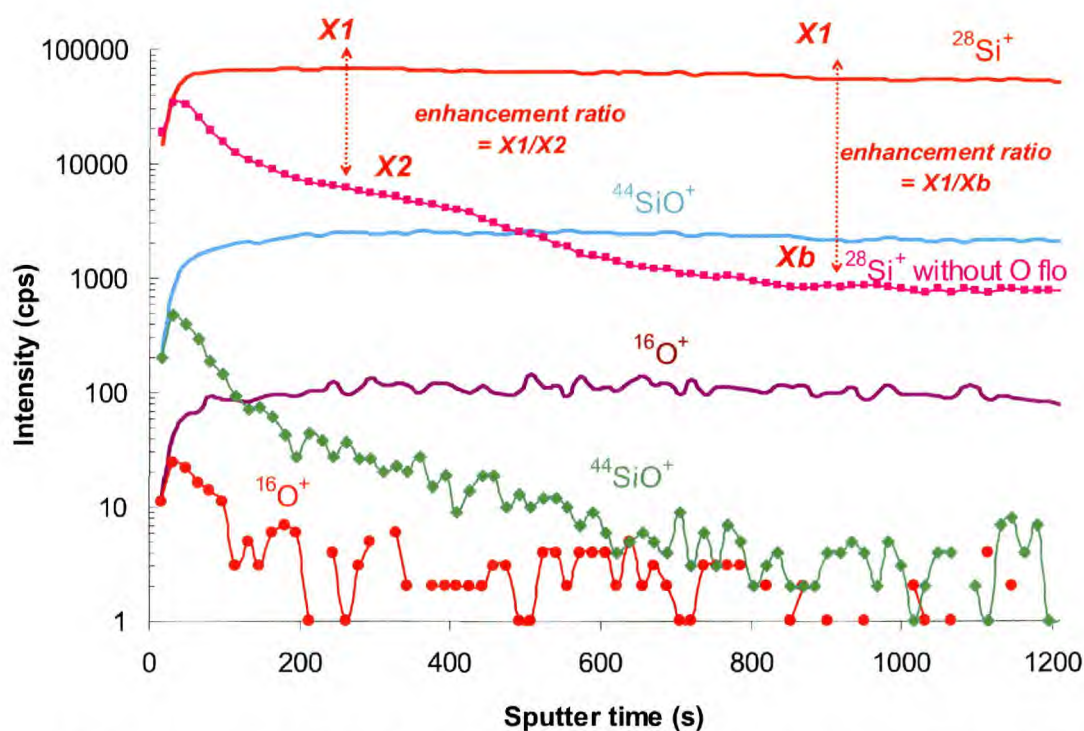


Figure 5.31 Depth profiles of several secondary ions with and without oxygen flooding in the altered layer formed by an oxygen dose of $3 \times 10^{16} \text{ O/cm}^2$. $X1/X2$ is the ion yield enhancement produced by oxygen flooding over nitrogen produced, and $X1/Xb$ is the ion yield enhancement produced by oxygen flooding.

To investigate how oxygen flooding pressure affects the $^{42}\text{SiN}^+$ layer and the correlations between the $^{42}\text{SiN}^+$ and the $^{44}\text{SiO}^+$ signal intensity, the 1.25 and 2.5 keV nitrogen induced altered layers were sputtered with oxygen flooding at different pressures namely: 1×10^{-5} and 4×10^{-6} mbar. As figure 5.32 shown, the $^{28}\text{Si}^+$ signals under the different oxygen pressures were the same, they quickly reached the steady state and stayed constant throughout the analysis. The implantation at different nitrogen energies had no effect on the $^{28}\text{Si}^+$ ion yields due to the oxidation of the substrate. In the $^{16}\text{O}^+$ depth profiles the intensity at an oxygen pressure of 4×10^{-6} mbar was slightly lower than that at the oxygen pressure 1×10^{-5} mbar despite the difference nitrogen implantation energy.

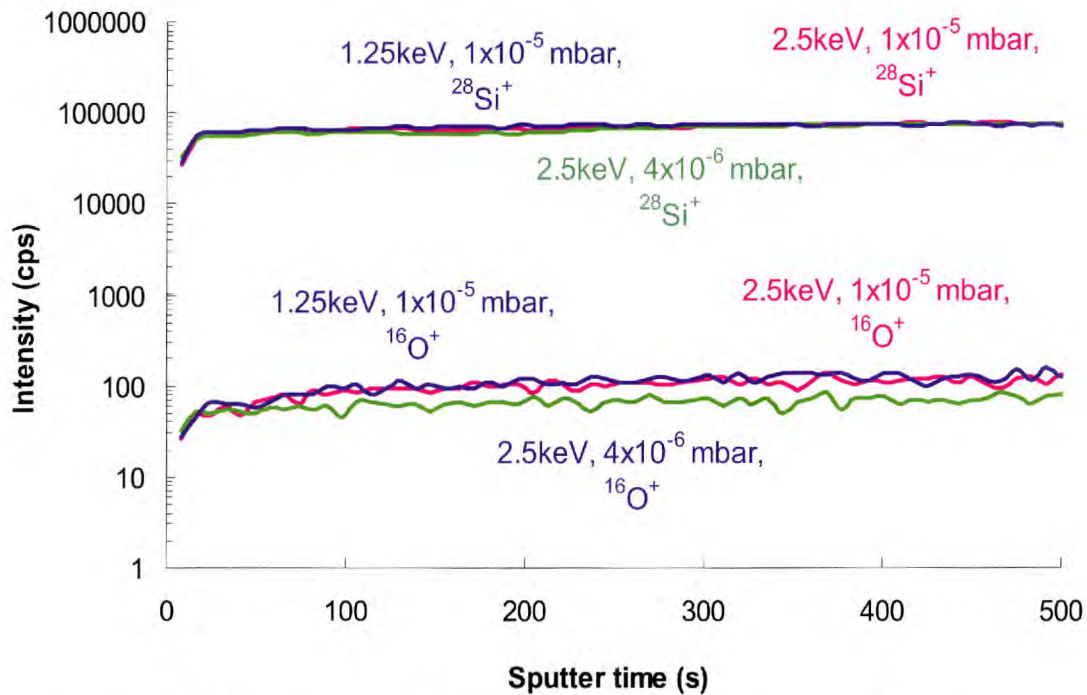


Figure 5.32 The intensity of $^{28}\text{Si}^+$ and $^{16}\text{O}^+$ as a function of oxygen flooding pressure. The analysis area was set in the altered layer, depth profiled with the ION-TOF IV.

The $^{44}\text{SiO}^+$ (solid lines) and $^{42}\text{SiN}^+$ (dot lines) depth profiles were plotted in figure 5.33. The $^{44}\text{SiO}^+$ intensity of 1.25 and 2.5 keV formed altered layers under oxygen pressure 1×10^{-5} mbar were similar. One could argue that for the first 450s, the $^{42}\text{SiN}^+$ intensity of 1.25 keV was slightly lower than that of 2.5 keV, which could be due to the different nitrogen implantation energy. But the difference is minor which can be ignored. When the pressure changed to 4×10^{-6} mbar, the $^{44}\text{SiO}^+$ intensity decreased indicating that less oxygen was introduced into the chamber. The $^{42}\text{SiN}^+$ depth profiles of the 2.5 keV formed altered layers under 1×10^{-5} and 4×10^{-6} mbar showed the same shape, and the $^{42}\text{SiN}^+$ intensity decreased very slowly to the steady state. The $^{42}\text{SiN}^+$ signal of 1.25 keV nitrogen formed silicon nitride layer gained under oxygen pressure 1×10^{-5} mbar decreased quicker compared with the other two. This suggested that oxygen flooding had no effect on the thickness of the nitrogen induced altered layer. As shown previously, the thickness of the altered layer is controlled by the implantation energy. The thickness produced by 1.25 keV nitrogen beam is smaller than that produced by the 2.5 keV nitrogen beam. The smaller the altered layer thickness is the faster the $^{42}\text{SiN}^+$ signal drops. Thus, the dependence of the altered layer thickness on implant energy was shown. Comparing the two $^{42}\text{SiN}^+$ profiles gained inside the 2.5 keV nitrogen induced altered layer at the oxygen

pressures of 4×10^{-6} and 1×10^{-5} mbar, they were almost identical and the thickness of the altered layers were the same.

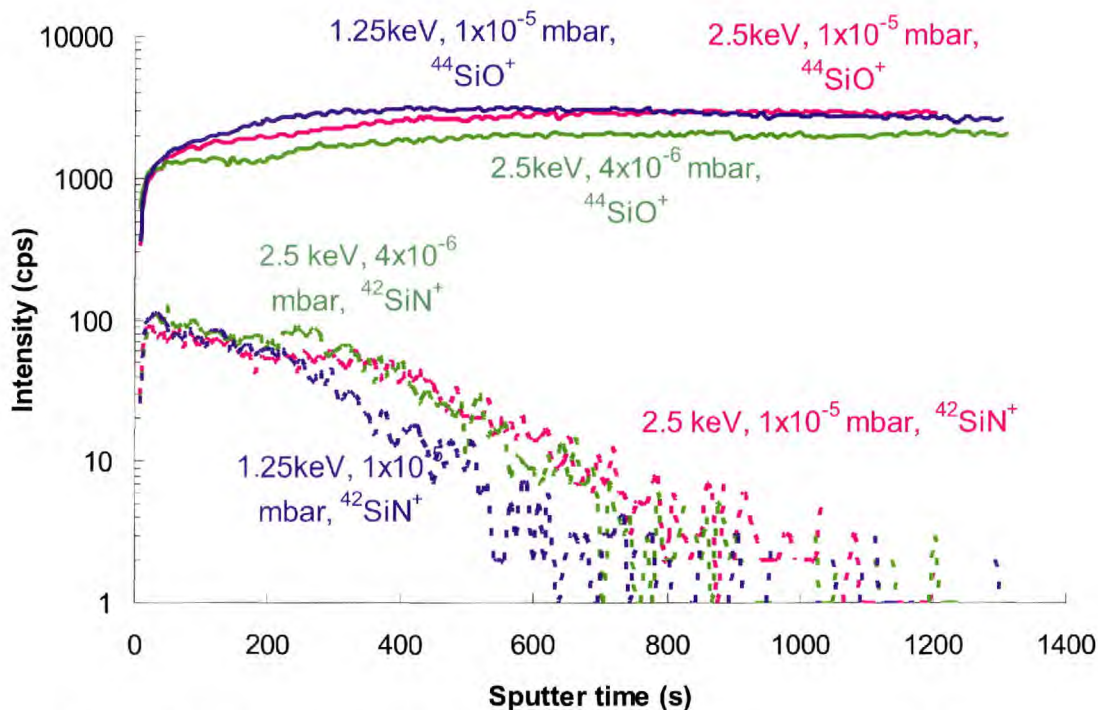


Figure 5.33 The intensity of $^{44}\text{SiO}^+$ and $^{42}\text{SiN}^+$ as a function of oxygen flooding pressure. The analysis area was set in the $500 \mu\text{m}^2$ altered layer. The nitrogen was implanted at 2.5 keV and 1.25 keV to form altered layers prior to ION-TOF IV measurement.

It was of interest to look at ion images from the nitrated region with and without oxygen flooding. Figure 5.34a shows the ion images inside the 1.25 keV nitrogen formed layer with very little oxygen flowing into the analysis chamber (3×10^{-7} mbar). Some contaminants were also seen. The great usefulness of this ion image is that it helps analysts to avoid the contaminated areas when the reconstruction of the depth profile is being made, so the analyst can actually select the area that they decide in which to do the depth profile. Figure 5.34b shows the ion image with oxygen flooding (1×10^{-5} mbar). 90% of the image was formed inside the 2.5 keV nitrogen crater and 10% was formed outside the crater (sample surface), the $^{42}\text{SiN}^+$ ion image showed that the intensity inside the crater was higher than that outside the crater. A huge amount of oxygen flooded onto the sample surface as seen in the $^{16}\text{O}^+$ image, The $^{28}\text{Si}^+$, $^{44}\text{SiO}^+$ and $^{72}\text{Ge}^+$ intensities were clearly enhanced by the oxygen flooding comparing with image (a), the $^{28}\text{Si}^+$ image appeared almost white. Again, this observation confirmed that oxygen provides better ion yield enhancement than

nitrogen. Another interesting observation is that, for $^{44}\text{SiO}^+ (^{72}\text{Ge}^+)$ image for instance, that the ion intensity inside the crater (90% of the image) was slightly lower than the one outside but it was almost the same.

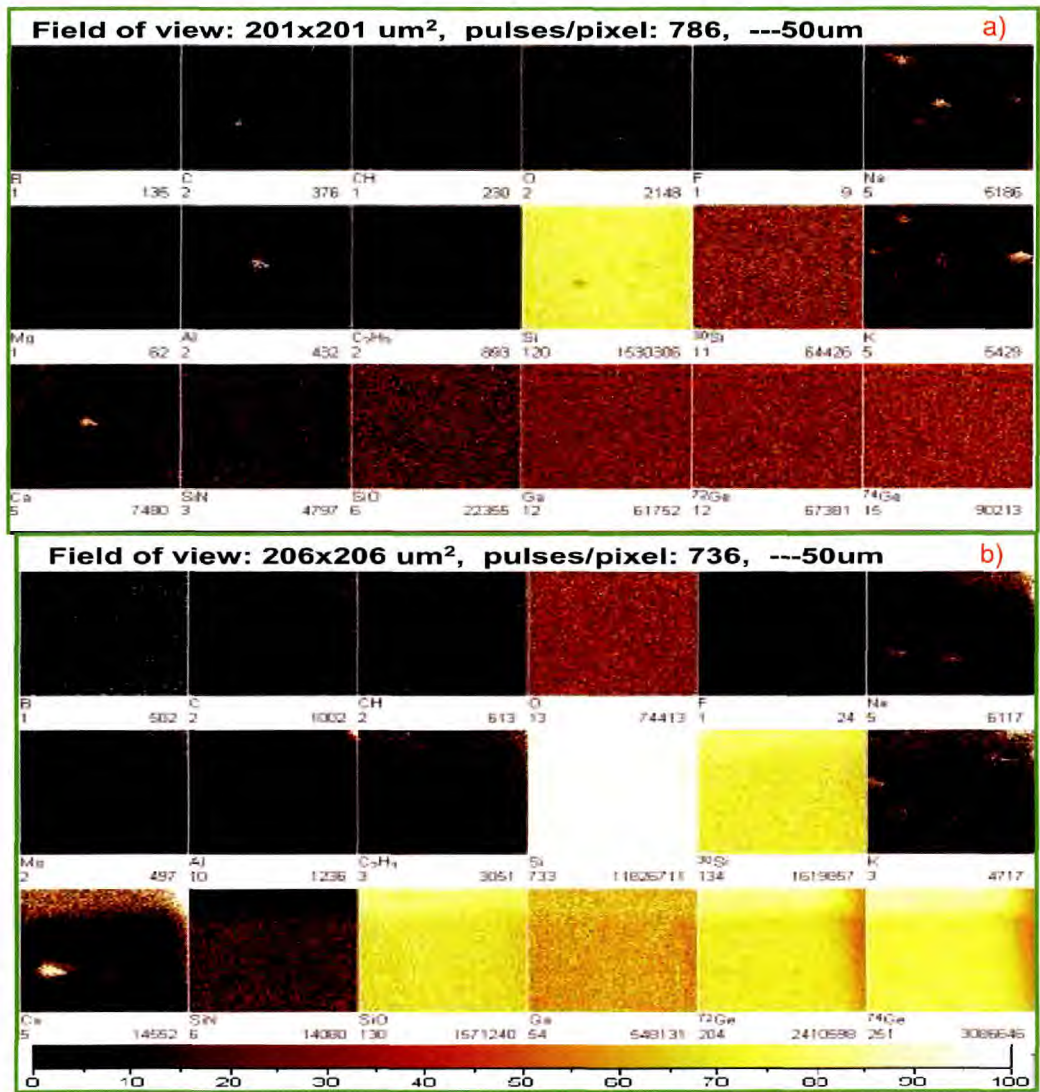


Figure 5.34 Ion images of selected ions of a) with no oxygen flooding, b) an oxygen flooding pressure of 1×10^{-5} mbar. Images were taken on the ION-TOF IV.

5.9 Conclusions

In conclusion, the positive ion yield was enhanced with oxygen flooding. It increased with oxygen pressure, and the ion yield enhancement depth showed the same effect. This effect can be simply explained for as the oxygen flooding pressure increases, more oxygen is introduced into the analysis chamber and the coverage of the oxygen on the sample surface is larger resulting in a higher ionisation probability. Equally important, under a dynamic SIMS conditions, a large amount of adsorbed oxygen on the surface is implanted into the material leading to oxide formation. In

consequence, the positive ion yield is enhanced. Under intermediate oxygen pressure conditions, the positive ion yield is not enhanced as much as that under high oxygen pressure. The crater bottom roughness was also observed at this level of oxygen pressure (figure 5.25a). At high oxygen pressure or with no oxygen flooding, the crater bottom was much smoother. With oxygen implantation, the ion mixing is higher at high ion implantation energy, and the whole profile is shifted away from the surface. Analysing the nitrogen induced altered layers with oxygen flooding shows that the ion yield enhancement due to the nitrogen implantation was overshadowed by the oxygen flooding. The ion yield was enhanced by the oxygen flooding but the thickness of the altered layer ($^{42}\text{SiN}^+$) was not dependent on the oxygen pressure but the nitrogen implantation energy. Furthermore, the $^{44}\text{SiO}^+$ signal intensity was not suppressed by the nitride layer. The oxygen implantation provided the same ion yield enhancement ratio as the oxygen flooding (at 1×10^{-5} mbar) did which was about two orders of magnitude and, nitrogen implantation provided a lower ion yield enhancement ($\sim \times 30$) as the ionisation efficiency provided by the nitrogen is not as good as oxygen. The main advantages of oxygen flooding are that it provides an unlimited enhancement depth, reduces the crater roughness, and most importantly, it is much cheaper! However, with oxygen flooding the features will also be distorted and the depth profile may not be 'real'. For oxygen implantation, the most important advantage is that it allows the analyst to direct the oxygen beam only on the area of interest, and the implantation area and depth can be precisely controlled without any hassle.

5.10 Reference

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Chapter Six

6. Damage During Chemical Modification

6.1 Introduction

It is very important that the strategies for chemical modification of the surface described in chapter 5 do not themselves impart unacceptable levels of damage into the material to be measured. A specially grown AlGaAs/GaAs test structure was used to investigate the damage induced by the primary beam implantation by using the SIMS analysis and cross-sectional TEM techniques. The great advantage of this material is the quality of the interface which can be easily resolved in SIMS. Moreover, the typical roughness for MBE AlGaAs/GaAs structures lies in the range of 0.5 to 1.5 nm ^[1]. These strategies were very useful in understanding the effect of chemical modification of the sample surface.

The AlGaAs test structure used was a GaAs sample with 12 delta layers grown by Professor M.Hopkinson at the University of Sheffield. The structure was grown by MBE with a growth temperature of ~590°C, at which diffusion would be completely negligible. The growth rate for GaAs was 0.226 nm/s and the GaAs has a density of 4.5×10^{22} atoms/cm³ (or a surface density of 1.25×10^{15} atoms/cm²). The growth rate for AlGaAs is a bit more, and a good interface was achieved. The delta layers were nominally doped at 4.2×10^{13} (Al_{0.042}Ga_{0.958}As) and 1.25×10^{14} atoms/cm² (Al_{0.1}Ga_{0.9}As). The structure starts with five deltas, separated by a spacing of 5 nm, followed by five deltas at a 10 nm separation, then the two further deltas with spacing of 15 nm respectively. A schematic view of AlGaAs delta layers in GaAs is shown in figure 6.1.

