Abstract

LOESING, RAINER, Development of High Resolution Depth Profiling Of Ultra Shallow Dopant Implants with SIMS (under the direction of Phillip E. Russell)

Secondary Ion Mass Spectrometry (SIMS) is considered a reliable technique for precise and accurate dopant depth profiling in Si with respect to junction depth and implanted dose. The junction depths of source drain extension structures are predicted to be between 19-33nm for the 0.1μm MOSFET generation. Accurate high depth resolution analysis of these ultra-shallow junctions by SIMS can only be provided if atomic mixing caused by energetic primary ion bombardment is minimized and extensive beam induced crater bottom roughening is avoided. For quantitative measurements, the influence of primary ion implantation, sputter rate changes and beam induced crater bottom roughness on secondary ion intensities has to be known. In this work SIMS was used to develop techniques for the accurate analysis of ultra shallow B, P and As implants in Si.

Low energy O$_2^+$ primary ion bombardment was found to give the highest depth resolution for the analysis of B and P in Si, while low energy Cs$^+$ and CsC$_6^-$ primary ion bombardment resulted in the highest depth resolution for the analysis of As in Si. To obtain a more accurate profile shape and depth scale it was found to be essential to limit beam induced crater bottom roughness by means of sample rotation, variations of primary ion angle of incidence or change in sample chamber vacuum conditions. Beam induced crater bottom roughness was investigated for low energy O$_2^+$, Cs$^+$ and CsC$_6^-$ ion bombardment using atomic force microscopy (AFM) and optical profilometer (OP) measurements. OP was found to be a valuable tool for investigating small changes in
sputter rate in the initial stages of a SIMS depth profile. It was shown that dose measurements of ultra shallow implants can be improved by using a correction procedure based on bulk doped standards. SIMS was proven to be a valuable tool for the characterization of ultra shallow implants in Si, but careful consideration of analysis conditions and SIMS artifacts is required for accurate analysis.
DEVELOPMENT OF HIGH RESOLUTION DEPTH PROFILING OF ULTRA SHALLOW DOPANT IMPLANTS WITH SIMS

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

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Chair of Advisory Committee
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RAINER LÖSING, was born in Flörsheim, Germany, in 1970, and raised in Weilbach, Germany from 1970-1989. He attended Gustav Heisenberg High School in Rüsselsheim, Hessen Germany from 1986-1989. From 1989-1990 he served his obligatory military service in Kassel, Germany. In the fall of 1990 he began to study Mineralogy at the Technical University of Darmstadt, Germany. After completing his preliminary studies in Mineralogy in the spring of 1993, he continued studying in the Materials Science Department at the Technical University of Darmstadt, Germany. From 1993-1994 he worked toward his M.Sc. degree in Materials Science at the Technical University of Tampere, Finland as a visiting scholar. In the spring of 1997 he graduated from the Technical University of Darmstadt, Germany with a M. Sc. in Materials Science. In the fall of 1997 he began work on his Ph.D. degree in Materials Science and Engineering at North Carolina State University with the Analytical Instrumentation Facility under the guidance of Dr. Phillip E. Russell and Dr. Dieter P. Griffis.
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List of Symbols, Terms and Acronyms

A = Electron Affinity
AFM = Atomic Force Microscopy
ALE = Atomic Layer Epitaxy
CVD= Chemical Vapor Deposition
$D_{x,y} = \text{Surface Diffusivity Terms}$
$\epsilon = \text{Constant describing ion yield dependence on normal particle escape velocity}$
$E_F = \text{Fermi Level}$
EM = Electron Multiplier
FC = Faraday Cup
FLIG = FLoating Ion Gun
$g_o = \text{Statistical weight of the atom state}$
$g_i = \text{Statistical weight of the ion state}$
FWHM = Full Width at Half Maximum
I = Ionization potential
IMS = Ion MicroScope
ITRS = International Technology Roadmap for Semiconductors
LAD = Laser Ablation/Deposition
LVDT = Linear Variable Differential Transducers
$\lambda_d = \text{Decay length}$
$\lambda_r = \text{Rise length}$
$\lambda = \text{Ripple wavelength}$
$\lambda = \text{Wavelength of light}$
MBE = Molecular Beam Epitaxy
MOSFET = Metal Oxide Semiconductor Field Effect Transistor
NA = Numerical Aperture
OP = Optical Profilometry
$\phi = \text{Sample work function}$
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1 Introduction and Problem Overview

1.1 Dissertation Structure

Chapter one covers the motivation for this work and the context in which it was performed. Chapter two describes the history of secondary ion mass spectrometry and the fundamentals of the SIMS technique focusing on various aspects of high depth resolution depth profiling of ultra shallow features using SIMS. Chapter three focuses on the details of the experimental methods used in this work. Chapter four discusses details of depth scale and impurity distribution accuracy when using low energy O\textsubscript{2}\textsuperscript{+} ion bombardment for ultra shallow analysis of B in Si. Chapter five examines some alternatives for analysis of ultra shallow P ion implants in Si with SIMS using low energy Cs\textsuperscript{+} and O\textsubscript{2}\textsuperscript{+} primary ion beams. Chapter six introduces a different approach for ultra shallow P analysis with SIMS employing negative cluster ions for the primary ion analysis beam. Chapter seven compares the advantages and disadvantages of magnetic sector and quadrupole type SIMS instruments with respect to the analysis of ultra shallow n-dopants. The chapter eight describes a method for improving depth scale calibration and correcting procedures for ion yield changes in the transient zone during SIMS depth profiling. Then conclusions and future work are given in chapter nine.