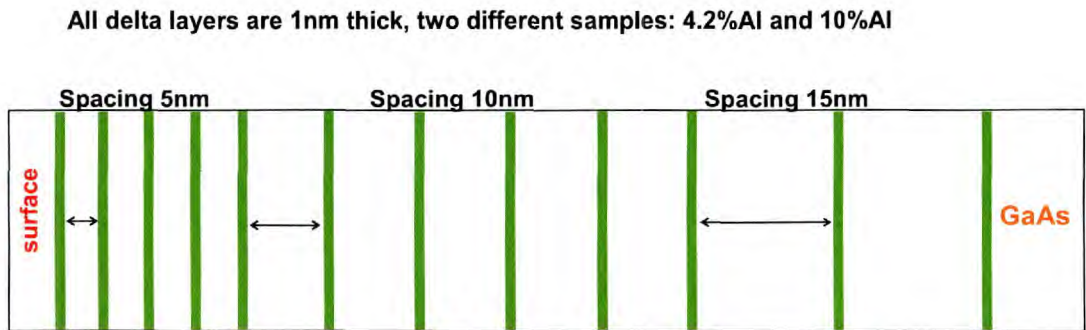


Figure 6.1 AlGaAs delta layers in GaAs

The samples were depth profiled in the Atomika 6500 and the ION-TOF IV. In the Atomika 6500, a nominal concentration of Al 10% Al(10) sample was bombarded with $^{16}\text{O}_2^+$ and $^{14}\text{N}_2^+$ beams at normal incidence. The crater edge effects were minimised by using 6.3% area electronic gating positioned at the centre of the crater. The Al(10) sample was also used in the ION-TOF IV, the incident angle of the sputter gun Ar^+ and the analysis gun Ga^+ was fixed at 45° , and the analysis was done in the interlace mode. The fixed incident angle is just at the boundary of the on-set of roughness, as was revealed in a detailed study of the depth resolution of sputtering with O_2^+ and Cs^+ bombardment at different energies and incident angles ^[2, 3]. The secondary ions monitored were $^{27}\text{Al}^+$, $^{71}\text{Ga}^+$, $^{74}\text{As}^+$ and $^{139}\text{Ga}_2^+$. The sputtering conditions are summarised in table 6.1. The final depth was measured on the Zygo. For 5% nominal concentrations, see appendix 3.

Beam	Energy (keV)	Area (μm^2)	Current (nA)
O_2^+	0.5, 1.25, 2.5	500x500	~60
N_2^+	0.5, 0.625, 1.25	500x500	~60
Ar^+	0.5, 1, 3	300, 200	14, 2.5
Ga^+	25	150, 100	0.001

Table 6.1 Sputtering conditions used on the Atomika 6500 and the ION-TOF IV.

6.2 FIB TEM Specimen Preparation

FIB TEM specimen preparation has been widely used in the preparation of specimens for TEM due to several advantages such as large thin areas of uniform thickness, and specific regions of interest that can be located with precise accuracy ^[4-7]. However, because of the high Ga^+ energy used (30 keV), lattice defects and regions of amorphous materials can be created. The damaged layers can be present on both sides of the specimens and sidewall and bottom wall. The width of the amorphous layer can be as large as 50 nm ^[8]. The large damaged layer presented in the thin TEM specimens can cause significant reduction in the TEM resolution. Many methods have been developed to reduce the FIB damage to TEM samples such as gas-assisted etching (GAE), low energy FIB, wet/dry etching and cleaning by broad argon beam ion milling ^[5, 9-11]. Figure 6.2 shows some results of reducing the FIB damage, (a) shows the TEM specimen prepared by the FIB milling, the damaged and undamaged

layer was resolved, (b) shows the side-wall of a specimen fabricated by gas-assisted etching (GAE). GAE uses a combination of a FIB and a reactive halogen (Iodine) gas. In the FIB system, halogen gas is delivered to a specimen surface via a nozzle while the beam is scanned over a defined area ^[12]. However, the damage seemed not reduced dramatically by this technique, (c) shows the specimen prepared by low energy FIB milling. In this technique, the final thinning was done by a 10 keV Ga beam rather than 30 keV, as a result, the damage was much reduced, (d) uses broad ion beam milling, that is after the fabrication by 30 keV FIB milling, the specimen is 'cleaned' by a broad Ar beam for a short time, (e) the most effective method was claimed to be the wet etching, after the fabrication by the FIB, the specimen was dipped in a mixture of nitric and hydrofluoric acid in the ratio of 199:1 for several seconds ^[5]. However, the degree of the damage removed depends on many experimental conditions and aspects, and a simple conclusion seems difficult to make.

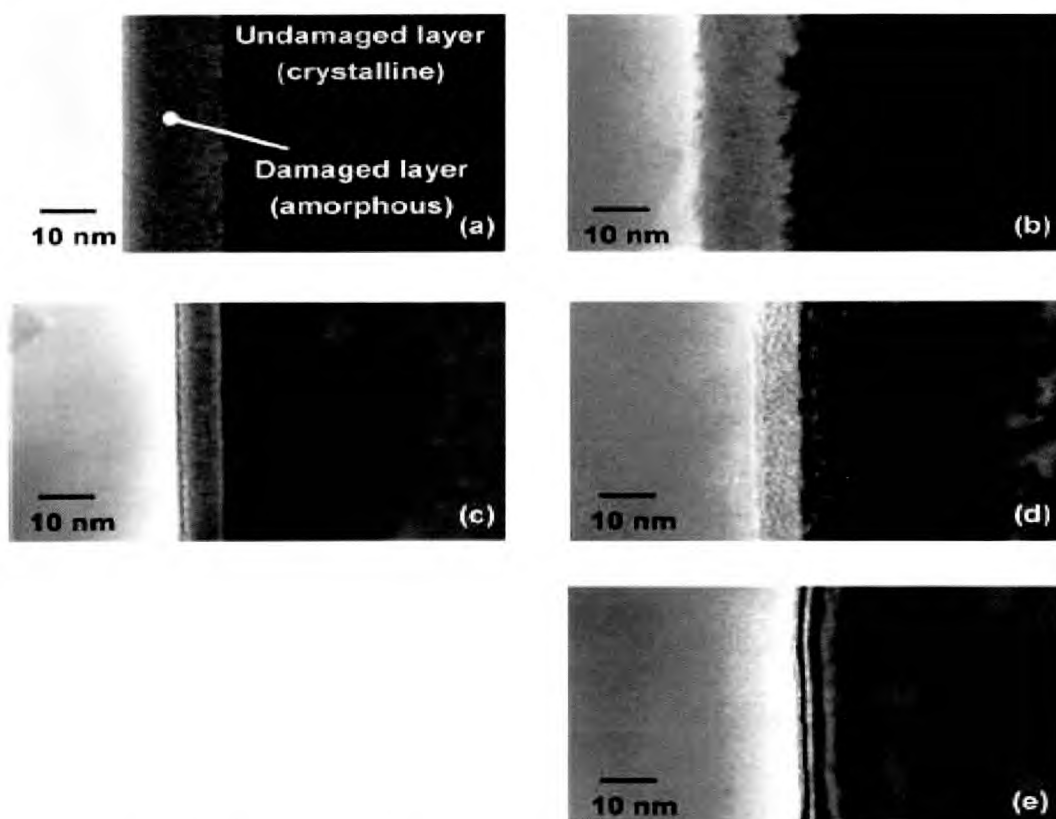


Figure 6.2 TEM images of a FIB prepared Si sample: a) 30 keV FIB etched without gas, b) 30 keV FIB etched with iodine gas, c) 10 keV FIB etched without gas, d) milled with a broad Ar^+ beam after 30 keV FIB etching, e) wet etched after 30 keV FIB etching ^[5].

In this project, the FIB TEM specimen preparation involves deposition of platinum (Pt) strip on the top of the area of interest to protect this area from beam

damage. FIB imaging was used for this purpose (i.e. locate the area of interest, and the deposition of the Pt strip). However, the near surface region of the specimen may be damaged during FIB imaging and the deposition of the Pt strip. Therefore, it is necessary to coat the sample surface with a protective metal film (e.g. Au, Cr) prior to any FIB examination ^[13]. Gold was used for FIB TEM specimen preparation in this project.

The gold sputter coating was carried out at a 20 mA plasma current in an argon atmosphere with the pressure at approximately 1×10^{-2} mbar, the final thickness of the gold layer is about 70 nm. It has been reported that sputter coating of gold can result in amorphous films with non-uniform thickness ^[13]. The sample rotation technique can be used to avoid non-uniform coating. The required thickness of the protective film (e.g. gold) should depend on the material used and be greater than implantation length of gallium ions in this material. It was found that the application of a gold layer at least 60 nm in thickness should be made prior to any FIB processing.

The most difficult and important step was to locate where the beam formed craters were after the deposition of the gold for FIB “lift-out”. It was impossible to see the gold covered craters in the FIB 200. Luckily, they were seen under the Zygo. The procedures to locate the craters and put Pt bars on the areas of interests are as follows: first of all, the gold covered sample was seen under the Zygo, and the craters were located. Secondly, a glass probe was used to scratch the sample surface around the crater (caution must be taken in order to avoid damaging the crater, glass probe not shown in figure 6.3). Thirdly, the sample was put in the FIB for Pt deposition, and the location of the crater was estimated in accordance with the scratches on the sample surface, then Pt was deposited. Fourthly, the sample was taken out from the FIB and, then put under the Zygo to make sure the Pt bar was deposited on the place of interests. If so, FIB TEM specimen preparation was carried on, otherwise, the craters were relocated. Figure 6.3 shows a gold coated crater with Pt deposition right on the edge of the crater wall, scratches around the crater were used as markers for finding the crater in the FIB 200. FIB TEM specimen preparation was carried out using the FIB 200 system with a 30 keV Ga^+ primary ion beam. The beam current used for sputtering varies from nA to pA, and the angle of incidence is usually set between 0° and 2° so that the etched surfaces of the thin area are parallel to each other. Figure 6.4 shows a schematic diagram of a TEM specimen fabrication procedure.

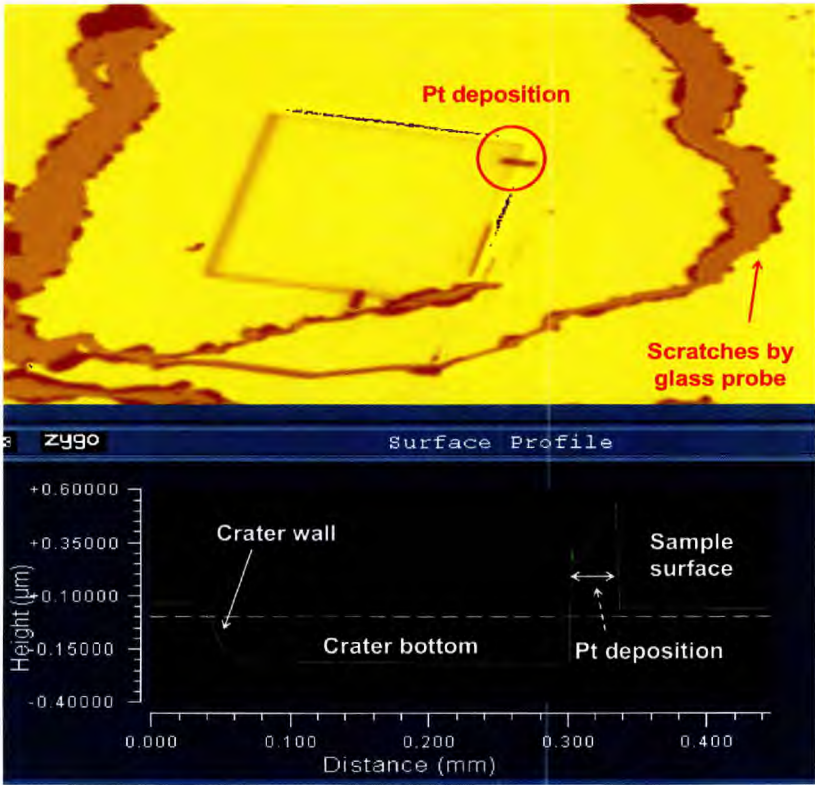


Figure 6.3 Zygo image and surface profile of the gold coated crater.

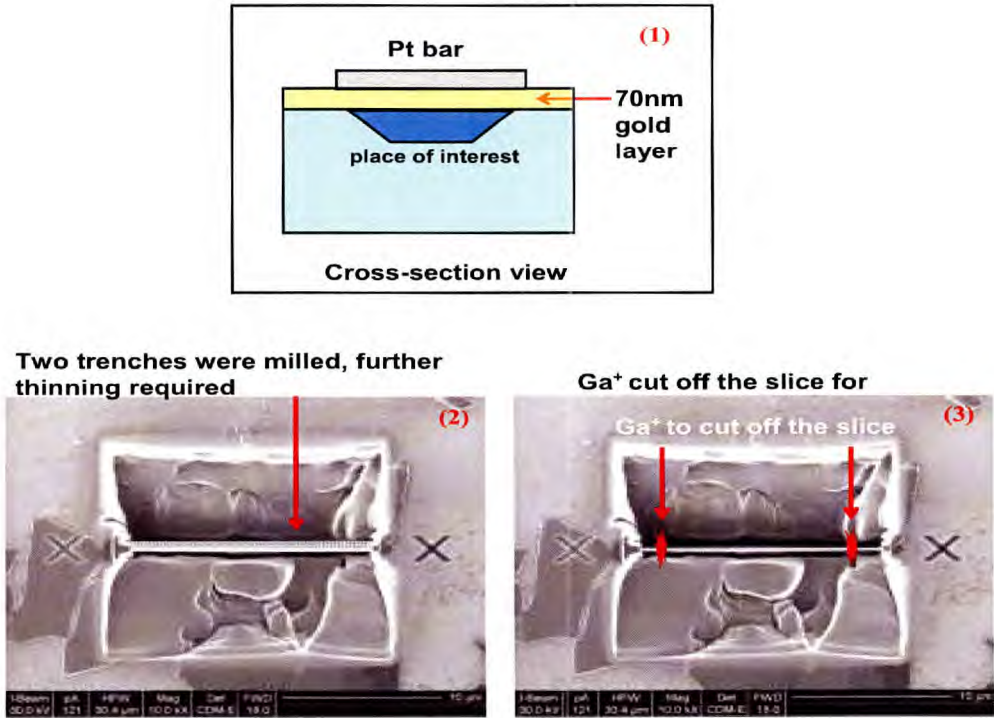


Figure 6.4 Shows (1) a cross-section view of the area of interest and deposition and, (2) and (3) FIB lift-out procedures.

SED imaging was used to locate the area of interest first. A 29 μm long platinum bar was then deposited on the top surface of the area of interest for protection. The deposition current and energy was 314 pA and 30 keV. Two trenches were milled on each side of the Pt bar to form a thin slice of material. Further thinning of this thin slice of material using a low beam current of 30 pA at $\pm 0.8^\circ$ was required to achieve an 80 nm thin electron transparent membrane. The EXLO is done by using a glass probe, shown in figure 6.5. The sample was now ready for TEM imaging

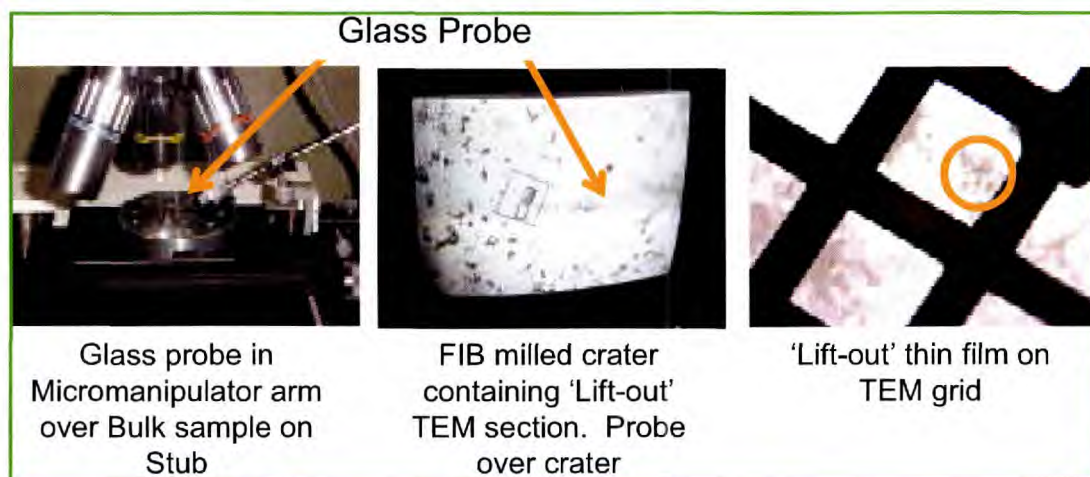


Figure 6.5 The ex-situ lift out using the glass probe. The glass probe was firstly positioned in micromanipulator arm over the bulk sample on the stub. The glass probe was then moved over the FIB milled crater containing the 'Lift-out' TEM section. Finally 'Lift-out' of a thin film on a TEM grid was carried out.

In section 6.1 and 6.2, the sample conditions and analysis conditions used for investigation of beam induced damages were introduced. The FIB TEM specimen preparation procedures used in this project was also documented. The results are shown in the following sections.

6.3 Damage Induced by $^{14}\text{N}_2^+$ Bombardment

By depth profiling the delta layers with $^{14}\text{N}_2^+$ and $^{16}\text{O}_2^+$ at different sputter energies, the beam induced roughness and atomic mixing effects in the vertical domain can be measured. Surface roughening is mainly responsible for a decrease in peak intensity and peak broadening, while atomic mixing is often demonstrated by measuring the decay length of the trailing edge. This is very useful to investigate the in-depth damage caused by the primary beam during the chemical modification of the sample surface. We have shown that the thickness of the beam induced altered layer increased with increasing beam energy, and that this results in a larger ion yield enhancement depth. However, it is also well known that deeper ion penetration and a higher degree of atomic mixing occurs at higher beam energy. Hence, the possibility of the beam induced damage during ion bombardment can be revealed during this study. Figure 6.6 shows the $^{27}\text{Al}^+$ depth profiles obtained at different nitrogen beam energies at normal incidence.

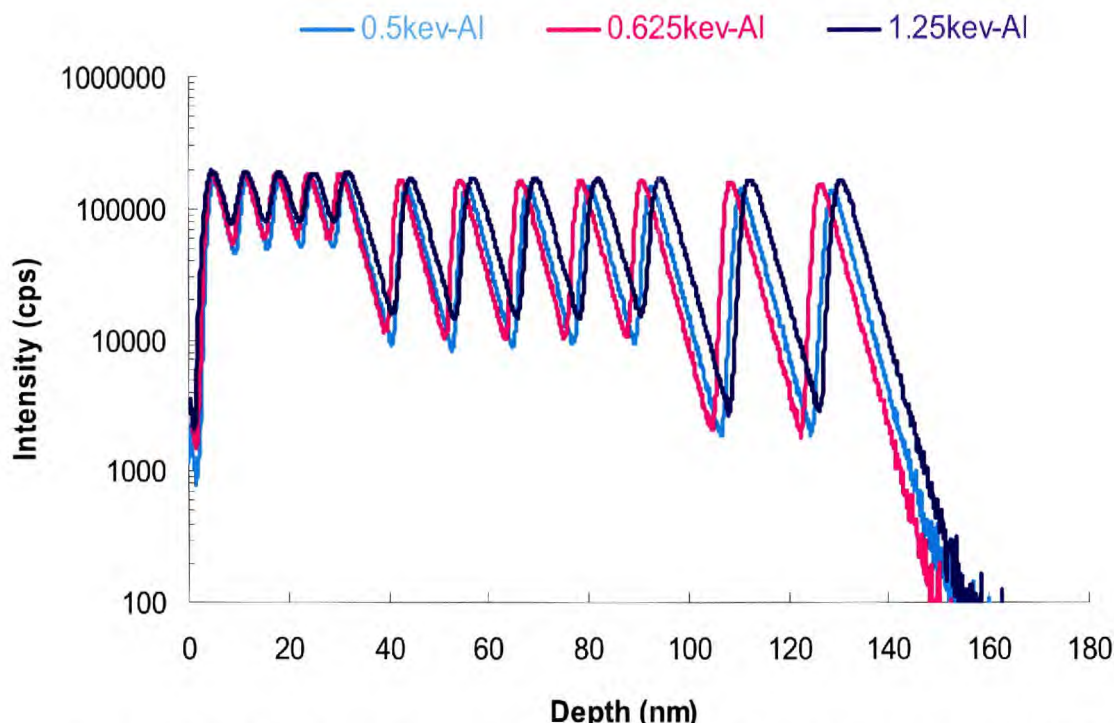


Figure 6.6 $^{27}\text{Al}^+$ depth profiles obtained at normal incidence bombardment with $^{14}\text{N}_2^+$ ions at energies of 0.5, 0.625 and 1.25 keV.