1.2 Introduction and Motivation

Recent advances in semiconductor technologies have largely been achieved by scaling down the lateral and vertical dimensions of device features. The next generation of very large scale integrated (VLSI) and ultra large scale integrated (ULSI) devices will contain device features on the order of 0.1\mu m. These devices will require source and drain extension (SDE) junctions, according to the International Technology Roadmap for Semiconductors (ITRS), that are below 33 nm deep. These junctions are classified as ultra-shallow junctions (1)(2). A schematic of a MOSFET with SDE is shown in Figure 1-1.
Figure 1-1: Schematic of a MOSFET with Source/Drain Extensions

Most commonly formation of p/n junctions in state of the art MOSFET devices is achieved using ion implantation. Ion implantation allows excellent control of the amount of dopant introduced into the sample and the depth over which the dopant is distributed and hence junction depths. Sputter depth profiling in combination with Secondary Ion Mass Spectrometry (SIMS) has been shown to provide accurate and reproducible analysis for high and medium energy ion implants with respect to implanted dose, junction depth and profile shape. Dose measurement precision, a value describing the repeatability of SIMS measurements, of better than 1 percent is obtainable (3). Dose measurement accuracy, a statement which describes how closely a measured value represents an actual value, is achieved by measuring a standard with a well characterized dose under the same analytical conditions as the unknown specimen and applying the dose calibration to the measurement. In general at least one substrate (matrix) signal is measured together with the dopant signal as a function of time throughout the SIMS depth measurement. The ratio of dopant to matrix signal is then converted to dopant concentration by applying a Relative Sensitivity factor (RSF) (4), obtained from the calibration standard. The time axis of the depth profile is converted into a depth scale by applying a constant sputter rate obtained from final crater depth measurements. Since the peaks for high and medium energy ion implants are well below the surface, changes in the initial part of the depth profiling process have only a limited influence on dose measurement and depth calibration for these implants.
The accuracy and precision provided by SIMS for high and medium energy ion implants will also be required for ultra shallow implants to allow reliable production (requires precision) and further development of device theory and modeling for improvement of device design (requires accuracy) of future MOSFET generations. State of the art SIMS depth profiling can not provide measurements of ultra shallow junction implants that are not compromised by ion beam induced mixing, and by changes in secondary ion yield and sputter rate during the depth profile. Sputter rate and secondary ion yield changes occur in a complicated and not well understood way due to implantation of primary ions into the sample and removal of surface layers, which complicates quantification. These changes are most prominent in the top few nanometers of the sample. The region over which sputter and ion yield changes occur is called transient zone.

With the peak concentration of ultra shallow implants lying in the immediate vicinity of the surface, accurate quantification is more difficult compared to deeper ion implants. Ion yield and sputter rate changes can be reduced, but not eliminated, by using e.g. lower primary beam impact energies or flooding the sample surface with $O_2$. It is essential that methods are developed which enable quantification in the near surface (transient) region of a SIMS depth profile to achieve the same dose accuracy for low energy ion implants that can be achieved for medium and high energy ion implants. Existing correction as well as newly developed models are applied in this work to improve quantification accuracy of ultra shallow ion implants.

The determination of profile shapes and junction depths of ultra shallow ion implants with SIMS requires that the depth resolution of the measurement is sufficient to reveal subtle changes in the profile. Depth resolution in SIMS depth profiling is most often quoted as decay length, which is the drop of a measured secondary ion signal by one over e ($e = 2.718... = \text{Euler’s number}$) on an exponentially decaying slope, usually the trailing edge of an implant (5). For shallow depth profiling atomic mixing and beam induced crater bottom roughness plays a dominant role and must be minimized to achieve high depth resolution and an accurate depth scale (6). Atomic mixing can be decreased by reducing primary ion impact energy, with the minimum practical energy currently limited by source stability and extraction efficiency (7). Other ways to reduce primary
ion range and therefore atomic mixing are to increase the primary ion angle of incidence, to minimize normal impact energies or to use cluster ions with each atom in the cluster carrying an energy according to the mass fraction of the ion in the cluster (8)(9). Beam induced crater bottom roughness can be reduced by rotating the sample (10)(11)(12), which results in an improved depth resolution and a more constant sputter rate throughout the profile and hence a more accurate depth scale.

In this work special emphasis will be given to the dopants phosphorus (P) and arsenic (As). As has a lower diffusivity in Si compared to P and hence will be the likely choice for ultra shallow junction formation (13). However, the semiconductor industry is also interested in shallow P analysis, since due to the overall reduction in device dimensions shallow P analysis will become important. SIMS is also used to measure unintentional dopant cross contamination by P produced during ion-implantation. This measurement requires accurate concentration determination, with the depth of the cross contaminant typically being less than the depth of the intentionally implanted species.

Characterization of P and As dopant profiles by SIMS requires high mass resolution (M/ΔM ~4000) to eliminate mass interferences between $^{30}$SiH and $^{31}$P and between $^{29}$Si$^{30}$Si$^{16}$O and $^{75}$As. Consequently SIMS depth profiling of P and As is essentially limited to magnetic sector or Time Of Flight (TOF) SIMS instruments, which have the capabilities to resolve these mass interferences (14). Exceptions are applications where P and/or As are of sufficient high concentration so that quadrupole instruments can be used effectively or samples are pumped down in UHV for extended periods (around 10 hours or over night) to reduce the respective mass interferences mentioned above. However, while interference separation is important, minimization of transient zone width, beam induced crater bottom roughness and atomic mixing are at equally important for measuring P or As secondary ion intensity with high accuracy during a depth profile.

Analysis of n-dopants like P and As using SIMS depth profiling is primarily done using a Cs$^+$ primary ion beam and extraction of negative secondary ions. Cs$^+$ is used because Cs lowers the work function of the surface, which increase negative ion yield. To extract negative ions the sample is biased negatively in magnetic sector SIMS. Since the primary beam and sample polarities are opposite, Cs$^+$ is accelerated towards the sample, limiting the possibilities for low energy primary ion bombardment. Since low
energy primary ion bombardment is one of the most important parameters for high depth resolution profiling, the possibilities and limitations of using Cs\(^+\) ion bombardment for the analysis of P with the CAMECA IMS 6F are investigated.

O\(_2\)^{+} primary ions and positive secondary ion extraction provide an alternative for analysis of P with SIMS. The positive sample bias used to extract the positive secondary ions repels positive primary ions, which reduces their total impact energy. The impact angle of positive primary ions onto the positively biased sample is increased as a result of the repelling sample potential, which reduces normal primary ion impact energies and atomic mixing and hence should improve depth resolution as stated above. This possible gain in depth resolution using O\(_2\)^{+} and positive secondary ion extraction instead of Cs\(^+\) and negative ion extraction is not often utilized for the analysis of P with SIMS, because the positive ion yield of P under O\(_2\)^{+} ion bombardment is about one order of magnitude lower compared to the negative ion yield of P under Cs\(^+\) bombardment. The increased levels of dopant concentration in ultra shallow junction formation to reduce depletion layer width may make O\(_2\)^{+} ion bombardment a more feasible alternative to Cs\(^+\) bombardment for high depth resolution measurements. The use of Cs\(^+\) and O\(_2\)^{+} bombardment is compared for the analysis of P with the CAMECA IMS 6F. The effect of glancing angle O\(_2\)^{+} bombardment on beam induced crater bottom roughness and its influence on depth resolution was investigated using a B delta doped structure. The use of B instead of P doped samples is possible, since due to the low dopant concentration results are assumed to be independent of dopant type and should apply to all investigated dopants.

As described above, Cs\(^+\) and negative secondary ion extraction gives the lowest detection limits for P and As, while sample potentials which repel the incoming primary ions as in the case of O\(_2\)^{+} primary ions and positive secondary extraction can give better depth resolution. In principle Cs containing negative primary ions and negative secondary ion extraction can be employed to combine the advantages of both primary ions. The use of negative primary ions other than O\(^-\) for sputter depth profiling is a new and challenging field of SIMS and part of this work involves the investigation of possible negative primary ions for ultra shallow depth profiling of n-dopants, employing a sputter negative ion source. From this study the most promising primary ion for this purpose
appears to be CsC₆⁻. CsC₆⁻ is used in this work for depth profiling of P and As in Si and compared with depth profiling of P and As in Si using O₂⁺ and Cs⁺ primary ion beams.

1.3 References

3. B.W. Schueler and D.F. Reich, proceedings of the 6th International Workshop on Ultra Shallow Junctions, Napa, CA, USA (2001)
2 Secondary Ion Mass Spectrometry (SIMS)

2.1 Introduction

In the last two decades the analytical demand for high elemental sensitivities down to parts per million (ppm) and parts per billion (ppb) as a function of depth has significantly increased. SIMS has developed during the last 30 years into a major technique that can provide this information for the surface analysis of solids (and sometimes liquids) (1). In SIMS a surface is bombarded with energetic particles, usually ions. Momentum is transferred to the atoms in the sample via a serious of binary collisions between the primary particle and sample atoms as well as solely between sample atoms. This is often described as a collision cascade. Some of the sample atoms that are set in motion during the collision cascade follow trajectories that reach the surface of the sample. Atoms that arrive at the surface with an energy that exceeds the surface binding energy can leave the sample and a fraction of these atoms are ionized. The theoretical description of ionization is complicated due to the simultaneous occurrence of sputtering and ionization and the use of reactive primary particles, which alter the sample matrix to increase ionization efficiency. Ionization models are described in section 2.3.6. Secondary ions of a selected polarity are extracted from the surface, separated by mass to charge ratio in a mass spectrometer and detected. Types of analyses that can be performed using SIMS include mass scans (secondary ion intensity versus mass), depth profiles (secondary ion intensity versus time) and secondary ion images (two dimensional secondary ion intensity distributions of selected species versus position on the sample surface). The depth profile time can, at least to a first approximation, be converted to a depth scale by measuring the total depth of the sputtered crater or by applying a known material removal (sputtering) rate. Quantification of concentration is usually done by applying conversion factors obtained from ion implanted or bulk doped standards. A schematic of a basic SIMS experiment is shown in Figure 2.1
2.2 History Of Secondary Ion Mass Spectrometry

The development of Secondary Ion Mass Spectrometry began in 1910, when Sir Joseph Thomson observed and identified the emission of positive secondary ions when he bombarded a metal surface with primary ions in a discharge tube (2). Woodcock recorded the first spectrum of negative secondary ions twenty-one years later in 1931 when he bombarded NaF and CaF$_2$ with 500eV Li$^+$ ions. In 1949 Vieböck under the supervision of Herzog constructed a SIMS instrument that used electric fields to accelerate primary ions to the sample and an electric field parabola spectrograph to separate the secondary ions and record a secondary ion mass spectra from metal oxides (3,4).

Rapid development of SIMS began in the 1960’s facilitated by progress in ion optical design by Liebl and Herzog. These advances in ion optical design led to the development of a prototype ion microscope by Castaing and Slodzian in (5, 6) 1960. This instrument used a broad ion beam to bombard the sample, but ion optics were used
to stigmatically extract secondary ions and to project a magnified secondary ion image onto a fluorescent screen, thus producing the first ion microscope. This instrument was able to achieve a spatial resolution of about 1 μm. A commercial version of this instrument was developed by Rouberol et al. at CAMECA instruments and commercially introduced in 1968 as the IMS-300 (7). The IMS-300 used a retarding field electrode for energy separation and a magnetic prism for mass separation. At about the same time (1967) Liebl developed an ion microprobe that used a finely focused ion beam rastered over a surface to erode the surface and produce a chemical map of the sample (8). This instrument, which was able to achieve a spatial resolution of 1 μm, was made commercially available in 1967 as the Ion Microprobe Mass Analyzer (IMMA) by Applied Research Laboratories. In the early 1980’s the obtainable lateral resolution on ion microprobe type instruments was vastly improved by the introduction of liquid metal ion sources that operate by field ionization of metals from a sharp tip (9). Lateral resolution of 20nm and below can now be obtained using liquid metal ion sources (10). In 1975 Wittmaack developed the first secondary ion mass spectrometer with mass separation based on a quadrupole (11). The ATOMIKA differential in-depth analyzer (ADIDA), based on the design by Wittmaack, was commercially introduced in 1976 by ATOMIKA GmbH of Germany(12,13,14).

In both magnetic sector and quadrupole type instruments, the surface is usually eroded rapidly to obtain secondary ion intensity distributions versus depth with high sensitivity, which makes “true” surface analysis impossible. This type of analysis is usually referred to as dynamic SIMS. To analyze the elemental composition of the first monolayer Benninghoven introduced in 1970 a variation of SIMS using low primary ion beam densities, so that the damage cross sections introduced by the primary ions did not overlap and the lifetime of the first monolayer was in excess of the time required for the analysis (15). This analysis technique is called static SIMS. Secondary ion mass separation and detection in the static SIMS mode is often achieved using a time of flight mass spectrometer (16), because of their high collection efficiency and high mass resolution. The advantage of static SIMS is that it gives not only elemental composition, but also gives chemical structural information of the surface via the analysis of molecular ions.
In 1977 CAMECA introduced IMS 3f as a replacement of the IMS 300. Design changes from the IMS 300 included the incorporation of a transfer optical system that improved the matching of the ion optics to the size of the analyzed area. In the IMS-3F, the double pass spectrometer was also replaced with a double focusing mass spectrometer. In a double focusing mass spectrometer an electrostatic sector and a magnetic sector are utilized in serial arrangement, so that the chromatic aberrations of each sector cancel each other and the mass dispersive properties of the magnetic sector are retained (17). This arrangement provides mass resolution over a range from 300 to 10000 $M/\Delta M$ (18). The next generation in what became now the CAMECA F-series was introduced by H.N. Migeon of CAMECA in 1985 as the IMS-4F. While based on a design similar to that of the IMS 3-F, capabilities such as a normal incidence electron gun and scanning ion image capability were added (19). The IMS-4F was replaced with the IMS-5F in 1991 (20). Improvements introduced on the 5F included digital control of the instrument, continuously adjustable sample potential from −5kV to +5kV to allow more flexibility in impact energy, a newly designed thermal ionization ion source for a Cs$^+$ microprobe (21) and improvements in the vacuum system to allow analysis of gaseous species with improved sensitivity. The next generation in the CAMECA F-series was introduced in 1996 as the CAMECA IMS-6F. In the IMS-6F, the magnet for secondary ion mass separation was replaced by a laminated magnet. The use of a laminated magnet reduced hysteresis which dramatically reduces the time necessary to switch between masses, especially at high mass resolution. Rapid mass switching capability reduces mass switching time which increases the amount of secondary ion acquisition time improving secondary ion sensitivity and/or depth resolution. Later improvements for the IMS-6F include a post acceleration system which enhances the conversion efficiency of the electron multiplier detector for low impact energies, a rotating stage which minimizes beam induced crater bottom roughness and a system for the duoplasmatron ion source of the instrument which allows low voltage primary ion extraction from the source with higher efficiency.