Clearly, very good depth profiles were obtained at all the energies used. The delta layers were nicely resolved and sharp. However, before the trailing edge of the first peak reached the background intensity level, the leading edge of the next peak

begins. This is a result of the ion mixing depth being comparable to the inter-delta layer spacing. For the first three delta layers, the profiles of all three energies were very close to each other, as the depth got deeper, the 1.25 keV depth profile shifted further from the surface. Comparing the peak-to-valley ratio (PVR), the 1.25 keV had the smallest PVR, the PVR of 0.5 and 0.625 keV was very similar but 0.5 keV was slightly better. The ion mixing effect due to high ion energy bombardment was observed. In addition, there was no coalescence or baseline drift seen here since these effects were often reported [2, 14, 15]. The roughness due to low energy bombardment at oblique angles is commonly observed. Since all the samples were bombarded at normal incidence in this project, roughness was not expected though Atomic Force Microscopy (AFM) could be used for further investigation. However, peak broadening with increasing depth and beam energy was seen, and this suggested that sputter-induced roughening occurred. Figure 6.7 shows the fourth Al delta layer obtained at different nitrogen energies. The peak broadening effect with increasing beam energy, the trailing edges at all three energies were always longer than the leading edges, this was due to the ion beam mixing effects.

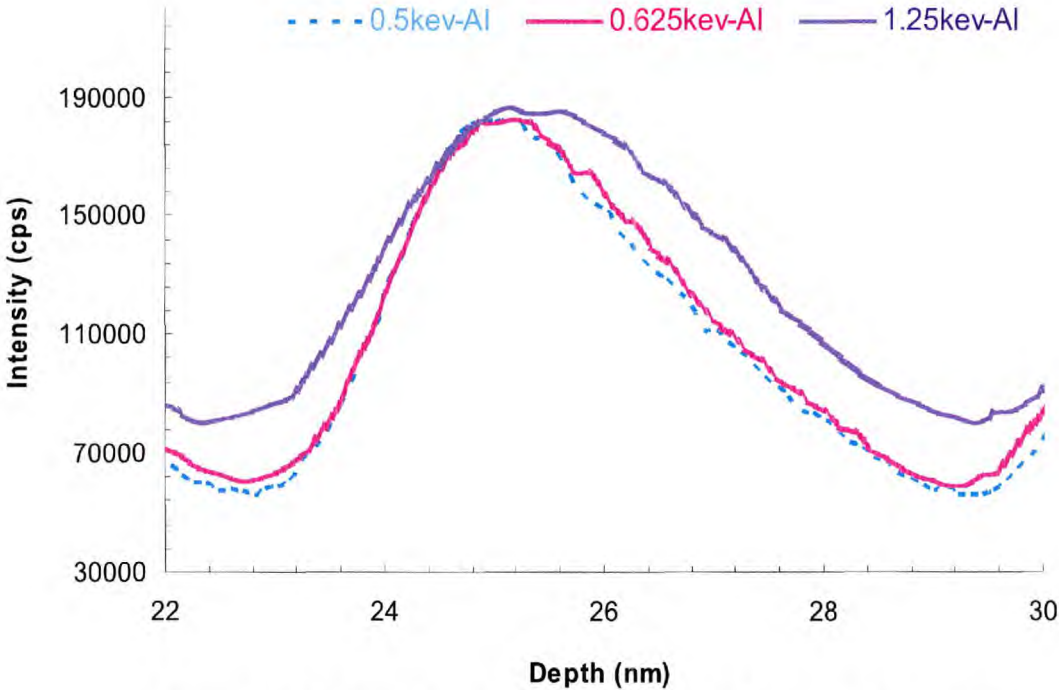


Figure 6.7 The fourth Al delta layer obtained at 0.5, 0.625 and 1.25 keV.

In the SIMS depth profiles of the delta layers, the ion mixing and roughness induced by primary ion bombardment are often measured by the decay length, λ_t (nm), which is the distance over which the intensity drops by a factor of e (2.7) or the decay

slope, Λ_d (nm/decade), which is the depth over which the signal changes by a factor of 10 and Full-Width-Half-Maximum (FWHM). Figure 6.8 shows the parameters that are commonly used to measure the ion mixing and roughness.

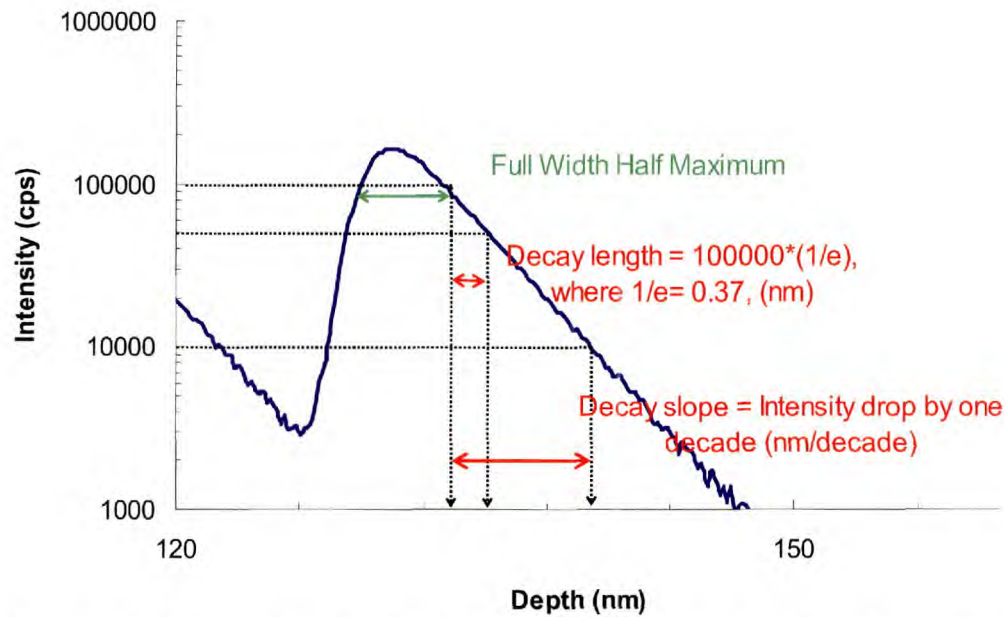


Figure 6.8 The parameters that are used for ion mixing and roughness measurements.

Figure 6.9 shows the decay length of the $^{27}\text{Al}^+$ peaks obtained at various nitrogen sputtering energy at normal incidence against delta layer index.

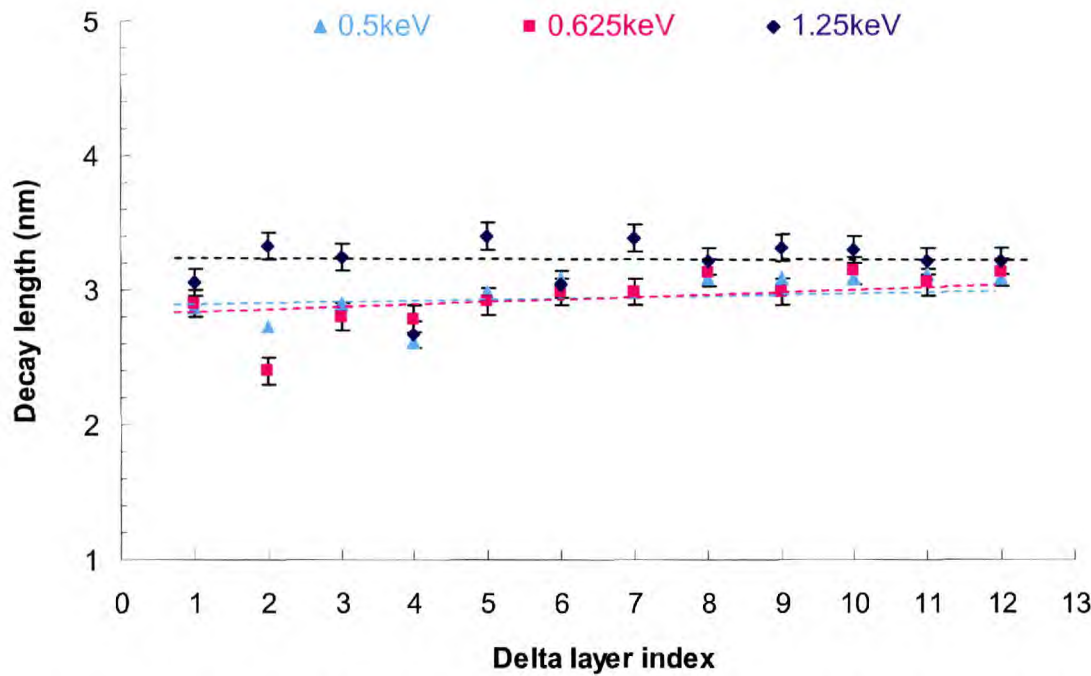


Figure 6.9 The decay length of the Al delta layers as a function of delta layer index for 0.5, 0.625 and 1.25 keV $^{14}\text{N}_2^+$ bombardments.

At a bombarding energy of 1.25 keV, the decay length was the largest, and the average value for this energy was about 3.20 nm. The difference in decay length between the lowest and the highest was about 20%. The 0.5 and 0.625 keV decay length was very similar (0.5 keV was slightly better) with no more than 3 nm throughout the analysis depth. The difference between the lowest and the highest was about 20%. The difference could be due to the fact that the deeper delta layers have longer diffusion times during growth. A general trend was obtained that was the decay length of all three energies stayed almost constant throughout the analysis with negligible increase with increasing depth. At higher beam energy the ion mixing effect becomes severe. Figure 6.10 shows a plot of decay slope against projected range of different nitrogen sputter energies.

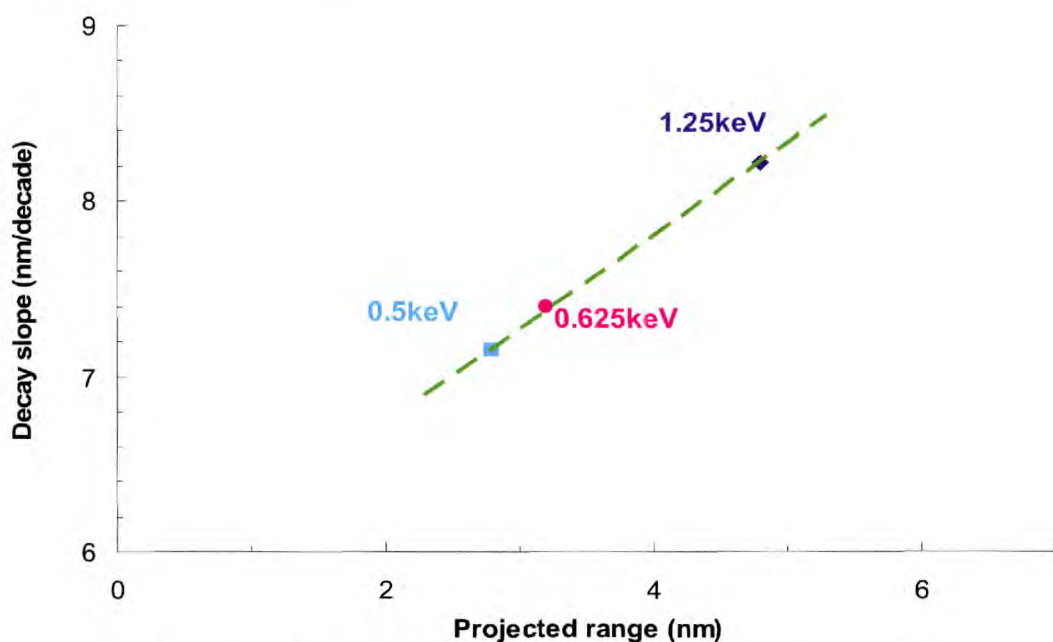


Figure 6.10 Decay slope as a function of nitrogen ion projected range.

The relationship between the ion mixing and projected range at different beam energies was clearly demonstrated although there were not many data points available. The same results were reported using boron delta layers in a silicon substrate bombarded with oxygen^[16]. The decay slope increased with increasing beam energy, or projected range. With energies lower than 0.5 keV, the projected range of ions is smaller and ions are resting on the surface, in consequence, deposition takes on instead of sputtering. The averaged λ_t of delta layers, its standard deviation, σ , and FWHM were tabulated in table 6.2. The 8th layer was used for the decade/nm, and the 3rd, 8th and 12th layers were measured for FWHM and then were averaged.

$^{14}\text{N}_2^+$ (keV)	Averaged λ_t (nm)	Standard deviation, σ	Decay slope nm/decade	FWHM (nm)
0.5	2.97	0.16	7.15	4.13
0.625	2.94	0.2	7.4	4.17
1.25	3.2	0.2	8.22	4.96

Table 6.2 Summary of averaged decay length, its standard deviation, decay slope and FWHM of different nitrogen energy bombardments.

As table 6.2 shows, the largest decay length and FWHM were gained at 1.25 keV, thus, confirming that at a higher beam energy, ion mixing and roughness was worse.

6.4 Damage Induced by $^{16}\text{O}_2^+$ Bombardment

In this section, we discuss the in-depth damage on the AlGaAs samples bombarded by an oxygen beam at different energies, namely 0.5, 1.25 and 2.5 keV. All the depth profiling was done at normal incidence. Figure 6.11 shows the $^{27}\text{Al}^+$ depth profiles obtained at different oxygen beam energies at normal incidence.

All the delta layers were nicely resolved with the oxygen energies used. The peak-to-valley ratio obtained when using 2.5 keV was smaller compared to that at 0.5 and 1.25 keV at all depths, while the PVR observed at 0.5 keV was the largest. Looking at the height of all the peaks, at 0.5 keV the heights were all equal. At an energy of 1.25 keV the 1st peak was higher than the rest. At 2.5 keV the 1st and 2nd peaks were higher than the others with the 2nd peak being the highest. This could be due to some degree of coalescence (the intensities of two peaks in the region where they overlap have been combined and increased in its apparent peak height, this coalescence effect becomes severe at higher beam energy) at a high beam energy.

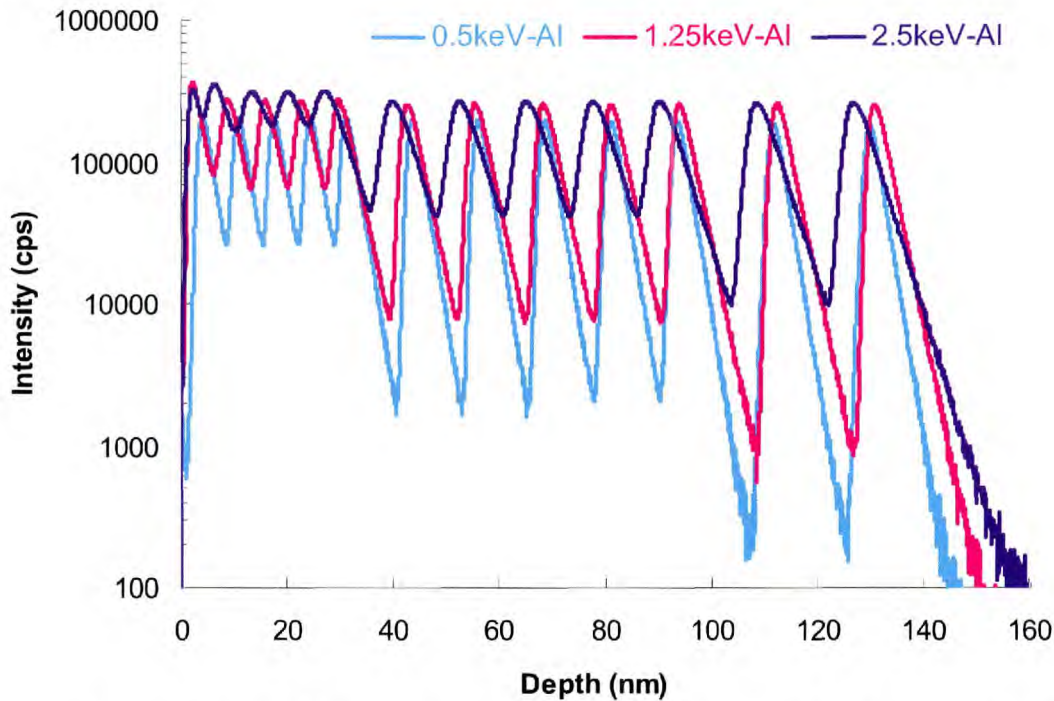


Figure 6.11 $^{27}\text{Al}^+$ depth profiles obtained at normal incidence bombardment with $^{16}\text{O}_2^+$ ions at energies of 0.5, 1.25 and 2.5 keV.

Comparing every peak position at all three energies, for the first 5 delta layers spaced 5 nm from each other, the 2.5 keV peaks were the closest to the surface, followed by 1.25 keV, then 0.5 keV. After the first five deltas, the peak position of

1.25 and 0.5 keV was very similar, the 2.5 keV peak position was gradually catching up with the two lower energies as the sputtering continued, but still being the closest to the surface. This was due to the differential shift effect, at higher energy bombardment the ion penetration was higher than that of lower energies, thus it took much less time (or fewer data point) to reach the first delta layer, as the sputtering depth continued to increase, ion mixing at higher energy became severe. Also as the oxygen energy increased, the thickness of the altered layer increased, the transient region increased, hence the sputter rate in this region was unknown which could affect the depth calibration. Furthermore, as we have demonstrated in the previous section, the onset of roughening formed with a higher beam energy, and as a consequence, peak broadening occurred. Figure 6.12 compares the 3rd Al delta layer obtained at different oxygen energy. The peak broadening increased with increasing beam energy, 0.5 keV has the narrowest profile shape and the highest PVR ratio. Ion mixing and roughness induced by high beam energy was clearly seen.

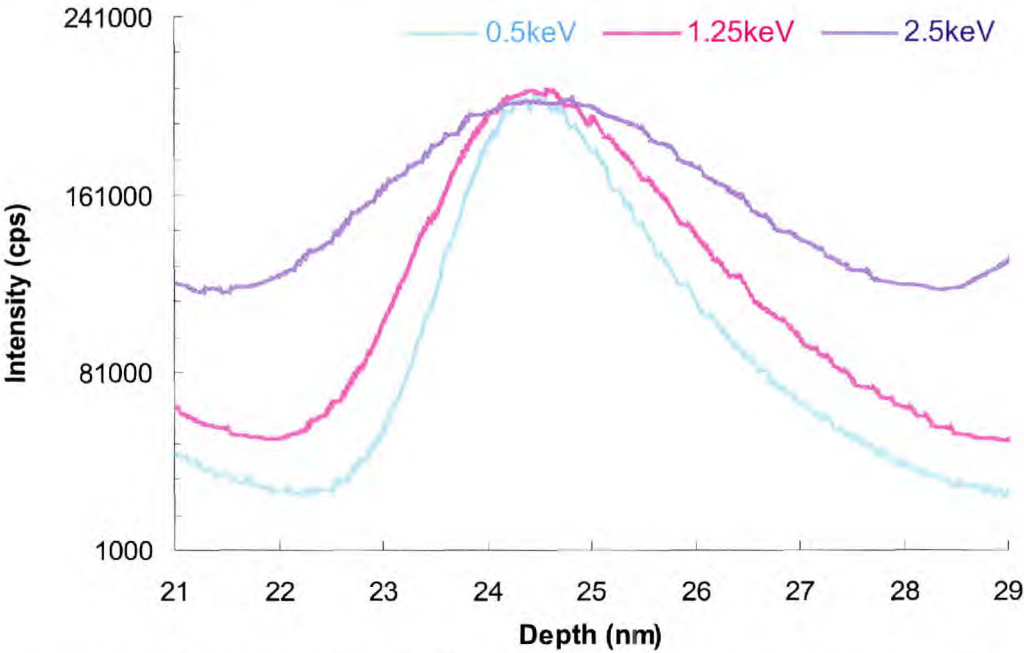


Figure 6.12 The third Al delta layer obtained at 0.5, 1.25 and 2.5 keV. The peak position and height was modified in order to guide the eye.

The decay length of the $^{27}\text{Al}^+$ delta layers obtained at different oxygen sputtering energies was plotted as a function of delta layer index in figure 6.13. At a bombarding energy of 2.5 keV, the decay length was the largest, the averaged value for this energy was about 3.79 nm. The largest error was obtained at the first layer which was about 30%. The decay length at 0.5 keV was the smallest with less than 2 nm throughout the

analysis. The decay slope at 0.5 keV was also the smallest which agreed well with the decay length. The difference between the lowest and the highest was about 6% which could be neglected. The largest λ_i and FWHM both was gained at 2.5 keV, the dependence of ion mixing and roughness on beam energy was shown.

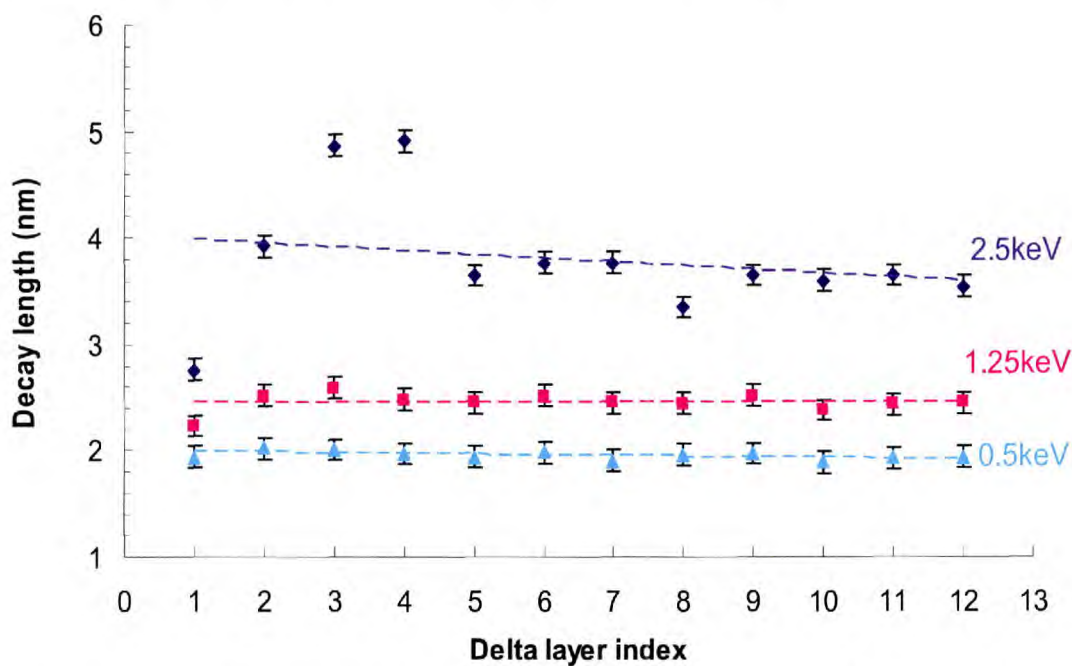


Figure 6.13 The decay length of the Al delta layers as a function of delta layer index for 0.5, 1.25 and 2.5 keV $^{16}\text{O}_2^+$ bombardments.

The averaged λ_i of delta layers, its standard deviation, σ , and FWHM were tabulated in table 6.3. The 8th layer was used for the decade/nm, and the 3rd, 8th and 12th layers were measured for FWHM and then were averaged.

$^{16}\text{O}_2^+$ (keV)	Averaged λ_i (nm)	Standard deviation, σ	Decay slope nm/decade	FWHM (nm)
0.5	1.95	0.04	4.77	2.98
1.25	2.46	0.09	5.54	3.83
2.5	3.79	0.59	8.38	5.96

Table 6.3 Summary of averaged decay length, its standard deviation, decay slope and FWHM of different oxygen energy bombardments.

Figure 6.14 shows a plot of decay length against projected range for different oxygen sputter energies, the observation is also compared with the literature in the figure. It is obvious that the decay length gained from this project is better than the literature. The reason was thought to be due to the angle of incidence and energy used.

Normal incidence was used for the analysis of delta layers in this project. Linnarsson *et al* ^[17] used the incidence angles from 77° to 42°, where Cirlin *et al* ^[18] used much higher ion beam energy at a fixed incidence angle of 40°.

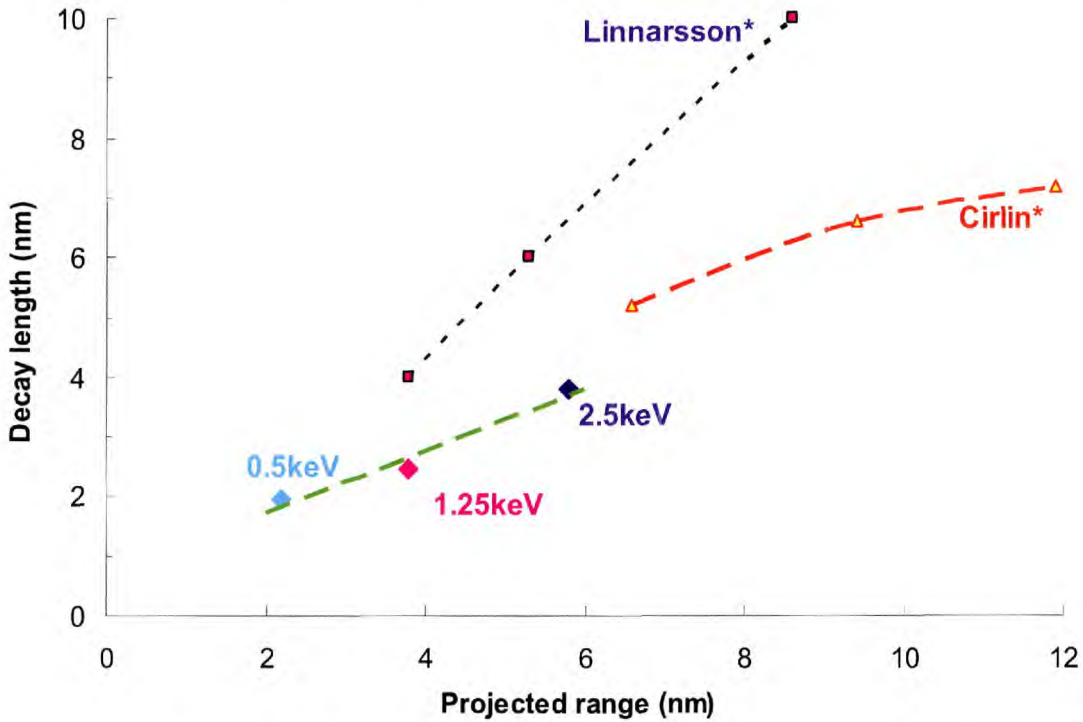


Figure 6.14 Decay slope as a function of oxygen ion projected range.

The decay length was correlated to the projected range, which was beam energy dependent. The ion mixing and oxide thickness both showed that with increasing beam energy, the ion penetration and the thickness of the altered layer increased as well. Hence, one would demonstrate the relationship between the decay length and the altered layer thickness. It was compared but no useful information was revealed since both parameters were energy dependent, and so was the projected range energy. In addition, with oxygen or nitrogen sputtering, diffusion is always expected as we have shown in the previous chapter. Thus, it would not provide any useful information by plotting the two against each other.

6.5 Comparison of $^{14}\text{N}_2^+$ and $^{16}\text{O}_2^+$ Bombardment

Comparing oxygen and nitrogen sputtering, it was found that at the same beam energy, oxygen was better in terms of decay slope and FWHM as shown in figure 6.15a. The lighter mass of the nitrogen ion has a slightly larger ion projected range than that of oxygen, at the same beam energy, and nitrogen is expected to travel further than oxygen ions do. We have shown in chapter 5, the nitrogen induced altered layer

thickness was always slightly larger than that of oxygen (the difference increases with increasing beam energy). This can be checked with the TEM measurement. The decay lengths under different beam energies sputtering obtained from this experiment were also compared with the literature ^[18-21] in figure 6.15b.

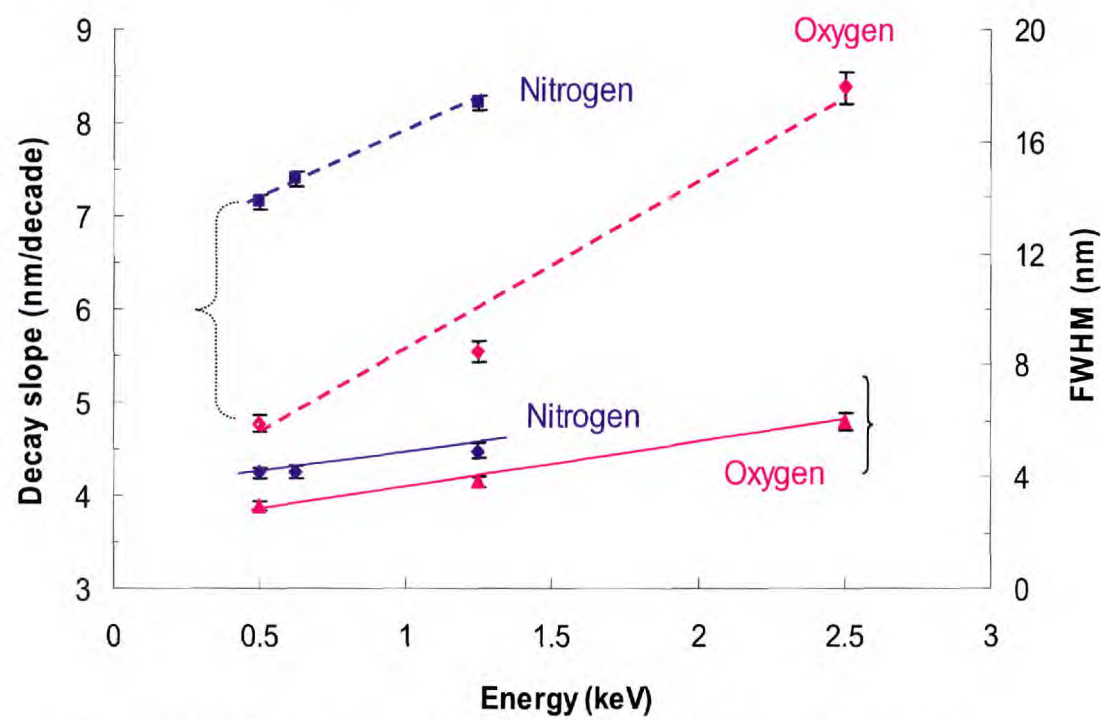


Figure 6.15a) Decay slope and FWHM of $^{14}\text{N}_2^+$ and $^{16}\text{O}_2^+$ as a function of energy.

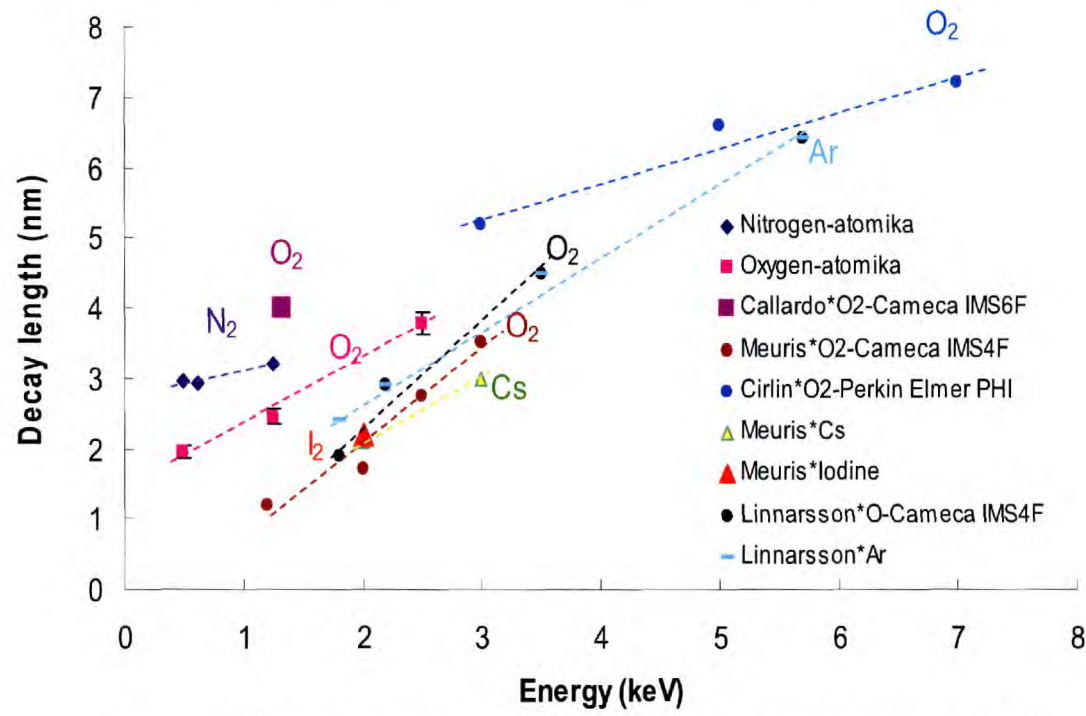


Figure 6.15b) Decay length obtained from this project and the literature ^[17-20].

Though the experimental conditions used were different the trend is more or less the same. That is, as beam energy increases the ion mixing becomes severe and that leads to a higher decay length. It also allowed us to study the effect of sputtering conditions on the ion mixing and from the instrumental point of view, it is interesting to compare the capability or reliability of the different machines.

After depth profiling the samples, the nitrogen and oxygen beam formed craters were imaged in the Joel 2010 FX TEM to investigate the correlations between the ion sputtering energy and ion projected range, and the TEM measurements were compared to the TRIM^[22] results. The TEM specimens were prepared using the FIB TEM technique as described in Section 6.2. Figure 6.16 shows the TEM image of the crater formed by the 1.25 keV oxygen beam (see Appendix 5 for 2.5 keV $^{16}\text{O}_2^+$ and 0.5 and 1.25 keV $^{14}\text{N}_2^+$).

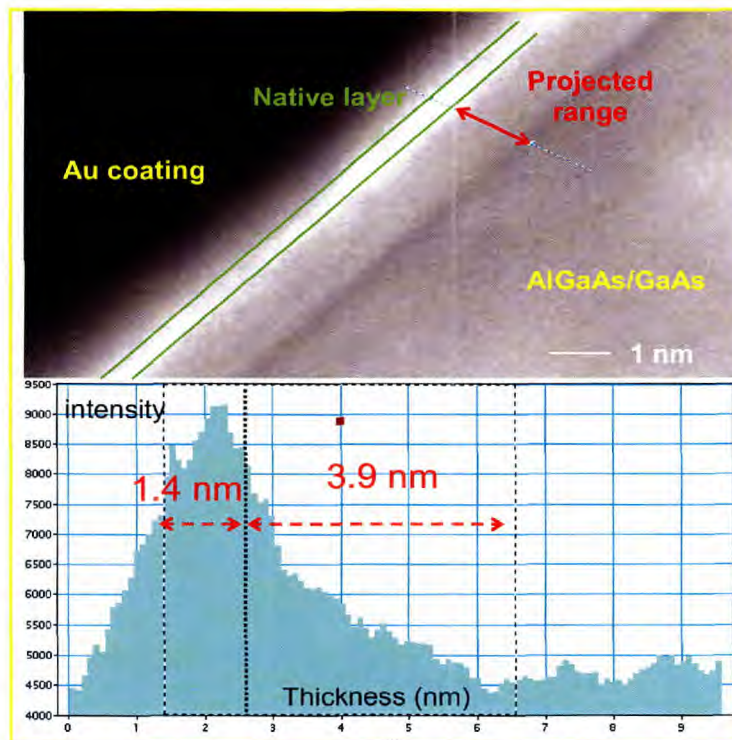


Figure 6.16 TEM image of the crater formed by the 1.25 keV oxygen beam, the ion projected range and the native oxide layer was measured in the DigitalMicrograph software. The imaging was done in a Jeol 2010 TEM at 200 keV, bright field mode.

The white stripe appeared between the gold coating and the crater bottom and is the native oxide layer which is about 1.4 nm. The dark line which is about 3.9 nm away from the native oxide layer is the end of the ion project range of the primary oxygen ions sputtering at the energy of 1.25 keV, this is the same as obtained in the

TRIM. The ion projected range of nitrogen and oxygen beam at different energies are compared and plotted in figure 6.17.

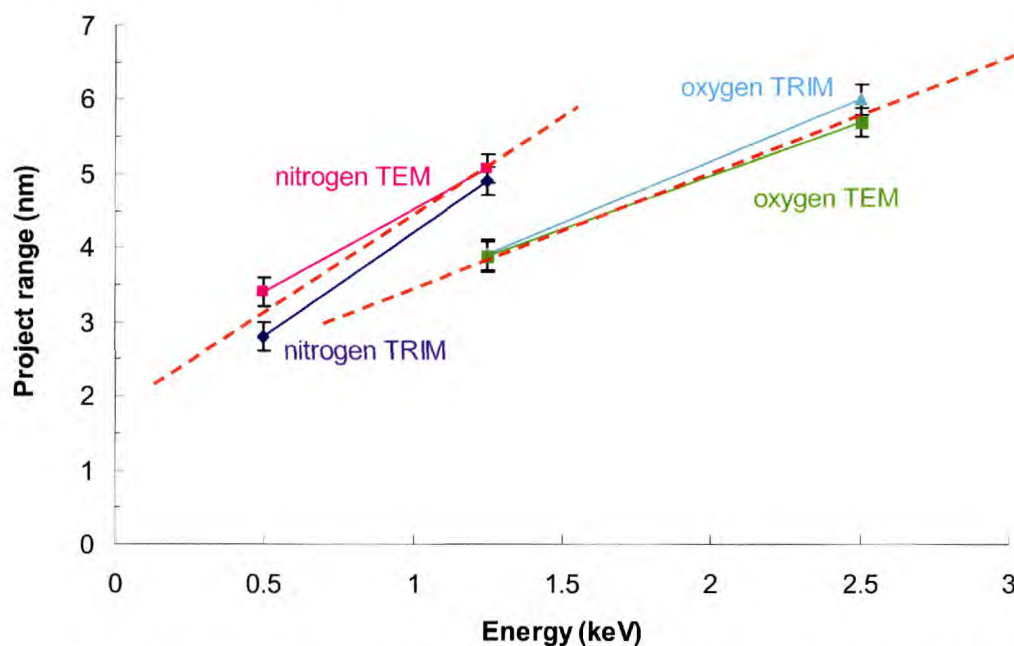


Figure 6.17 The ion projected range at different beam energies obtained in the TEM and TRIM.

The ion projected range at different nitrogen and oxygen sputtering energies measured in the TEM and TRIM have a very good agreement, though there are not many data point shown but the general trend is seen. As the beam energy increases, the projected range increases. At a beam energy of 1.25 keV, the projected ion range of the nitrogen beam is higher than that of oxygen, which resulted in a larger altered layer thickness and larger ion mixing.

Low oxygen and nitrogen beam energy bombardment was carried out to investigate the beam induced damage on the sample surface by using the AlGaAs test structure with 12 Al delta layers. Since all the samples were measured at normal incidence and low energies, ion mixing and roughness were expected to be compressed. We have demonstrated the benefit of using low energy beam bombardment by measuring the decay length and roughness of the delta layers. At high beam energy, the ion penetration increased (higher ion project range) causing a wider ion mixing depth, this can be seen from the TEM image. It was also seen that peak broadening occurred with increasing beam energy suggesting sputter-induced roughening formed (Appendix 4 for decay length comparison between N_2^+ and O_2^+).