For quadrupole instruments in 1996 Dowsett developed (22) a floating low energy ion gun (FLIG) which was introduced to the SIMS community by ATOMIKA in 1998 (23). This design allows the ion beam to be transported through the primary ion column
at high energy before deceleration of the primary ions near the sample, allowing impact energies as low as 150eV (24). With the increasing need for analyses of more and more shallow features, interest in dopant depth profiling with Time-Of-Flight (TOF) type instruments, which were traditionally only used for static SIMS, has increased. In 1998, Niehuus of ION-TOF developed a TOF instrument which uses two primary ion beams for depth profiling, one beam for rapid removal of material and a short-pulsed beam for the creation of secondary ions (25).

### 2.3 Fundamental Concepts in Secondary Ion Mass Spectrometry Related to High Resolution Depth Profiling

There are three major factors that determine the attainable depth resolution using SIMS. These factors are ion beam mixing, surface roughness, which can be either initial (prior to SIMS analysis) or primary ion beam induced surface roughness and instrumentation related factors. Other described phenomena are the transient zone (the initial part of a sputter depth profile where removal rates and ionization efficiencies change), ion yield models which describe the theoretical treatment of ionization of sputtered particles and oxygen flooding of the sample surface, which is a method to increase ion yields and reduce transient zone width.

#### 2.3.1 Ion Solid Interaction

Ion-Solid interactions include the transfer of momentum from the primary ion to target atoms as well as radiation-enhanced segregation and radiation enhanced diffusion. If ion beam induced crater bottom roughness and redistribution of the analyzed species via segregation and diffusion under the primary ion beam bombardment are avoided, ion beam or cascade mixing will be the limiting factor for the obtainable depth resolution. Ion beam induced mixing is a direct consequence of the slowing down of the primary ion due to a series of energy transferring collisions with target atoms. Generally the energy directly transferred by the primary ion to a target atom (primary recoil atom) is sufficient
for the primary recoil to describe a trajectory of a certain length in the target. These primary recoils will set other target atoms in motion (secondary recoils) as long as their transferable energies exceed a certain threshold value that is for most elements in the order of 20eV (26). The vast majority of the higher order recoil atoms have lost the directional character dedicated by momentum conversation of the first one. The movement of the recoiled atoms causes intermixing of the different elements of a sample and thus limits the depth resolution of SIMS. Deeper penetration of the primary ion beam species results in a larger volume over which recoil mixing can occur increasing primary ion beam induced mixing of the sample. The mixing depth is proportional to the projected range plus straggle of the primary ion beam. The mixing depth is also affected by primary beam species, energy, mass and angle of incidence. A schematic of the collision cascade caused by the incoming primary ion is shown in Figure 2-2 (27).
Simulation of the ion induced primary ion interaction with the sample matrix is useful for gaining an understanding of beam sample interactions. Because of the large number of particles involved in SIMS (or ion implantation), simulations are most often done using Monte Carlo methods, which simulate processes based on probabilities. SRIM (Stopping and Ranges of Ions in Motion) is a widely used Monte Carlo program for simulation of ion implantation (28). It consists, like all Monte Carlo simulation programs for ion-solid interaction, of calculating the trajectories and energy losses for a large number of primary ions in the target. SRIM assumes an amorphous target and treats the interaction of incoming ions and target atoms as binary collisions, i.e. it ignores the influence of neighboring atoms. Initially each primary ion starts with a given energy,
position and direction. Only nuclear collisions are assumed to be able to cause changes in direction of primary ions or target atoms that were set into motion, while between collisions particles are assumed to fly in a straight path. Ions lose discrete amounts of energy in nuclear collisions and lose energy continuously due to electronic losses. Nuclear and electronic energy losses are assumed to be independent. To calculate energy losses and angular deflections due to nuclear scattering the program uses the universal ZBL (Ziegler, Biersack, Lindhard) interatomic potential derived from solid state electron distributions (28). Electron stopping at low velocities, which are important for SIMS, are calculated based on the formalism of Lindhard and Scharff (29). In SRIM simulation the path of the ion ends either when the ion leaves the sample or when its energy drops below that necessary to displace target atoms. Because an amorphous target is assumed, no crystallinity affects are taken into account and thus neither directional effects on sputtering rates nor channeling are simulated.

In addition to cascade mixing, primary ion implantation introduces defects in the crystalline material. These defects can cause radiation enhanced segregation of impurities in the target. Radiation-enhanced segregation is a non-equilibrium process, since ion bombardment causes the defect concentration in the material to greatly exceed its equilibrium concentration. The increase in defect concentration also leads to a greatly enhanced diffusion in ion bombarded materials, as the diffusion coefficient is proportional to the point defect concentration. The effect of ion bombardment on diffusion is often described by an effective temperature, which is the temperature at which the sample would have to be heated to obtain the same mobility as without ion bombardment (30). As primary ion implantation also changes the surface composition, segregation of elements to or from the surface can occur due to thermodynamic forces to minimize the surface free energy. This segregation process is called Gibbsian segregation (31)(32).
2.3.2 Changes in Surface Topography due to Ion Bombardment

The initial physical characteristics of the sample to be analyzed can strongly influence obtainable depth resolution. The best depth resolution can only be achieved if the sample has a perfectly flat surface. Dust particles that act as local erosion masks and/or scratches in the sample surface lead to unacceptable distortions in SIMS depth profiles, but proper sample handling and/or cleaning can be used to avoid this problem. For dopant and impurity depth profiling of Si wafer having surfaces with a surface roughness of 0.1nm RMS and where minimum surface contamination is readily achievable, depth resolution is often not limited by the initial surface characteristics. However, in SIMS depth profiling, depth resolution can still be severely compromised by the formation of sputter induced surface topography.