6.6 Damage Induced by ION-TOF IV Ar⁺ Bombardment

In addition, we investigated the damage left on the AlGaAs test structures by ION-TOF IV Ar⁺ bombardment at different energies, namely: 0.5, 1 and 3 keV. The incident angle of the Ar⁺ and Ga⁺ beam was fixed at 45°. At an energy of 0.5 keV, the beam current was 2.5 nA at maximum, the sputter area was 200x200 μm² and the analysis area was 100x100 μm². At an energy of 1 keV, sample rotation was also used to compare the results gained without sample rotation. Figure 6.18 shows the ²⁷Al⁺ depth profiles obtained at different argon beam energies at an incident angle of 45°.

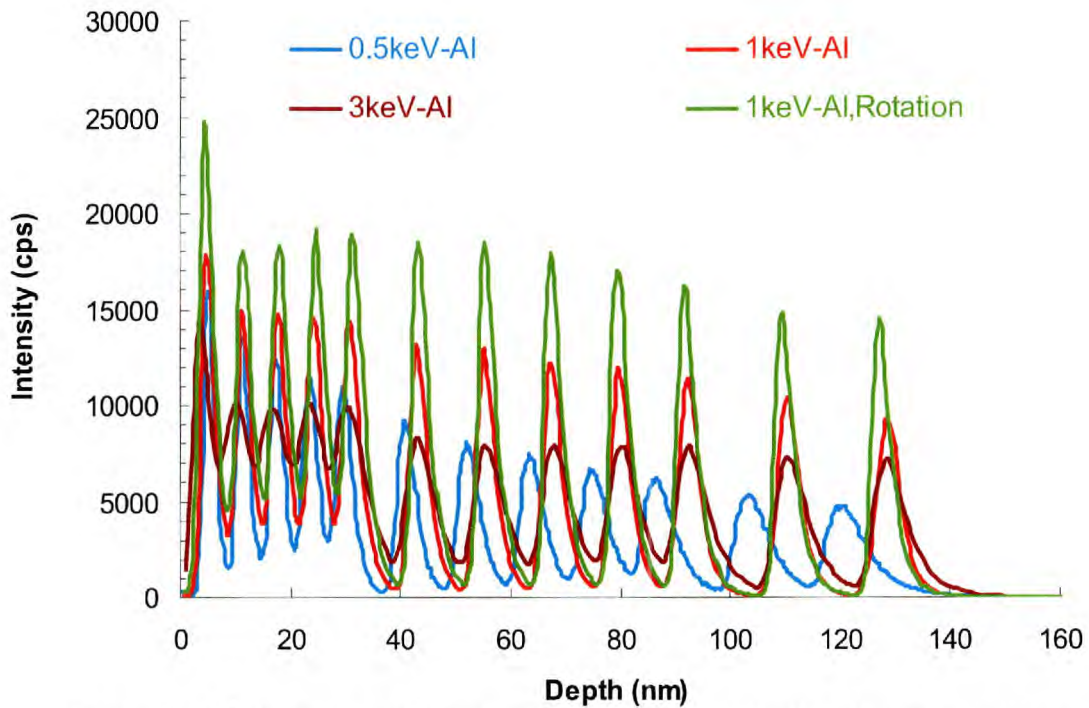


Figure 6.18 ²⁷Al⁺ depth profiles obtained with argon ION-TOF IV bombardments at different energy at an incident angle of 45°.

All the Al deltas were well resolved at all the energies used, and there is no differential shift in the depth profile since the primary beam was an inert beam. In other words, there was no altered layer formed during the sputtering. It was obvious that 1 keV provided the best result overall. For the first four delta layers, the layer peak position of all three energies was very close. As the sputtering depth gradually increased, the 1 and 3 keV profiles moved further away from the 0.5 keV profile. The same observation was seen in the nitrogen and oxygen bombardment. However, what was not seen previously was profile converging, that was the peak tops and bottoms of the delta layers are converging. At higher energy 1 and 3 keV, the profiles suffered

this effect slightly but at 0.5 keV, the converging became severe. Figure 6.19 shows the Al deltas measured at 0.5 keV argon sputtering at 45°.

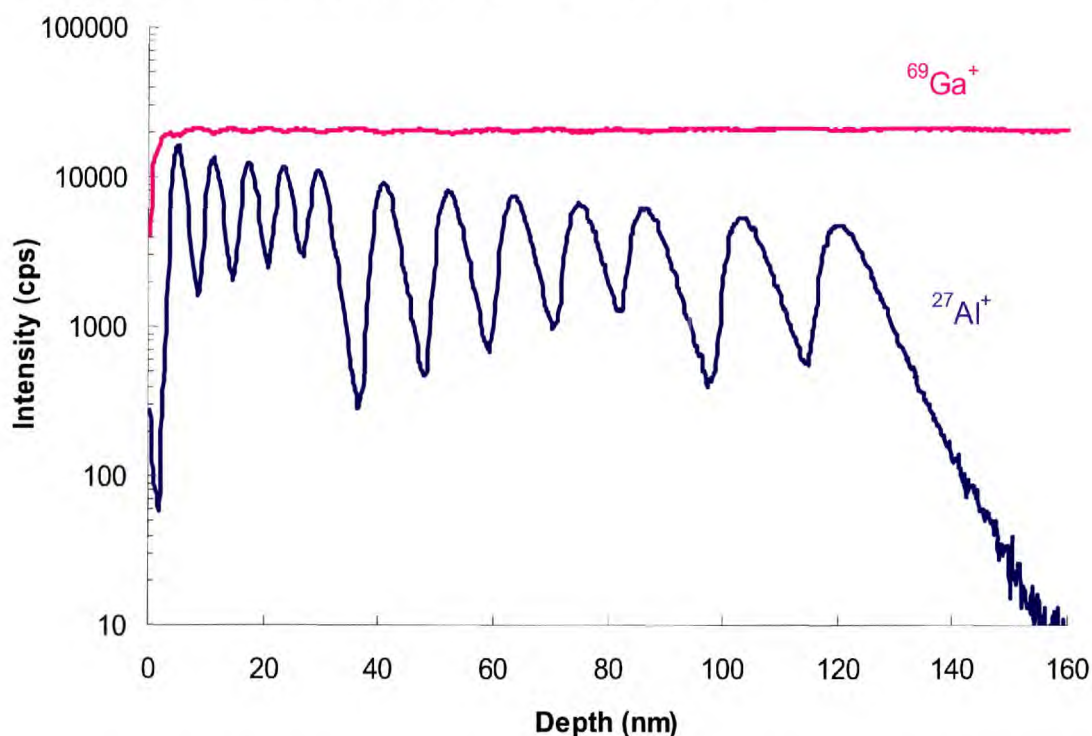


Figure 6.19 $^{27}\text{Al}^+$ and $^{69}\text{Ga}^+$ depth profiles obtained with the Ar^+ ION-TOF IV bombardments at 0.5 keV at an incident angle of 45°.

The cause of this profile converging was thought to have several reasons. Firstly, the argon beam energy of the ION-TOF IV was rarely used at 0.5 keV, there were no default values or ready-to-use set-up for the experimental parameters. The errors (e.g. beam alignment, beam focus, low current) in the system configuration could cause problems for the experiments. Due to this low beam energy the maximum current that could be achieved was about 2.5 nA, and the energy beam was very difficult to focus. On top of this, the small sputter area was $200 \times 200 \mu\text{m}^2$, and the analysis area was $100 \times 100 \mu\text{m}^2$. The sidewall effect could play a big role in this. Finally, crater base unevenness would have occurred and would have affected the profiles if the change ratio in the peak height was similar to the change ratio in the peak bases ^[23]. It was found that the ratio was nearly the same. Looking at the PVRs, the smallest was obtained with the highest beam energy of 3 keV and the best was gained at 1 keV. This was similar to the nitrogen and oxygen bombardment. At 0.5 keV, for the first four deltas, the PVR was larger than that of the rest of the energies and then decreased afterwards. Despite the good and sharp profiles obtained for the first six deltas, the profiles obtained at 0.5 keV started to broaden aggressively after a depth of 60 nm and

became even larger than the profile of 3 keV at the last delta. This observation was very similar to that found by Liu *et al* [15], where an incident angle of 46° was used in their experiment. They suggested that the broadening effect was directly related to the onset of surface roughening according to the atomic force microscope measurement. Comparing the depth profile obtained with and without sample rotation at 1 keV the profiles were very similar, the PVR stayed almost constant throughout the analysis but the profile with sample rotation had a better PVR. From the 6th delta layer to the 10th delta layer, the peak intensity dropped slightly with no changes in the base peak intensity, accompanied by peak broadening. Surface roughening was thought to be responsible for this. At 3 keV, the PVR stayed constant throughout but the trailing edges were noticeably longer than the leading edges; this was due to the ion beam mixing effects as mentioned before. Figure 6.20 compares the PVR of 0.5, 1 (with rotation) and 3 keV as a function of delta layer index. Clearly, it was shown that at a beam energy of 0.5 keV, the PVR was not stable. For the first 4 deltas (the first was not included), the PVR at a beam energy of 0.5 keV was the largest, from the 6th delta to the 10th delta, the changes dropped significantly by a factor of 20, and in the end, the PVR was smaller than that of 3 keV. Hence, the on-set roughening at 0.5 keV was demonstrated. For 1 and 3 keV, the PVR was very stable, at the 7th delta, the PVR of 1 keV with rotation became the largest.

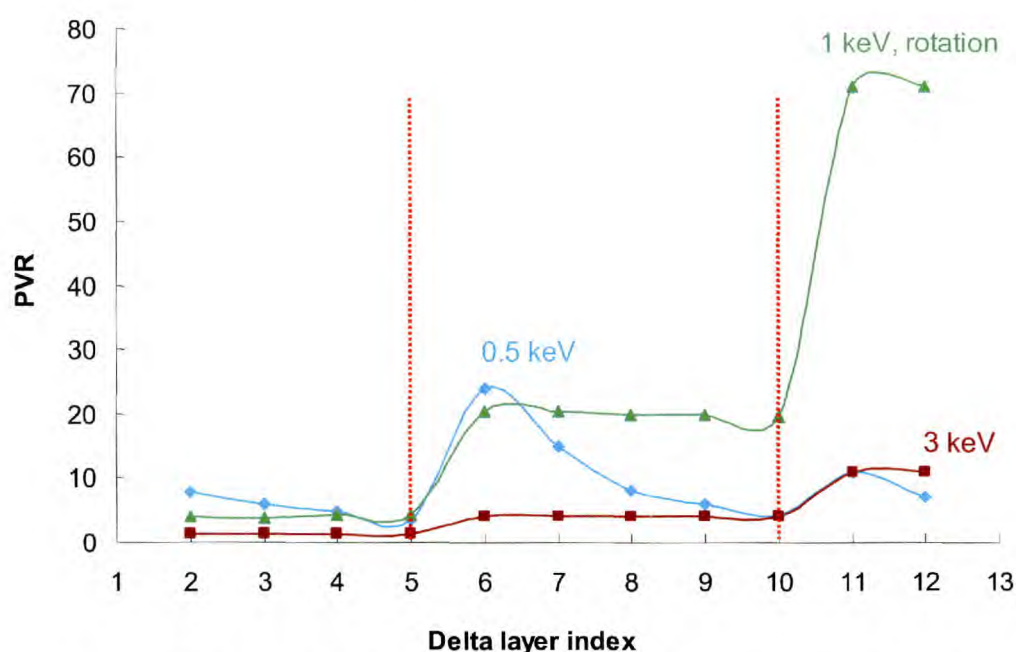


Figure 6.20 Peak-to-Valley ratio of 0.5, 1 and 3 keV as a function of delta layer index. The first delta layer was excluded in the figure due to experimental errors.

To study the ion mixing induced by different beam energies, the decay length was measured and plotted against delta layer index in figure 6.21.

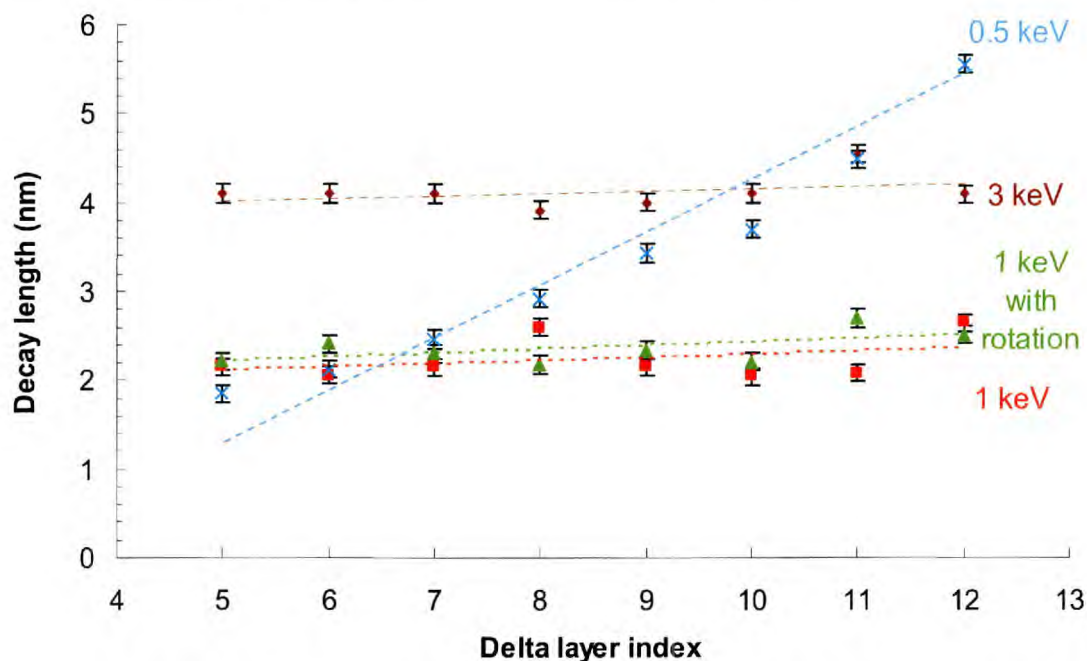


Figure 6.21 The decay length of Al delta layers as a function of delta layer index for 0.5, 1 (with and without sample rotation) and 3 keV Ar^+ bombardments. The decay length was measured from the fifth delta layer for all the energies used.

At a bombarding energy of 3 keV, the decay length was the largest apart from the last delta; the averaged value for this energy was about 4.12 nm. The difference between the largest and smallest decay length was about 14%. The decay length of 1 keV with/without sample rotation was very similar at 2.36 and 2.24 nm. The error was less than 23% in both cases. Surprisingly the profile gained without sample rotation resulted in a smaller decay length (the difference between the two was only 0.012 nm). At 0.5 keV the decay length increased with increasing sputter depth. At the 7th delta it became larger than that of 1 keV and at the 11th delta, the decay length was larger than that of 3 keV. The FWHMs measured from the 3rd, 8th and 12th delta layer were plotted as function of delta layer index in figure 6.22. Again, the FWHM of 0.5 keV increased with increasing sputter depth. This was thought to be due to roughening. The same observation was seen in the PVR measurement, the peak broadening became serious after 60 nm. For 1 and 3 keV, the FWHM was roughly constant with small variations throughout the analysis depth. There was not much difference between the rotation and no rotation at 1 keV. Despite the increasing trend in 0.5 keV, the FWHM was the largest at 3 keV with an average value of 7 nm.

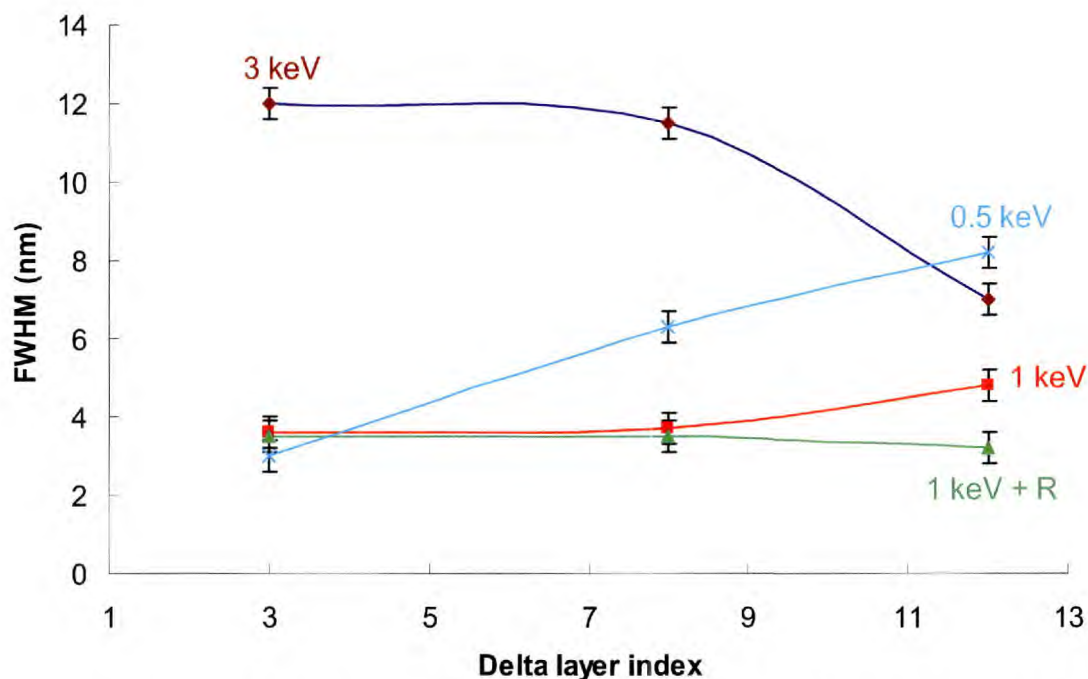


Figure 6.22 The FWHM as a function of delta layer index for 0.5, 1 (with and without sample rotation) and 3 keV Ar^+ bombardments. The 3rd, 8th and 12th delta layers were used.

Finally, the AlGaAs test structure was analysed at different Ar^+ sputter energies. All the Al deltas were well resolved at all energies used. Profile converging was seen at sub-keV energy bombardment. Moreover, the PVR decreased with increasing depth as well as the FWHM and decay length. The changes were related to the onset of surface roughening and ion mixing. At 1 keV, the sample was analysed with/without rotating. A better result was expected with the sample rotation technique. However, there was not much difference between the two profiles in terms of decay length and FWHM though depth profiling with rotation provided slightly better PVR and FWHM (figure 6.20 and figure 6.22). In other words, the surface roughness may be reduced slightly with rotation. The decay length plotted in figure 6.21 showed that the ion mixing effect was not simply reduced by rotation at 1 keV sputtering. Ng *et al* ^[24] investigated the crater roughness induced by 500 eV O_2^+ bombardment at 56° with sample rotation. It was found that surface roughening was reduced by rotation but ion mixing remained unchanged. Oxygen flooding was suggested as a better option for mixing suppress. Ion sputtering at 3 keV, the PVR, roughness and mixing appeared to the worst. The same observation was shown in nitrogen and oxygen bombardment with higher beam energy. Hence, a 1 keV beam energy provides the best results for the bombardment of Ar^+ ION-TOF IV at 45° (see Appendix 4 for the comparison between the Atomika 6500 and ION-TOF IV techniques).

6.7 Summary

These studies have shown that low energy ion irradiation introduces beam induced mixing into the sample, that is entirely consistent with theory, and similar to the range of the projectile. The studies also indicate that samples can rapidly roughen under low energy irradiation, under certain conditions, and that this should be borne in mind for dynamic situations. These investigations define the damage in the Z direction during low energy ion irradiation.

6.8 Reference

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Chapter Seven

7. Conclusions and Future Work

7.1 Conclusions

As the physical dimensions of electronic devices continue shrinking down and the analytical volume gets smaller and smaller, the conventional SIMS technique is facing severe problems. FIB SIMS involves the integration of a SIMS analyser into a FIB system. It combines the high spatial resolution of FIB (~5 nm) with the high elemental sensitivity of SIMS. This has made it possible to provide crucial small area elemental analysis for some systems such as semiconductors. Unfortunately the secondary ion yield on the FIB SIMS instrument at Imperial College is not optimized either in terms of the ionization probability of the secondary ion species or the secondary ion transmission. This could limit the range of applications of FIB SIMS. Methods of enhancing the secondary ion yield such as surface chemistry modification with reactive ion sources and oxygen flooding have been investigated.