Ion bombardment of a sample can form commonly known lattice imperfections like Frenkel and Schottky defects (33), dislocations (34) or defect cluster formation (35). If the damage introduced by ion bombardment exceeds a certain damage threshold, amorphization of crystalline samples occurs. For ion bombardment with fluencies of >1E16 ions/cm², many types of surface features have been observed, like cones, etch pits, facets, grain boundaries, cell structures, ripples or an increase in random roughness. Impurities with lower sputter yields compared to the surrounding matrix are often the reason behind cone formation, with the same often being true for grain boundaries. Facets are usually seen after eroding a poly crystalline sample resulting from the different sputter rate of different crystallographic planes.

Periodic ripple structures, which are often seen after oblique ion bombardment of solid surfaces, can be understood as the result of a linear surface instability due to a negative surface tension caused by curvature dependant sputtering as originally shown in the theory derived by Bradley and Harper (36) and further developed by Cuerno and Barabasi (37). They also showed that the formation of a negative surface tension under certain ion bombardment conditions can explain the formation of a periodic ripple structures on an originally flat surface. In curvature dependant sputtering under ion bombardment valleys are eroded faster than crests because of the greater amount of energy deposited near to the bottom of valleys compared to the amount of energy deposited at crests, as illustrated in Figure 2-3.
Figure 2-3: Illustration of curvature dependant sputtering

It can be seen that the energy deposited at point O by beams impacting at O, O_L and O_R is lower than the energy contributed by beams impacting at P, P_L and P_R to the total energy deposited at point P.

Bradley and Harper also postulated that ripple formation competes with surface diffusion and that this interplay generates ripples with wavelength in the order of

$$\lambda = \sqrt{D/\nu}$$

, where D is the surface diffusivity and ν a term describing the negative surface tension. To test Bradley and Harper's theory, McLaren bombarded GaAs with 17keV Cs^+ in the temperature range from –50 to 200°C (38). When decreasing the temperature from 200 to 55°C he observed the reduction in ripple wavelength according to the theory, with a ripple wavelength proportional to the square root of the diffusion constant. At 55°C the ripple wavelength stabilized, giving indication to a temperature independent, ion induced, surface diffusion constant. Temperature independent surface diffusion due to ion bombardment was termed effective surface diffusion. Based on angular dependant sputtering, curvature depending sputtering and surface diffusion terms, Makeev and Barabasi (39) derived the equation of motion of a single valued height function h(x,y,t) measured from an initial flat surface which lies in the x,y plane:

**Equation 1**

$$\frac{\partial h}{\partial t} = -v_o + \frac{\partial h}{\partial x} + \frac{\lambda_x}{2}(\frac{\partial h}{\partial x})^2 + \frac{\lambda_y}{2}(\frac{\partial h}{\partial y})^2 + \nu_x \frac{\partial^2 h}{\partial x^2} + \nu_y \frac{\partial^2 h}{\partial y^2} - D_x \frac{\partial^4 h}{\partial x^4} - D_y \frac{\partial^4 h}{\partial y^4}.$$

The first term ($v_o$) is the erosion rate, the second term ($\gamma(\delta h/\delta x)$) is for the predicted movement of surface features during sputtering in the x-direction, $\lambda_x$ and $\lambda_y$
represent slope depending sputtering, $v_x$ and $v_y$ are constant for surface tension terms induced by curvature dependent sputtering and terms for the effective surface diffusion.

Using the computer code COSIPO and a simplified model for surface diffusion based on the premise that atom jumps are irreversible and that atoms will jump to positions which will provide them with the maximum number of bonds to nearest neighbors, Koponen et al. (40) successfully simulated the formation of ripples for ion bombardment of amorphous carbon with 5keV Ar$^+$ primary ions at angles of incidence of 30° and 60°. The ability to simulate ripple formation supports the theoretical derived view of ripple formation and demonstrates a general improved understanding of ripple formation.

2.3.3 Instrumental Factors that Influence Depth Resolution in SIMS Depth Profiling

Ion sources commonly used in SIMS often produce other ion species in addition to the species to be used for depth profiling. Without mass filtering of these additional primary ions, simultaneous sputtering with different primary ions would occur. These ions would generally have different composition, primary ion range and/or momentum, which would lead to an increase in depth over which surface composition, and hence sputter and ion yield, changes occur compared to single species sputtering. This means a primary ion mass filter is a prerequisite for reliable analysis. Also proper focusing and rastering of the primary ion beam is necessary to get a reproducible flat crater bottom and avoid erosion inhomogeneity. Erosion inhomogeneity results in a decrease in depth resolution with depth ($\Delta z \propto z$) and can be the dominant factor controlling depth resolution. Erosion inhomogeneity can be significantly reduced by sample rotation.

2.3.4 The Transient Zone

The SIMS depth profile transient zone is the depth (time) over which the sputter rate and ion yield are changing and have not reached their equilibrium values. The
changes in sputter rate and ion yield result from primary ion implantation, changes in sample composition from the surface layers to the bulk or contamination of the sample. The width of the transient zone is often taken to be the point at which the secondary ion intensity of the matrix element has reached 90% of its steady state value.

**Figure 2-4: Illustration of the transient zone in SIMS sputter depth profiling**

Since the rate of change of the sputter rate and ion yields in the transient region is currently unpredictable, quantification of impurity concentrations in the transient region is impossible. Unfortunately, with the lower ion implant energies used to form ultra-shallow junctions by ion implantation, a large amount of the total implant dose comes to rest within the transient zone, making it necessary to develop and apply correction models to allow quantification within this zone. An effort will be made to develop a correction method, which will allow quantitative impurity analysis.

### 2.3.5 Secondary Ion Yield Models

A particle sputtered from the surface has a certain probability to be in an ionized state and leave the sample as a secondary ion. The ratio of secondary ions of a given element to the total number of sputtered particles of the same element is called secondary ion yield. Secondary ion yields largely determine the minimum concentration with which an element can be detected.

During ion bombardment, the bombarded material becomes amorphized at relatively low primary ion doses (approximately 1E14 to 1E16 atoms/cm²). The dose
required for amorphization depends on the mass and energy of the primary ion and the composition of the sample (41), (42). Even at the initial stages of ion bombardment the material is largely disturbed at the point of ion impact. Therefore, with respect to the effect of the material structure on ion yield, it seems more appropriate to not consider the electronic band structure of the material, but rather to consider the material as being amorphous with continuous energy states. There are essentially two models that discuss ionization probabilities in SIMS, the perturbation or electron-tunneling model and the bond-breaking model. Both of these models will be discussed below.

In the perturbation model (43), (44), ionization probability is believed to be highest close to the surface. However, neutralization probability is also high close to the surface and thus escape probability of the atom in the ionized state is low. As an ion moves further away from the surface, the coupling between ion and the surface becomes weaker and escape probability increases. However, if the sputtered atom or molecule is not already ionized, ionization probability also decreases. Thus at a distance a few Ångstroms away from the surface a point exists where the probability of ion escape is at maximum. Following this reasoning, the ionization probabilities can be shown to be proportional to:

$$P^+ \propto \exp\left[-\frac{I-\phi}{\epsilon_0}\right]$$

$$P^- \propto \exp\left[-\frac{\phi-A}{\epsilon_0}\right]$$

where $P^+$ and $P^-$ are positive and negative ionization probabilities, $I$ is the ionization potential, $A$ is the electron affinity, $\phi$ is the work function of the material and $\epsilon_0 = \hbar\gamma v/C\pi$, with $\hbar$ being Planck’s constant, $\gamma$ is a characteristic constant of approximately $2\AA^{-1}$, $v$ is the velocity of the leaving ion and $C$ being a constant.

The electron tunneling model (45) (46) is an extension of the perturbation model. In this model, for ionization to occur, the leaving particle must have an energy level equal to an energy level in the substrate at or below the Fermi level (metals) or valence band (semiconductors). The probability of having these isoenergetic levels is greatly enhanced by the excitation of electrons and the formation of a continuum of energy states which can occur during ion bombardment. This model can explain changes in positive and negative ion yield with changes in the work function of the material. It has been shown by this model and in practice that negative secondary ion yield can be increased by
reducing the work function of the material which can be for example achieved for a Si matrix via Cs implantation (47).

In contrast to the tunneling model which deals primarily with metal and semiconductor surfaces, the bond-breaking model (48) deals specifically with ion emission from ionic surfaces. If an element is already in an ionic state at the surface, the probability of the occurrence of a secondary ion depends simply on the probability of the atom or molecule remaining in a state that is more to an energetically favorable to the ionic state versus that of the neutral state as it moves away from the surface. Ionization probability will depend on the position at which the ionic and neutral potential energy curves cross. Figure 2-5 illustrates level crossing. The position of the crossing point is influenced by the ground state energies of the associated species, the difference between ionization potential and electron affinities of the positive and negative ions and the range over which electrostatic interaction occurs. If the ionic and neutral potential energy curves do not cross, a very high ionization probability results.

![Level Crossing Diagram](image)

**Figure 2-5: Illustration of level crossing. Example H\(^+\) to H**

Other ionization models are the molecular model which is based on the dissociation of neutral molecules some distance away from the surface to form ions or ions and neutrals or ions and electrons (49), and the desorption ionization model which
includes direct desorption of preformed positive and negative ions as well as fast ion/molecule reactions, electron ionization and molecular dissociation (50).

2.3.6 \( \text{O}_2 \) Flooding

Extensive reports detailing effects of \( \text{O}_2 \) flooding during SIMS depth profiling of Si have been published (51) (52). \( \text{O}_2 \) flooding in combination with \( \text{O}_2^+ \) primary ion bombardment is a method frequently used in SIMS to increase sensitivity, reduce transient zone width and eliminate or reduce the matrix effects in multi-layer analysis (53). \( \text{O}_2 \) flooding results in stochiometric \( \text{SiO}_2 \) at the surface similar to the \( \text{SiO}_2 \) surface layer formed by near normal \( \text{O}_2^+ \) ion bombardment often used in quadrupole SIMS in which case full oxidation occurs without \( \text{O}_2 \) flooding (54).

In ultra shallow depth profiling, the reduction in transient zone width with the use of \( \text{O}_2 \) flooding is especially important since a large fraction of the depth from which impurity information is desired is located in the top few nanometers of the sample. A reduction in transient zone will allow more accurate quantification in ultra shallow SIMS depth profiling.

The description of the effects of \( \text{O}_2 \) flooding on depth resolution in SIMS depth profiling varies. Both improvement (55) and degradation (56) of depth resolution has been found when \( \text{O}_2 \) flooding is used. Improvement in depth resolution is likely to be related to increased target swelling associated due to the additional O uptake resulting in a decrease in effective Si matrix mixing and/or a smoothening of the surface. Degradation in depth resolution may be connected with an increase in beam induced crater bottom roughness which occurs under certain bombardment conditions or from segregation of analyzed elements away from the O rich surface into the O depleted bulk or into the \( \text{SiO}_x/\text{Si} \) interface. A detailed study investigating the effect of \( \text{O}_2 \) flooding on high depth resolution profiling of selected ultra shallow dopants will be presented in this work. Segregation of elements into the bulk occurs as a result of the higher oxide heat of formation of Si compared to the oxide heat of formation of most other elements. This segregation is especially important for group Ia elements which have a high mobility in
Si (57). Some elements such as Mg or Be, which have a higher oxide heat of formations compared to Si, segregate into the oxide which results in a decrease in decay length or apparent but erroneous improvement in depth resolution.

For many species the positive ion yield shows a roughly 10-fold increase when O₂ flooding was used during the depth profiling Si with O₂⁺ primary ion beams (58). A higher enhancement in positive ion yield is seen for species with a high electronegativity, like As or P. When measuring the increase in positive ion yield as a function of oxygen surface concentration it is seen that most of the increase in positive ion yield occurs when the O surface concentrations is higher than 64%(59). It is assumed that at this oxygen surface concentration the SiO₂ band gap starts to form, which reduces neutralization of ions leaving the sample in accordance with the electron tunneling ion yield model described in chapter 2.3.5. An increase in sensitivity is essential for the measurement of ultra-shallow junctions in SIMS, since detection limits are reduced for high resolution depth profiling due to lower primary ion impact energies which reduces the amount of secondary ions produced per time interval and voltages which results in decreased secondary ion collection efficiency due to reduced secondary ion extraction.