In the first set of experiments, nitrogen and oxygen were implanted into the silicon wafer to form ion induced altered layers prior to FIB SIMS analysis. Different beam energies and doses were used in order to study how the ion yield changes with beam conditions. The ion yield on the FIB SIMS was enhanced with both primary ion species. The degree of the ion yield enhancement increased with increasing beam dose until the critical dose was reached. At the critical dose, all the beam energies used in the experiments were enough to provide the maximum ion yield enhancement. The thickness of the beam induced altered layer increased with increasing ion energy. The maximum ion yield enhancements observed were more than two orders of magnitude with prior oxygen implantation. Comparing the ion yield enhancements, the oxygen beam provided higher enhancements than the nitrogen beam did.

In the second set of experiments, the nitrogen and oxygen formed altered layers were analysed with the ION-TOF IV, which enabled us to compare and contrast the results obtained from two different techniques. The same observation was seen in which the ion yield enhancements were independent of the ion implantation energies and the altered layer thickness increased with increasing ion energy. Comparison of the ion yield enhancements and altered layer thickness gained from the two

techniques were made. The ion yield enhancement on the FIB SIMS due to nitrogen implantation was larger than that obtained with the ION-TOF IV (by more than a factor of two). However, with oxygen implantation, the ion yield enhancements were larger with the ION-TOF IV (by a factor of two). The reason is unknown though the author thinks that, the beam current varied during the nitrogen implantation which could enormously have affected the altered layer formation. Secondly, the nitrogen induced altered layers might have been damaged or exposed to different environment and chemically modified since the samples travelled a long way from the UK to Singapore. Finally, the FIB SIMS instrument has no gating system, hence, the sidewall effect might have affected the results. Further investigation is required. The thickness of the ion induced layers was much larger from the FIB SIMS measurements due to the high Ga^+ beam energy. The high Ga^+ energy results in a high degree of ion mixing which can push the depth profile away from the surface. In consequence, the thickness of the altered layer was overestimated. Therefore, the thickness of the altered layers measured from the ION-TOF IV was much more reliable and accurate.

A cross-sectional TEM technique was used to measure the thickness of the nitrogen induced altered layer. The TEM specimen was prepared in the FEI FIB 200 using the FIB 'lift-out' technique. The thickness obtained from this technique had a good agreement with the SIMS measurement. The altered layers were nicely resolved in the TEM with less than 0.5 nm measurement error. Although there was not many data points shown due to the difficulties in the FIB sample preparation process the general trend could be seen. The oxygen induced altered layer was not measured in the TEM since the experiments could be found in the literature. The thickness of the oxygen induced layers obtained from this project with the ION-TOF IV was almost the same as in the literature.

In the third set of experiments, the oxygen flooding technique was used with ION-TOF IV analysis. The aim of this experiment was to compare the ion yield enhancement of oxygen flooding and ion implantation. As an outcome, the ion yield enhancement was very similar between the oxygen implantation and oxygen flooding but nitrogen implantation was lower. The highest enhancement was over two orders of magnitude at an oxygen pressure of 1×10^{-5} mbar. Lower oxygen pressures were also used and showed the enhancements increased with increasing oxygen pressure. The

advantage of oxygen flooding over implantation is that as long as the oxygen flooding is on and at its maximum, the ion yield will not drop. In addition, the transient region and surface roughness are reduced. However, one big problem with oxygen flooding is that it introduces swelling, which could lead to distortion of the depth profile. With ion implantation one can control more precisely and accurately the depth and the area of the implant. Hence, the ion yield on the FIB SIMS can be enhanced by oxygen flooding and sub-keV energy ion implantation and the enhancement ratio is about the same.

Finally, an AlGaAs test structure was used to study the correlation of the implant beam energy and the damage induced by the oxygen and nitrogen beams. The results have shown that using a low beam energy reduced the roughness and ion mixing greatly. The best profile was gained at 0.5 keV for the two bombarding beams. The different beam energy formed craters were then analysed in the TEM and they showed that at higher beam energy the ion projected range was larger, which confirmed and partially explained the observation in the SIMS. At a sputtering energy of 0.5 keV both for $^{14}\text{N}_2^+$ and $^{16}\text{O}_2^+$, the ion projected range was the smallest. TRIM simulation was also used and it had a very good agreement with the TEM results. Comparing the nitrogen and oxygen, the ion mixing produced by the nitrogen sputtering was larger than that produced by the oxygen bombardment and the altered layer thickness was also larger by nitrogen sputtering due to the lighter mass of nitrogen ion which travels longer in the materials. We also investigated the damage induced by the Ar^+ ION-TOF IV bombardment at 45° ; the general trend was very similar to that of nitrogen and oxygen sputtering. However, profile convergence and coalescence was seen in the profile and, the profile worsens more dramatically with depth at a sub-keV bombardment energy (i.e. 0.5 keV). Hence, normal incidence again won out. At 1 keV, sample rotation was used to compare with no sample rotation. Interestingly, the roughness was only reduced slightly by the sample rotation technique, and ion mixing remains. The reason could be that the bombarding energy was already very small, therefore the damage was not so significant. The sample rotation technique works better with high energy ion bombardment. The results have shown that an 1 keV beam energy provided the best results for the sputtering with Ar^+ on the ION-TOF IV at 45° .

7.2 Future Work

Several oxygen and nitrogen beam energies, namely: 0.5, 0.625, 1.25, 2.5 and 5 keV were used in this project and the relationship between the beam energy and ion yield enhancement was investigated. It was also found out that at an ion energy of 1.25 keV, the degree of ion yield enhancement was dependent on the beam dose. However, could this observation apply to other energies remains an open question, and if the answer is yes, then what is the critical dose for each energy.

Cesium is a promising ion source for improving the negative ion yield. However, there are very few studies on the negative ion yield enhancement in the FIB SIMS. It is worth finding out how the negative ion yield in the FIB SIMS can be enhanced and by how much. TEM can potentially be very useful to measure the cesium induced altered layer (e.g. thickness, damages).

The AlGaAs test structure was SIMS depth profiled with $^{14}\text{N}_2^+$ and $^{16}\text{O}_2^+$ in the Atomika 6500 and with Ar^+ in the ION-TOF IV, and the ion mixing and roughness produced by different beam energies was investigated. The Atomic Force Microscopy is a very useful tool to measure the crater bottom roughness, a direct comparison between the AFM and the SIMS technique would be very helpful to confirm the results that were observed in the SIMS depth profile. In addition, it helps the SIMS analyst to gain a better understanding of the ion mixing mechanism.

The ion beam bombarded craters were imaged in the TEM after the SIMS analysis. The ion damaged area was seen in the TEM images. A fresh (not bombarded by any beam) TEM specimen was also prepared by the FIB TEM technique but, the buried thin AlGaAs delta layers were not resolved. The author thinks that there are three possible reasons, namely: one, the AlGaAs delta layers were too thin (1 nm) and lightly doped ($\sim 4.2 \times 10^{13}$ atoms/cm²), thus it made it impossible to see those layers in the TEM. The solution to this is to re-grow the test structure with thicker and higher dose of the deltas. Secondly, the TEM imaging principle is based on the scattering factor of the sample, unfortunately the AlGaAs has very similar scattering factor which means the contrast in the TEM is not good enough to resolve the deltas. The solution to this is to grow some AlAs layers near the layers of interest as marker layers since the AlAs has very good contrast in the TEM, this helps the analyst to pay attention to this part of the structure. With the help of an AlAs marker layer, the AlGaAs deltas could be easily located in the high resolution TEM. Thirdly, the TEM

specimen could have been damaged by intermixing with the Ga^+ beam during FIB milling, so they were not visible anymore. However, the author thinks that this is the most unlikely reason since special caution was taken during the FIB milling, also many TEM specimens were prepared but none worked. However, the solution to remove the damage or intermixing can involve several methods such as gas-assisted etching and wet etching as described in chapter 6. The difficulties of preparing the TEM specimens are well known and the investigation of the thin AlGaAs delta layers in the TEM can lead to another project.

It was found that the maximum absolute Si^+ intensity gained in the FIB SIMS was smaller compared to that gained in the ION-TOF IV. The transmission of the FIB SIMS is not optimised and the secondary ion optics of this technique needs to be developed. One approach is to design a secondary ion energy filter. The experiments have shown that oxygen flooding and oxygen implantation provide the same ion yield enhancements. Oxygen flooding gives unlimited ion yield enhancement depth and it is much cheaper (no more than a couple of thousand pounds). Thus, it would be very useful to mount an oxygen leak valve into the FIB SIMS. Furthermore, the high energy of Ga^+ leads to a high level of ion mixing, and the question is whether the oxygen flooding can reduce this effect and if so by how far.

FIB SIMS combines the high resolution of FIB and high sensitivity of SIMS, and it allows in-situ micro-milling and imaging. This gives a great advantage over other surface analytical tools for the compositional analysis of some special geometrical samples. For example, AlGaN multiple quantum wells (MQWs) were grown on GaN, grown by epitaxial lateral overgrowth (ELO), Figure 7.1.

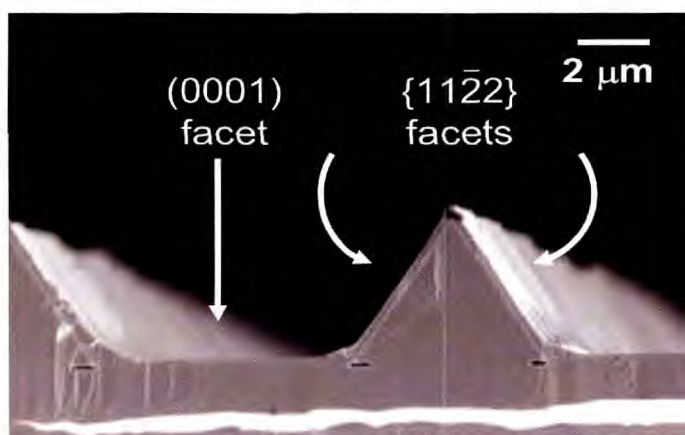


Figure 7.1 Scanning Electron Microscopy image of ELO GaN with AlGaAs/GaN MQW on the surface^[1].

The Al concentration, which is very important for GaN structures used in light emitting devices (LEDs), at the corner is difficult to measure by the ION-TOF IV due to its instrumental geometry limitations. It was found using the ION-TOF IV that the concentration of Al varies on different facets^[1], figure 7.2. Particularly at the corner between (0001) and (11 $\bar{2}$ 2) facets, there is a decrease of Al concentration. This gives a decrease of AlGa_xN barrier height, which can give rise to short circuit of the LED at these corners.

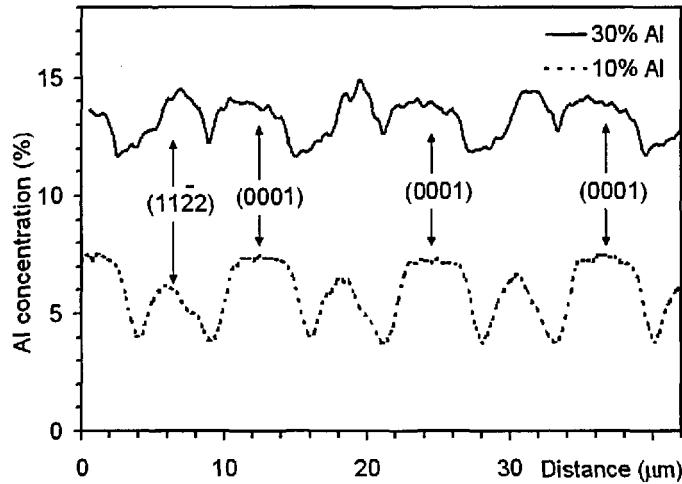


Figure 7.2 Lateral profiles of Al concentration integrated through the depth of MQW in samples with nominal 10% and 30% Al content^[1].

Taking into account the importance of the Al concentration for GaN based LED, it is necessary to make sure whether the observed variations of Al concentration are real. For FIB SIMS, with its high spatial resolution, 5 stage movements (x, y, z, tilt and rotate) and in-situ analysis, the task is easily done. Figure 7.3a shows the secondary electron image of the cross-section of GaN. The cross-section was made by FIB SIMS at an angle of 45°, the in-situ analysis allowed us to ion image the sample straight after the cutting, figure 7.3b. The sample was covered with a 60 nm layer of Au to protect the layers of interest from sputtering. Cross-sections were made by sputtering the samples at 45°. The stage was rotated so that the prisms were perpendicular to the tilt axis. The Ga⁺ beam was sputtered at an energy of 30 keV to a depth of around 1 μm, beam current 3 nA, raster area 26x7 μm². The elemental mapping was done by rastering the 30 keV Ga⁺ beam at a current of 500 pA for mapping of Al⁺, raster area 35x30 μm² and acquisition time around 7 minutes. The FIB SIMS analysis was done in SIMS lab, Imperial College London.

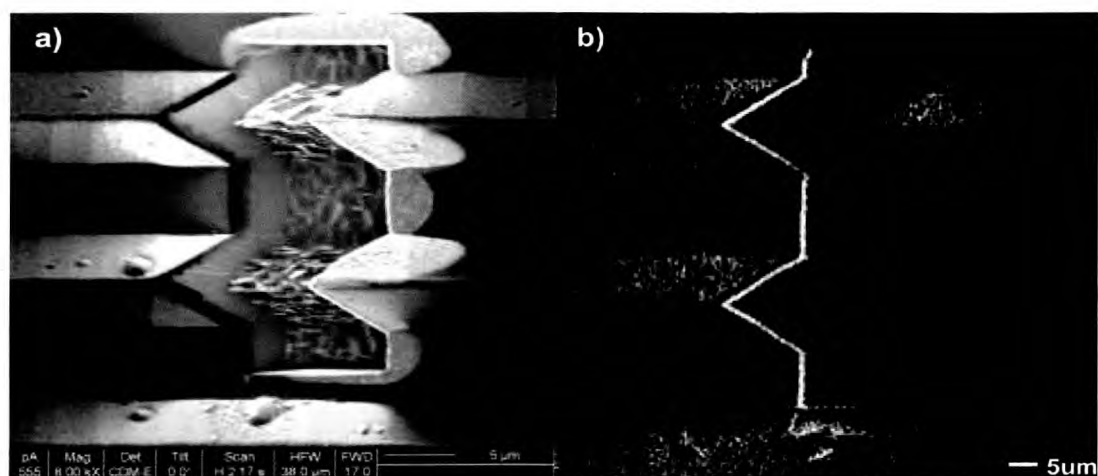


Figure 7.3a) FIB SIMS secondary electron image and b) Elemental mapping of $^{27}\text{Al}^+$ of the cross-section of GaN:Al/GaN sample with nominal 30% of Al.

The map of Al shows a distinct Al-containing layer and the $^{27}\text{Al}^+$ intensity looks uniform along the layer. Hence it allows us to conclude that the content of Al is generally uniform along the surface. It also suggests that the decrease of Al in the corners observed with the ION-TOF IV may be due to an artifact of TOF SIMS. FIB SIMS does enjoy relatively uniform secondary ion extraction from surfaces with non-uniform features. It is important, therefore, that if we do implement a secondary ion energy filter, that the uniform secondary ion transmission observed here is not compromised.

Hence, comparative studies of different materials can be made with other techniques and FIB SIMS. As an outcome, the reliability of the compositional analysis obtained by different techniques can be significantly enhanced.

7.3 Reference

1. AlGaIn/GaN multiple quantum wells grown on facet-controlled epitaxial lateral overgrown GaN/sapphire templates, Zhou, H.L., Chua, S.J., Tripathy, S., Yakovlev, N.L., Wang, L.S., and Liu, W., Journal of Physics: Condensed Matter. (5): p. 056005. 2007

Appendix 1 – Depth Profiles of Surface Contaminants

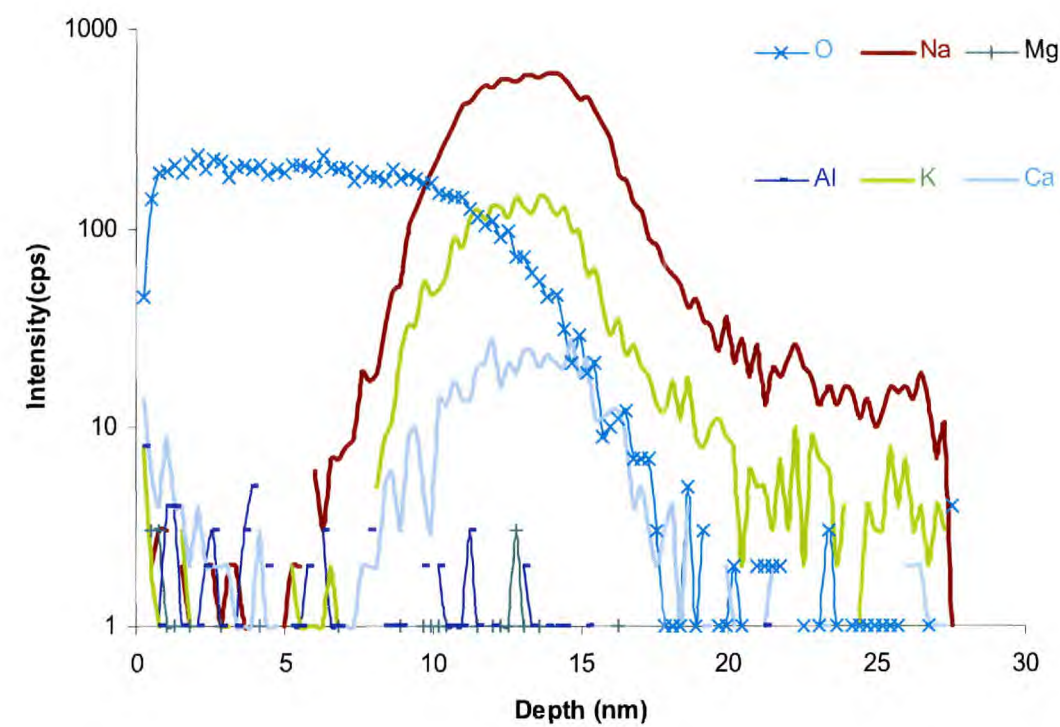


Figure 1.1 Shows surface contaminants $^{23}\text{Na}^+$, $^{39}\text{K}^+$, $^{40}\text{Ca}^+$ that have been detected in the crater formed by an oxygen beam energy of 5 keV.

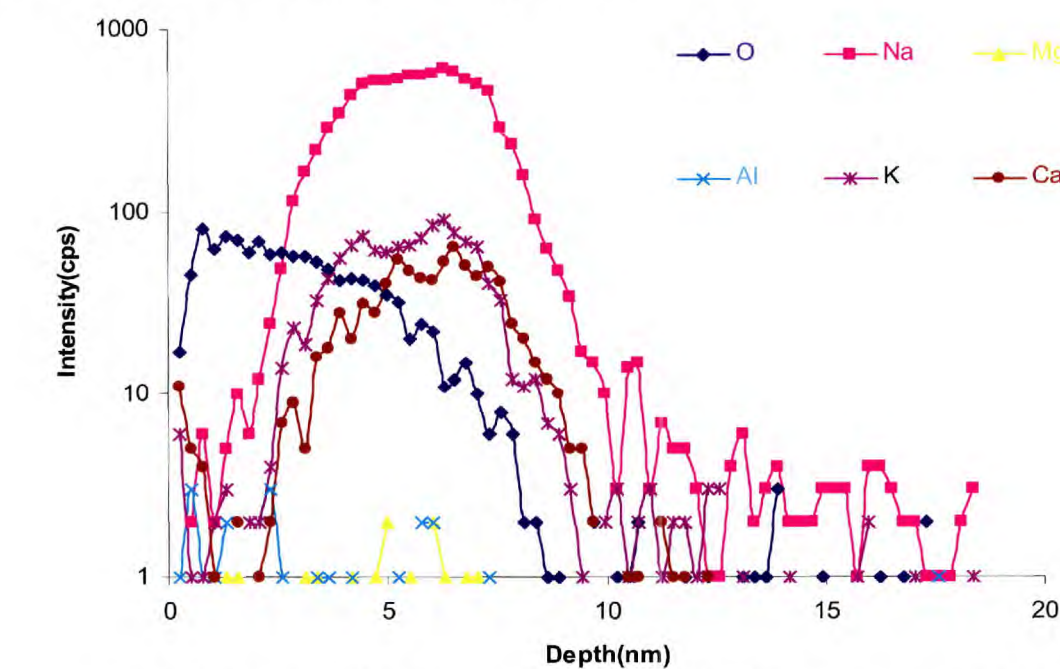


Figure 1.2 Shows surface contaminants $^{23}\text{Na}^+$, $^{39}\text{K}^+$, $^{40}\text{Ca}^+$ that have been detected in the crater formed by an oxygen beam energy of 1.25 keV.