2.3.7 Depth Resolution Criteria

SIMS depth resolution must be sufficient to reveal the structure of the impurity distribution to the degree required for the analysis. One criterion for depth resolution is the Raleigh criterion, which defines depth resolution as the minimum distance at which two closely spaced features can be visually resolved. In SIMS visually resolved is often defined as a 50 percent difference in intensity between two closely spaced delta layers and the valley in between. Similar to the Raleigh criterion, depth resolution can be also quoted as full width over half maximum (FWHM), which is the width over a peak at 50 percent of its maximum intensity. In SIMS depth profiling, intensity peaks obtained from delta layers are often not well defined due to atomic mixing and can be shifted in position due to sputter rate changes and/or crater bottom roughness. Hence depth resolution is generally quoted in SIMS depth profiling as decay length (λₐ) , which is defined as a
signal drop over \(1/e\) on an exponentially decaying slope, e.g. the trailing edge of an implant. While decay length \((1/e)\) is sometimes quoted as depth resolution, it gives an overoptimistic view of true depth resolution, i.e. distinguishability \((60)\). To resolve sharp features, their spacing has to be larger than \(3\lambda_d(61)\) or approximately the signal drop over one decade, \(\lambda_d(\text{decade})\). Figure 2-6 illustrates the decay length concept for \(\lambda_d(1/e)\) and \(\lambda_d(\text{decade})\).

![Figure 2-6: Illustration of decay length \(\lambda_d(1/e)\) and \(\lambda(\text{decade})\)](image)

2.4 References


2. J.J. Thomson, Phil. Mag., 20, 252, (1910)


5. R. Castaing and G. Slozdian, J. Microsc. 1, 395 (1962)


33. G.H. Kinchin, R.S. Pease, Rep. Prog. Phys, 18, 1 (1955)
34. N. Hermanne, Radiat. Eff., 19, 161 (1973)
3 Experimental Method

3.1 Introduction

Secondary Ion Mass Spectrometry is considered the most reliable technique for accurately analyzing dopant profiles with respect to junction depth and implanted dose. In each new transistor generation junction depth is reduced. Source drain extension structures are predicted to have a junction depth of 11-19nm by 2011 (1)(2). Accurate analysis of these ultra-shallow junctions by SIMS can only be provided if atomic mixing caused by energetic primary ion bombardment is minimized, and if extensive beam induced crater bottom roughening can be avoided. Lower primary ion energy and higher angle of incidence reduces atomic mixing. In addition, changes in sputter rate and ion yields in the transient zone, the initial part of the depth profile where ion and sputter yields are changing must be sufficiently understood. The CAMECA IMS 6F is a state of the art magnetic sector SIMS, a type of SIMS especially suited for analyses which require the combination of high depth resolution with high mass resolution. Recent development of the instrument improves its capabilities for high depth resolution analysis. High depth resolution analysis requires the minimization of surface topography development under primary ion beam bombardment. The nanometer scale changes in surface roughness that occur during ion bombardment can be investigated using AFM. While AFM can be used to analyze shallow sputter crater depths, optical and stylus depth profilometry are more suitable for investigating the relatively large craters (>150µm²) usually produced in SIMS. Samples used in this work were selected to allow the investigation of instrumentation and analytical parameters related to depth resolution, depth calibration and the transient zone.
3.2 The CAMECA IMS 6F

3.2.1 Ion Sources

In the most common configuration, a CAMECA IMS 6f is equipped with two ion sources: a duoplasmatron plasma ionization source and a Cs surface ionization source. In most cases $\text{O}_2^+$ primary ion ions are extracted from the duoplasmatron for the analysis of electropositive elements. In this case positive secondary ions are extracted from the sample which in magnetic sector SIMS requires a positive sample potential. The positive sample potential repels the incoming positive $\text{O}_2^+$ primary ions, which results in a more glancing angle of incidence. A more glancing angle of incidence results in lower penetration depth of the primary ions, a condition that is favorable for high depth resolution analysis (3)(4)

Cs$^+$ ion bombardment results in higher negative ion yields for elements that have a high electronegativity (5). In magnetic sector SIMS, the sample is negatively biased for extraction of negative secondary ions, which accelerates the positive primary ions towards the surface and result in impact energies higher than the initial primary ion beam energy. Since lowest Cs primary ion energy is 1.5keV and lowest practical sample potential is −1.0keV, resulting in a minimum Cs impact energy of 2.5keV, the possibilities for high depth resolution analysis using Cs$^+$ and negative secondary ion extraction are limited (6).

If negative primary ions are used instead of the positive Cs$^+$ for negative secondary ion detection, the negative sample potential repels the primary ions, which reduces primary ion impact energies. The use of sputter negative ion sources, described in detail in chapter 3.2.1.3, for production of negative primary ions is well documented in accelerator physics (7)(8)(9)(10)(11). Peabody Scientific has developed a sputter negative ion source for the use in mass spectrometry that is based on the design by Middleton (6,7). This source was employed in this study (see chapters 6 and7) to investigate the possible use of negative primary ions for high depth resolution SIMS analysis of n-dopants in Si.
3.2.1.1 Duoplasmatron

The first duoplasmatron ion source was developed by v. Ardenne in 1956 as a compact ion beam source which delivered high brightness and good beam quality at moderate cost (12). Gas is introduced into the source at a low pressure through a hollow cathode. The anode is kept at a potential difference of several hundred volts with respect to the cathode and a plasma is formed by an arc going from the cathode to the anode. A conical intermediate electrode, which is connected to the anode via a resistor, helps in creating and maintaining the ion discharge plasma. The plasma is densified close to the anode by an axial magnetic field produced by a coil between the intermediate electrode and the anode forming two plasma regions of different densities. The plasma extends through the anode due to pressure differences between the plasma region and the outside of the gun. Positive and negative ions can be extracted from the duoplasmatron depending on the polarity of the voltage applied on the anode. The most common ions extracted are O$_2^+$ and O$^-$ when using O$_2$ as a source gas and Ar$^+$ when using Ar as a source gas. An illustration of a duoplasmatron is shown in Figure 3-1 (13).

![Illustration of a duoplasmatron](13)
Ion extraction from a duoplasmatron is very efficient for high extraction potentials (>10keV). For lower extraction voltages, primary ion current extracted from the source decreases sharply as shown in Figure 3-2 (14). The low primary ion currents obtained using low extraction voltages make analysis using $O_2^+$ primary ions with primary beam energies below 3keV and impact energies below 1keV unfeasible. However, analysis of ultra shallow ion implants with SIMS requires lower impact energies. To allow SIMS depth profiling with $O_2^+$ primary ions with impact energies as low as 500eV on the IMS-6F, CAMECA introduced a modification to the duoplasmatron ion extraction system, the Accel/Decel system. Maximum $O_2^+$ current extracted from a duoplasmatron with and without Accel/Decel system as a function of extraction high voltage is shown in Figure 3-2. In this system primary ions are extracted from the source using high potentials before they are decelerated to the desired primary ion beam energy as shown in Figure 3-3. An additional lens was added between the duoplasmatron and the primary beam magnetic sector (PBMS) to further increase extraction efficiency.