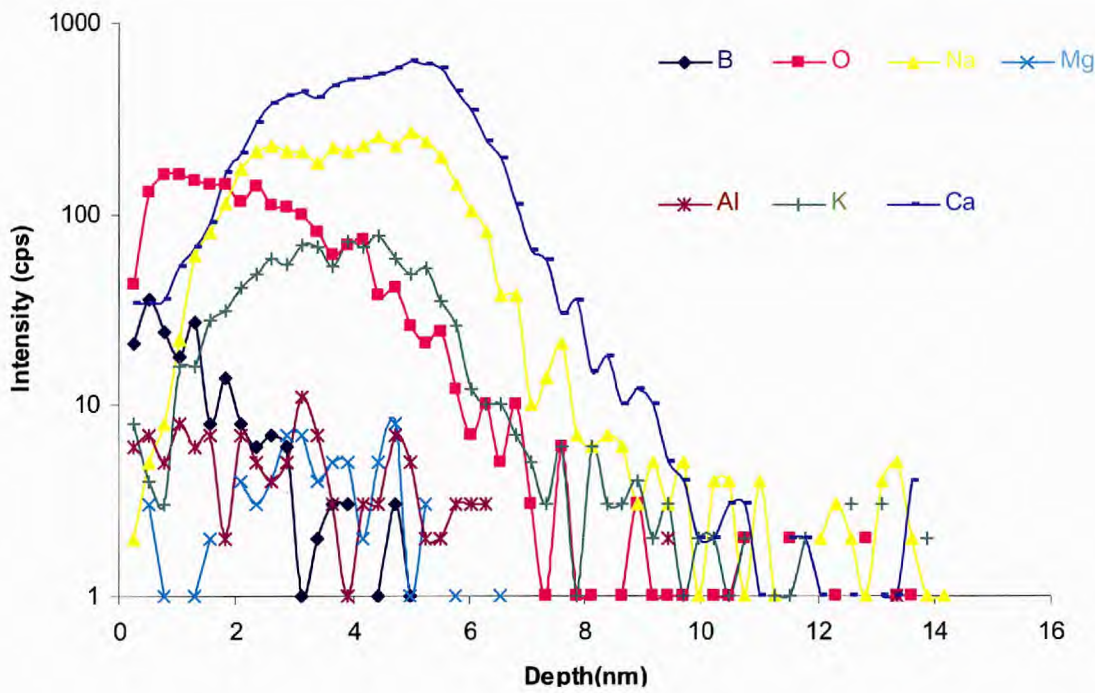


Figure 1.3 Shows surface contaminants $^{23}\text{Na}^+$, $^{39}\text{K}^+$, $^{40}\text{Ca}^+$ that have been detected in the crater formed by an oxygen beam energy of 0.625 keV.

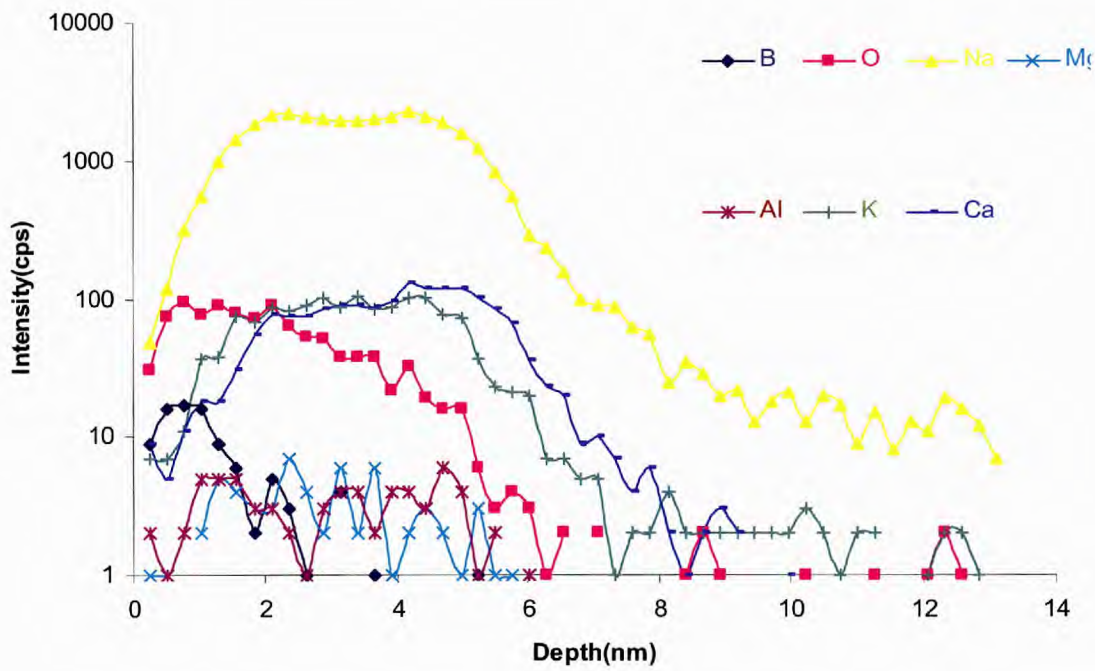


Figure 1.4 Shows surface contaminants $^{23}\text{Na}^+$, $^{39}\text{K}^+$, $^{40}\text{Ca}^+$ that have been detected in the crater formed by an oxygen beam energy of 0.5 keV.

Appendix 2 – Thickness of Nitrogen Induced Altered Layer by TEM

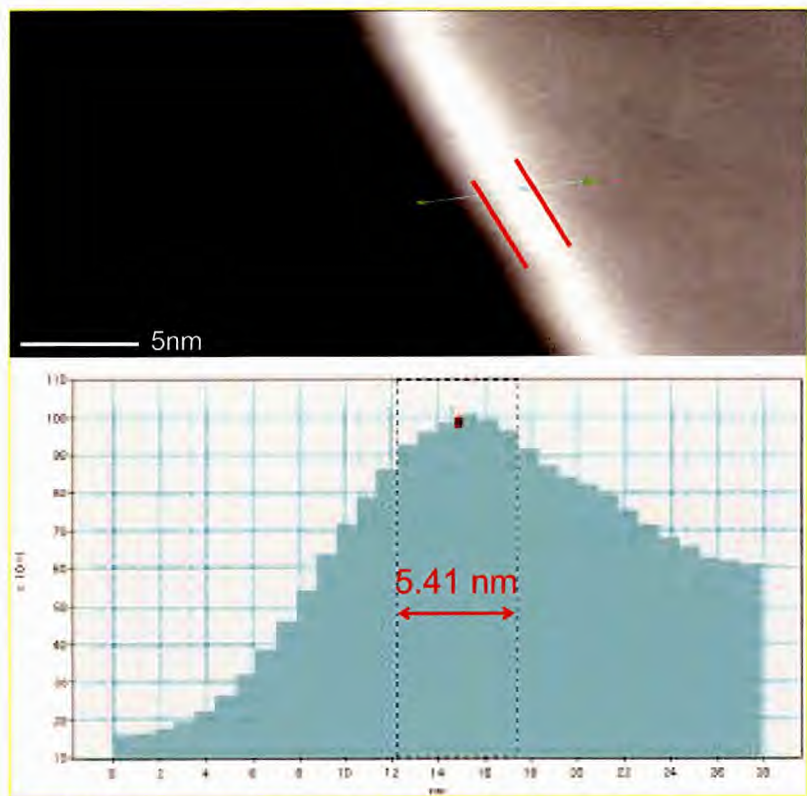


Figure 2.1 The thickness of a 0.5 keV nitrogen beam induced altered layer.

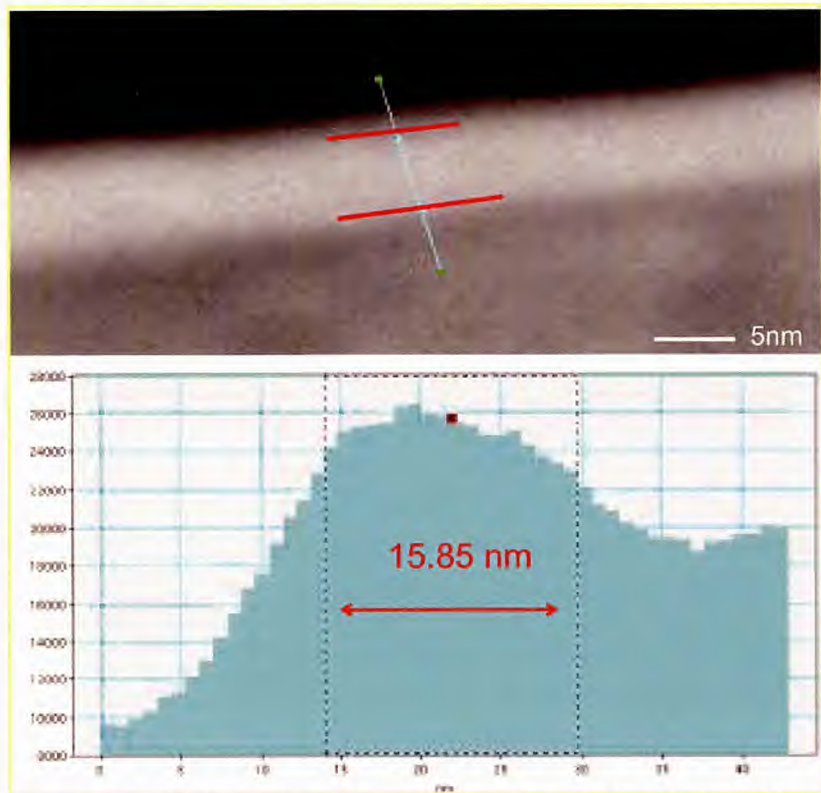


Figure 2.2 The thickness of a 5 keV nitrogen beam induced altered layer.

Appendix 3 – 5% AlGaAs Bombarded by $^{14}\text{N}_2^+$, $^{16}\text{O}_2^+$ and $^{39}\text{Ar}^+$

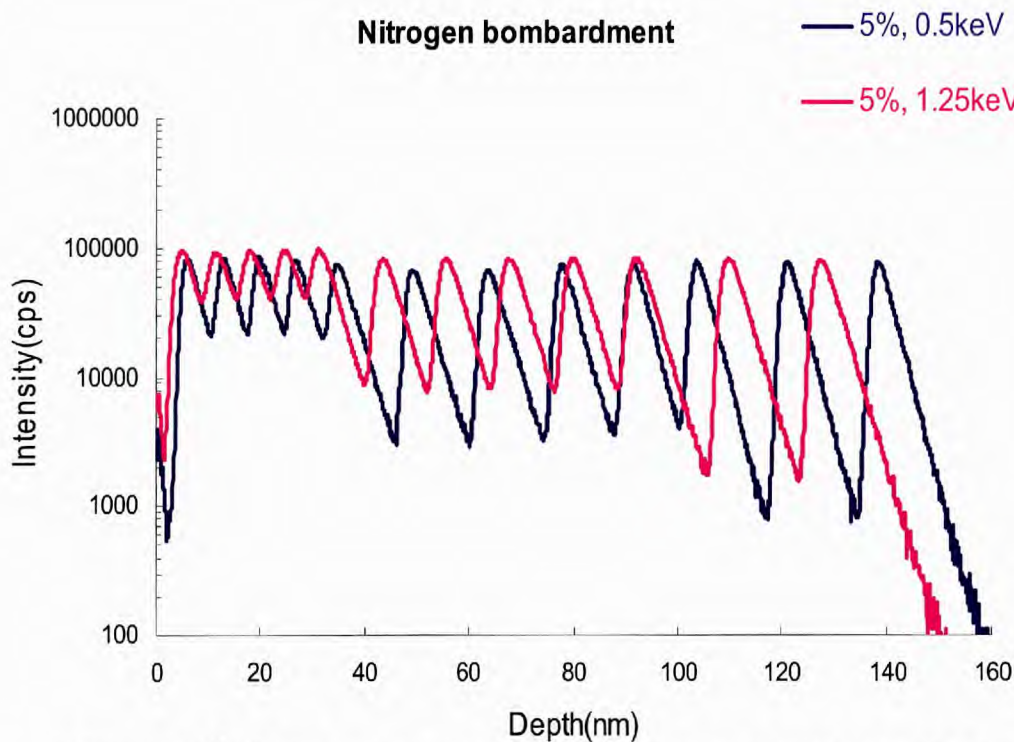


Figure 3.1 $^{27}\text{Al}^+$ depth profiles obtained with nitrogen Atomika6500 bombardments at different energy at normal incidence.

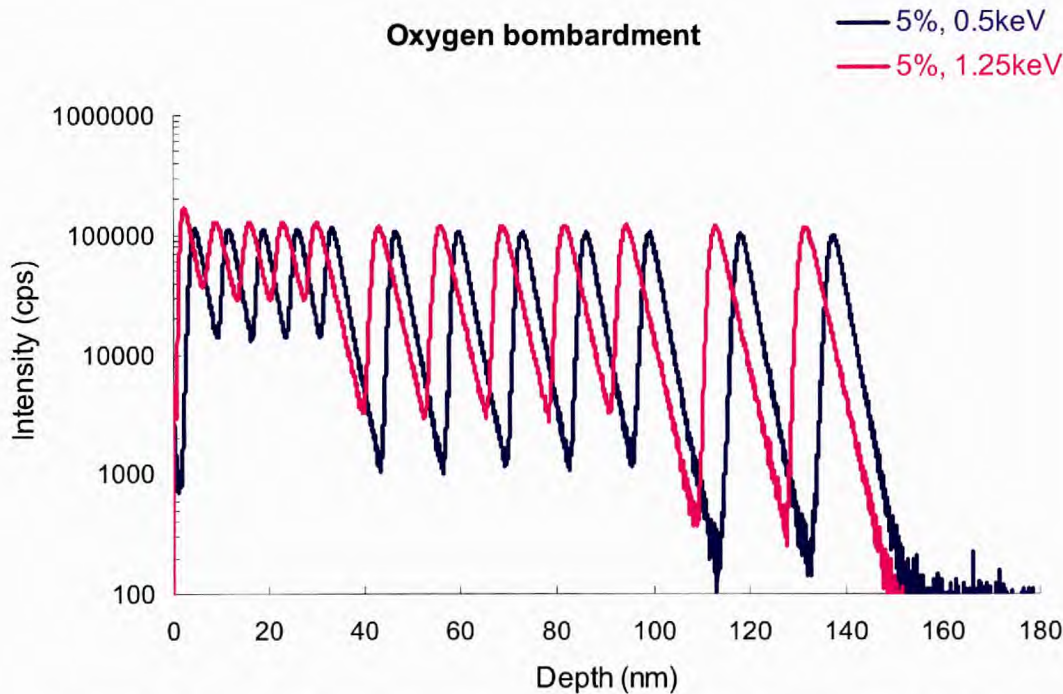


Figure 3.2 $^{27}\text{Al}^+$ depth profiles obtained with oxygen Atomika 6500 bombardments at different energies at normal incidence.

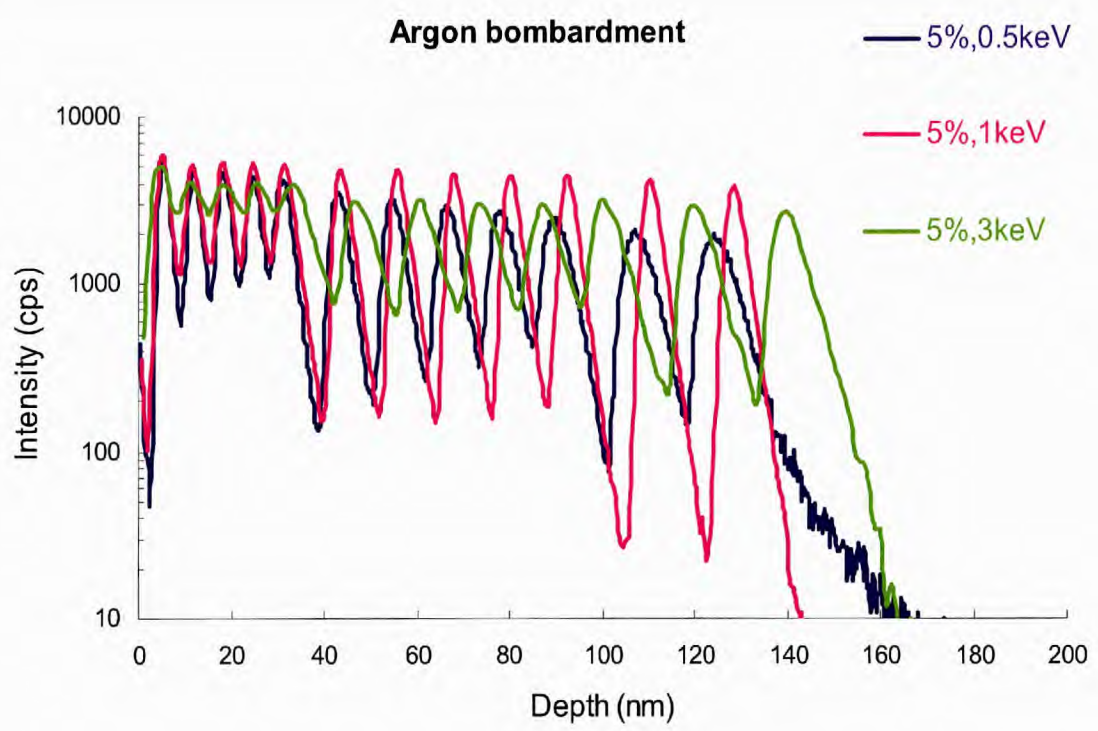


Figure 3.3 $^{27}\text{Al}^+$ depth profiles obtained with argon ION-TOF IV bombardments at different energy at an incident angle of 45° .

Appendix 4 – Comparison between Different Beams and Techniques

Decay length comparison between nitrogen and oxygen

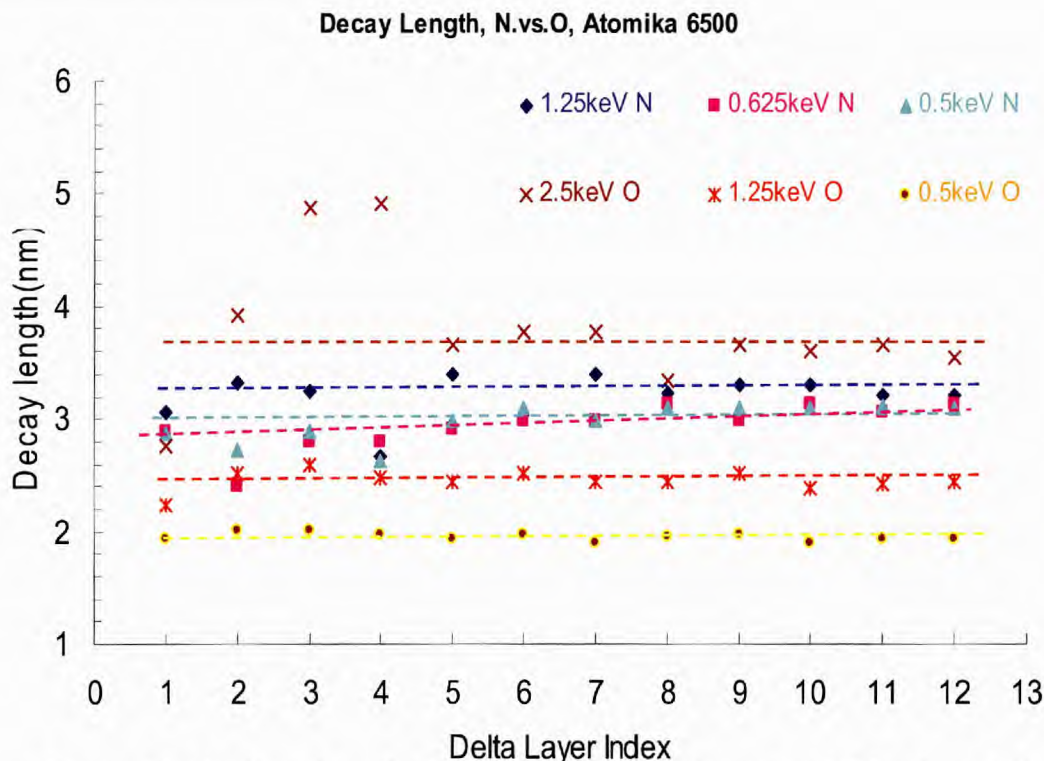


Figure 4.1 The decay length of Al delta layers as a function of delta layer index at different nitrogen and oxygen beam sputtering energies .

The comparison between the Atomika 6500 and ION-TOF IV techniques

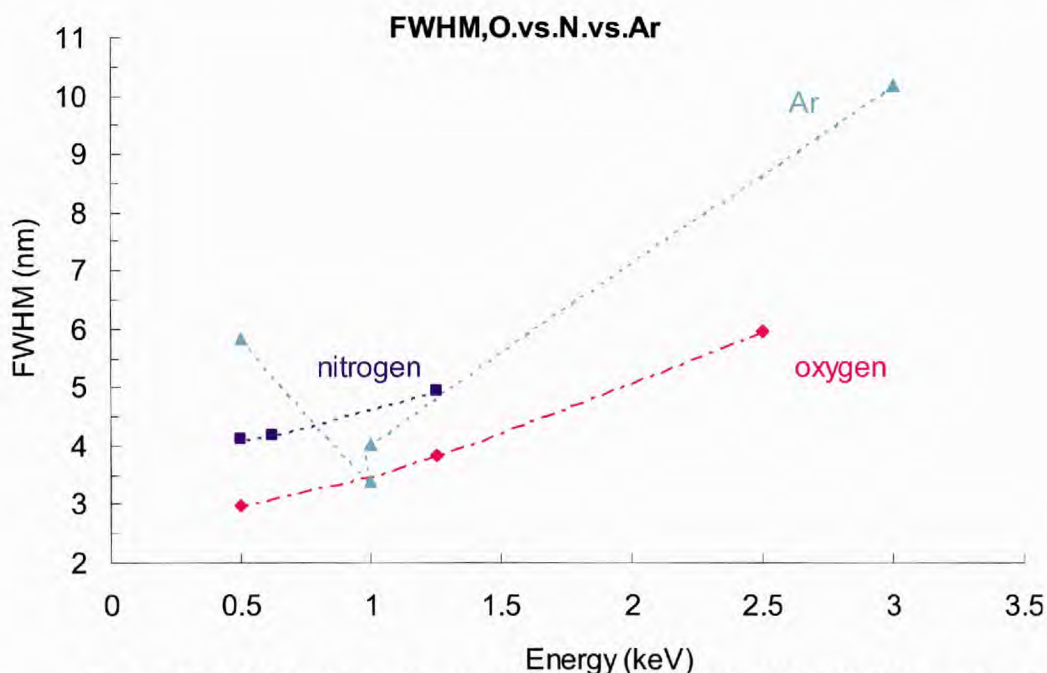


Figure 4.2 FWHM obtained in the Atomika 6500 and the ION-TOF IV as a function of beam energy.

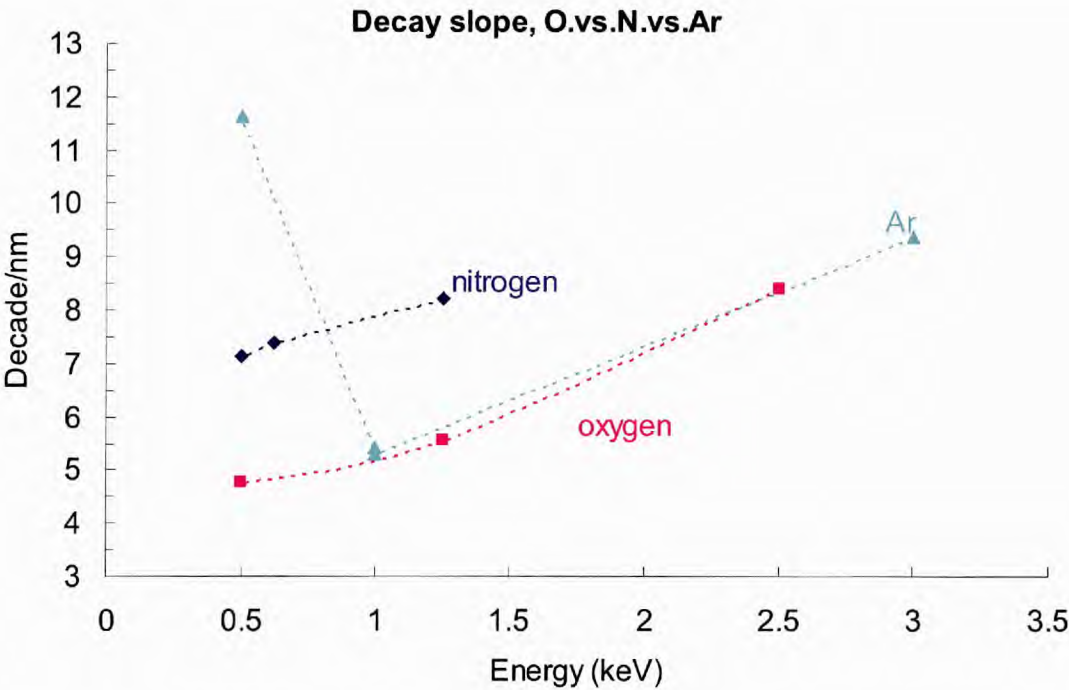


Figure 4.3 Decay slope obtained in the Atomika 6500 and the ION-TOF IV as a function of beam energy.

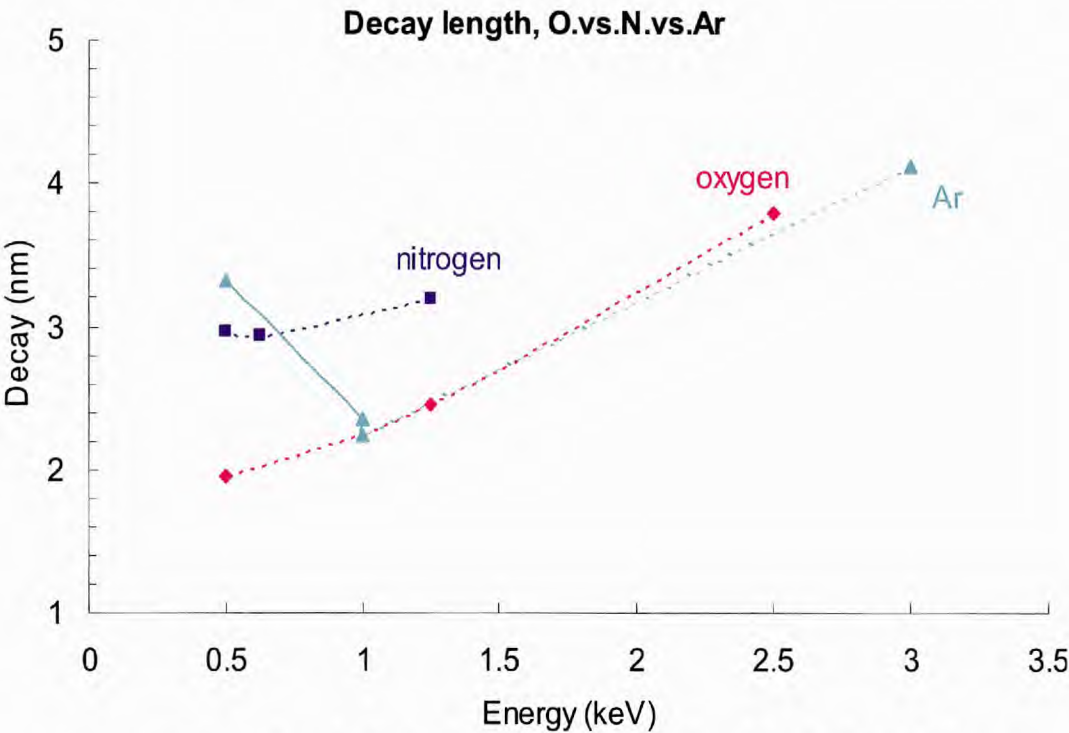


Figure 4.4 Decay length obtained in the Atomika 6500 and the ION-TOF IV as a function of beam energy

Appendix 5 – Ion Projected Range Measured in TEM

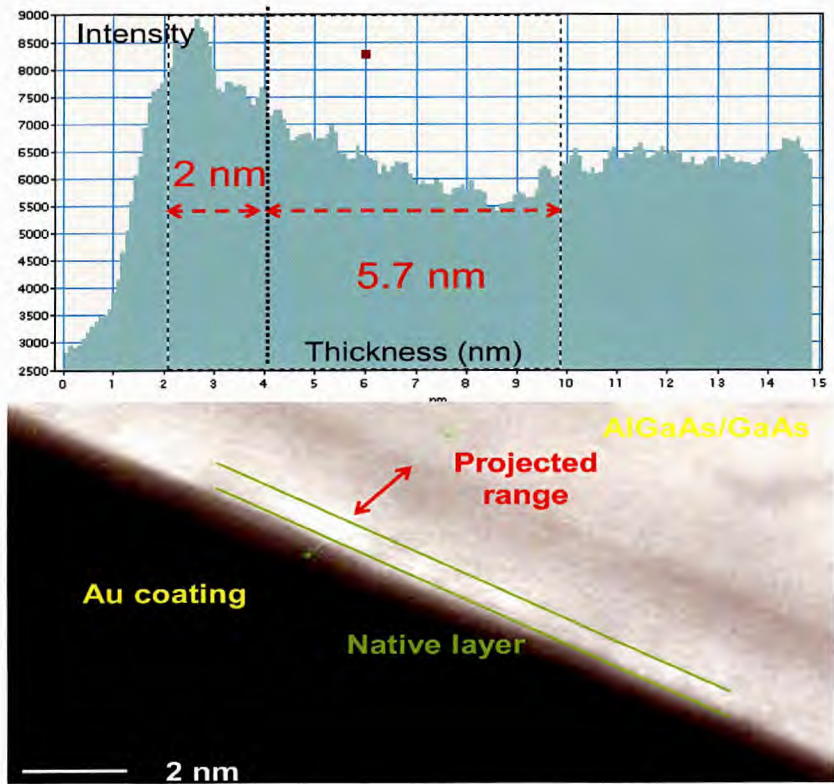


Figure 5.1 TEM image of the crater formed by the 2.5 keV oxygen beam.

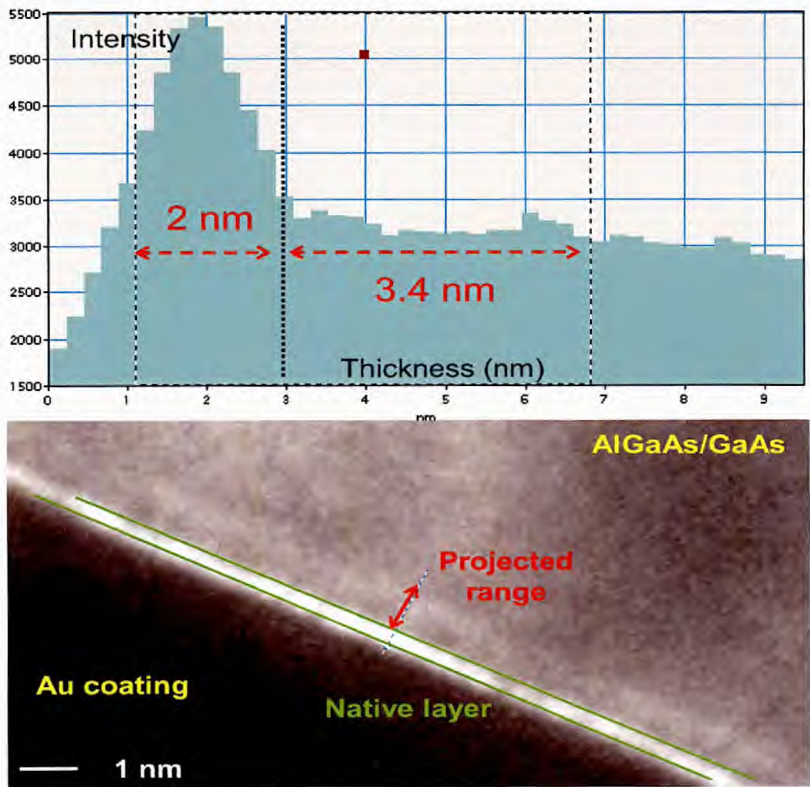


Figure 5.2 TEM image of the crater formed by the 0.5 keV nitrogen beam.

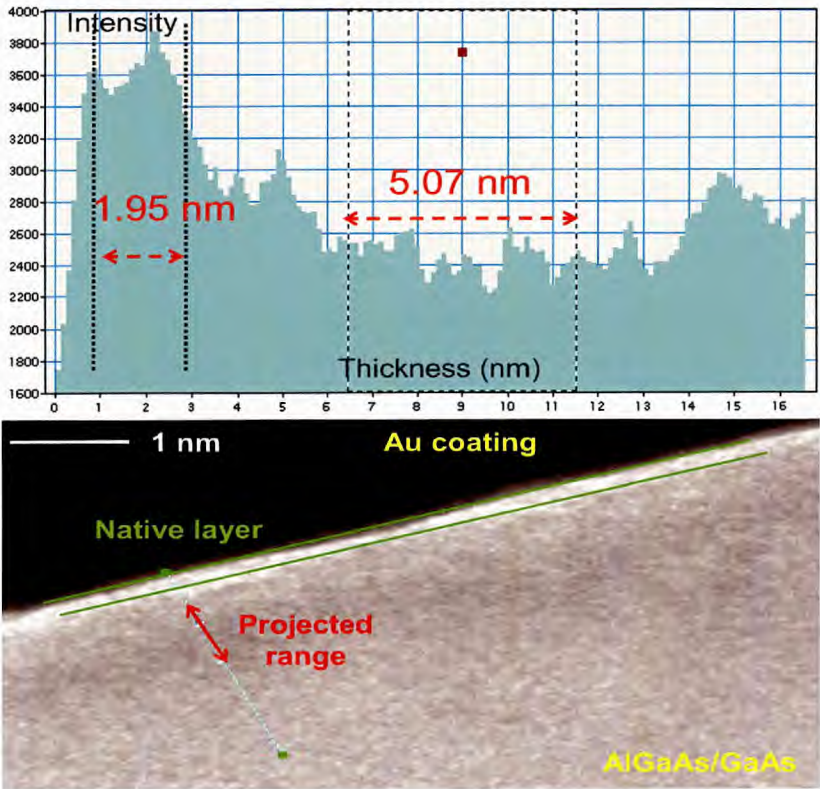


Figure 5.3 TEM image of the crater formed by the 1.25 keV nitrogen beam.

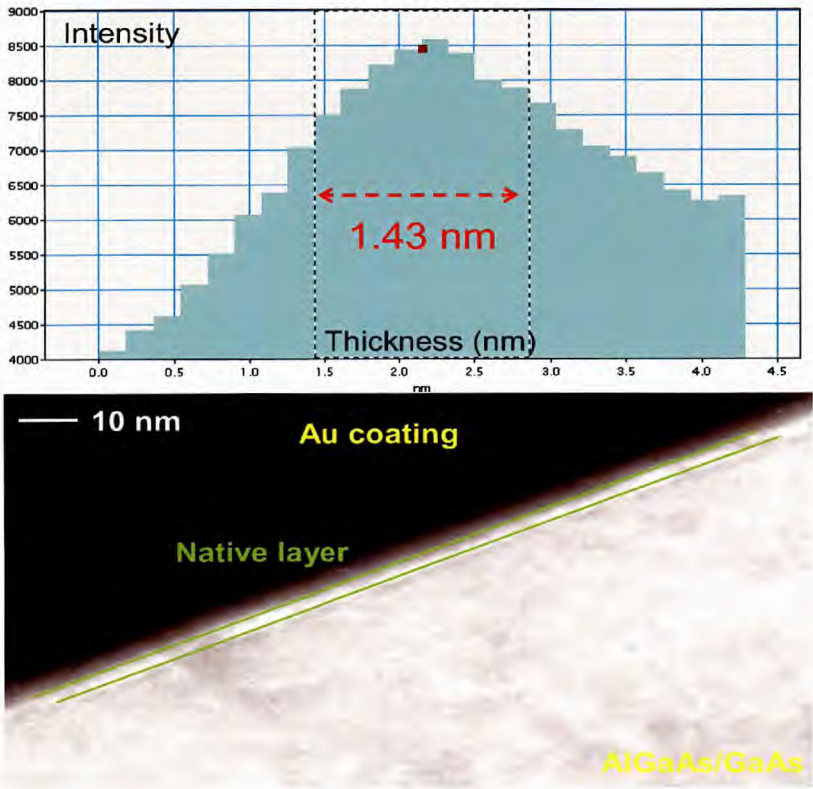


Figure 5.4 TEM image of a fresh surface, there is no dark line appeared in the image, the white line is the native oxide layer, its thickness is about 1.43 nm.

Publications

1. The ion yield enhancement for FIB-SIMS, 16th Surrey Ion Beam Centre (IBC) User Workshop, University of Surrey, poster presentation, 28/March/2007
2. The optimisation of focused ion beam secondary ion mass spectrometry (FIB-SIMS) for applications in Materials Science, European Microbeam Analysis Society (EMAS) conference, poster and oral presentation, 06/May/2007
3. Applications of FIB-SIMS in Materials Science, SIMS 16, Kanazawa, Japan, poster presentation, 28/10/2007
4. Secondary ion yield enhancement effect of $^{16}\text{O}_2^+$ and $^{14}\text{N}_2^+$ ion bombardment in Ga^+ FIB-SIMS and TOF-SIMS, Postgraduate Research day, Department of Materials, Imperial College London, UK, poster presentation, 23/March/2009
5. L.Li, D.S.McPhail, N. Yakovlev, H.Seng, Surface and interface analysis, *Strategies for improving the sensitivity of focused ion beam secondary ion mass spectrometry (FIB-SIMS)*, **in press**.
6. L.Li, D.S.McPhail, N. Yakovlev, H.Seng, Surface and interface analysis, *Ion yield enhancement effect in FIB-SIMS and TOF-SIMS*, **in press**.
7. L.Li, D.S.McPhail, N. Yakovlev, H.Seng, Surface and interface analysis, *Secondary ion yield enhancement effect of low energy oxygen implantation and flooding in TOF SIMS*, **in press**.
8. D.S.McPhail, L.Li, R.Chater, N. Yakovlev, H.Seng, Surface and interface analysis, *From FIBSIMS to SIMSFIB - The Prospects for a 10nm Lateral Resolution SIMS Instrument with Full FIB Functionality*, **in press**.
9. D.S.McPhail, R.Chater, L.Li, *Applications of focused ion beam SIMS in Materials Science*, Mikrochimica acta. 161(3): p. 387-397. 2008

Major Awards

1. Deputy Rector's Award 2006, Imperial College, Duration 3 years
2. Stephen and Anna Hui Fellowship 2006, Imperial College, Duration 3 years
3. 'Young Scientists' Award', European Microbeam Analysis Society conference, Antwerp, Belgium, 06/May/2007
4. President's Award for the best paper in the EMAS2007 Workshop Proceedings
5. SIMS XVII Student Award, Toronto, Canada, 14/September/2009
6. The Armourers & Brasier's Award
7. Hilary Bauerman Trust & Frank Merrick's Associates Award

8. UK Surface Analysis Forum travel grant, 2009
9. IOP Materials Characterisation Group travel grant, 2009