Figure 3-2: Maximum $O_2^+$ primary ion current extracted from a duoplasmatron ion source with and without the Accel/Decel system as a function of extraction high voltage (14)
3.2.1.2 Cs Surface Ionization Source

While in the IMS 6-F a duoplasmatron is used for the production of O$_2^+$ primary ion beams, as described in the previous section, a surface ionization source is used for the production of Cs$^+$ primary ion beams. Surface ionization, first considered by Langmuir and Kingdon (15), describes the ionization of atoms when they come in contact with a hot metal surface. If the residence time of the atom on the hot metal surface is long enough so that it can reach thermal equilibrium with the surface, the ionization probability is described by the Langmuir-Saha equation

$$P_i = \left(1 + \frac{g_0}{g_i} e^{\frac{(I - \phi)/kT}{}}\right)^{-1}$$  \hspace{1cm} (1)

where $g_0$ and $g_i$ are the statistical weight of atom and ion states, $I$ is the ionization potential of the atom, $\phi$ is the work function of the metal and $T$ is the temperature of the hot metal plate. The ionization probability of alkali metals on hot refractory metal surface can be close to 1.
A schematic of the micro beam Cs surface ionization source used in the CAMECA IMS 6F (16) is shown in Figure 3-4. Cesium chromate (Cs₂CrO₄) or Cesium Carbonate (Cs₂CO₃) is heated up to approximately 400°C (Cs₂CrO₄) or 150°C (Cs₂CO₃) and Cs vapor is released. The Cs vapor is transported to the W ionizer which is heated by electron impact to a temperature of 1100°C whereupon the Cs vapor is ionized to Cs⁺. The entire source is then raised to a potential between 1 and 12kV to allow extraction of Cs⁺ ions towards a grounded extraction electrode.
1): High Voltage Input, 2) Cesium Chromate (Carbonate) Pellet, 3) Reservoir
4) Ionizer 5) Tungsten Plate, 6) Reservoir Filament, 7) Ionizer Filament
8) Extraction Plate
Figure 3-4: Schematic of a Cs microbeam surface ionization source (16)
3.2.1.3 Peabody PSX-120 Sputter Negative Ion Source

The duoplasmatron and the Cs surface ionization source are the commonly used primary ion sources on the IMS-6F, but recently negative primary ions produced with negative ion sources have been used for SIMS sputter depth profiling. Negative ion sources can be divided into negative hydrogen producing sources and ion sources which produce ions other than hydrogen. The special interest in negative hydrogen ions arises from their use in high-energy accelerators and fusion research. For high depth resolution measurements in SIMS, hydrogen ions are not suitable because their small mass results in a deep penetration depth, which degrades depth resolution.

Sputter type negative ion sources, originally developed by Mueller and Hortig in 1969 for the use in tandem accelerators (17), are a type of negative ion source which can produce a large variety of negative primary ions. Mueller and Hortig were also the first to show that negative ions can effectively be produced on a cesiated surface by sputtering. Cs was supplied to the surface in the neutral state while an independent positive ion beam was used for sputtering. A few years later Middleton developed the universal negative ion sputter source (UNIS) (6). It uses a Cs surface ionization source, similar to the one described in chapter 3.2.1.2, to sputter a target cone with high-energy Cs ions and to enrich the target surface with Cs to lower its work function as described in chapter 2. The Cs concentration created on most target surfaces with this design was usually low and insufficient to significantly reduce the work function of the target surface to increase negative ion yield. In order to overcome the problem of insufficient Cs supply Middleton developed the versatile negative ion source (VNIS) (7). The Peabody PSX-120 sputter negative ion source is based on this design. A schematic of the PSX-120 is shown in Figure 3-5. Cs is heated in a reservoir to a temperature of ~150-200°C, transported into the source body and directed onto a cylindrical tantalum ionizer which is heated to a temperature of 1100°C. Neutral Cs will become ionized on contact with the 1100°C hot tantalum surface. A cooled target is placed in front of the ionizer and biased negatively, which accelerates the positive Cs+ ions towards the target. Negative ions sputtered from the target are extracted towards the grounded extraction electrode. The ionizer can be biased negatively to provide focusing of the negative ion beam. An Einzel
lens between the extraction electrode and the primary beam mass sector provides additional focusing capability.

![Diagram of the working principle of the PSX-120 sputter negative ion source](image)

**Figure 3-5: Schematic of the working principle of the PSX-120 sputter negative ion source**

### 3.2.2 The Sample Rotation Stage

Depth profiling by ion beam bombardment can increase the roughness of the surface being eroded by inhomogeneous removal of material. Recent investigations have shown that especially for low energy ion bombardment of Si, beam induced crater bottom roughness formation can be significant. For example, the beam induced roughness which forms during SIMS sputter depth profiling of Si using O$_2^+$ and SF$_5^+$ primary ion bombardment, both with and without O$_2$ flood, can significantly limit the achievable depth resolution (18)(19)(20)(21) (also see chapter 4). SIMS depth profiles acquired
employing a rotating stage indicate that sample rotation reduces surface roughness and, as a result, improves depth resolution and reduces interface width. Improved depth resolution is due to the “360 degree” bombardment for a given surface feature (22)(23)(24)(25). “360 degree” bombardment reduces preferential channeling, i.e. deeper penetration of primary ions into a sample when oriented along low Miller index crystallographic directions, in polycrystalline samples and reduces primary ion beam shadowing, i.e. less primary ions will hit the sample after an elevated surface feature. A rotating sample stage is an optional feature for the CAMECA IMS 6F. Using this stage the sample can be rotated with speeds of up to 60rpm. Synchronizing of the counting time for each recorded element during depth profiling with the time required for a full rotation is necessary to achieve good signal stability.

A significant improvement using sample rotation can be obtained on polycrystalline samples were grains with different crystallographic orientations show different removal rates which result in extensive beam induced crater bottom roughening. An example showing improved depth resolution using sample rotation is shown for the analysis of a Ni/Cr multiplayer structure in Figure 3-6 (25). The sample consisted of a Ni/Cr depth-profiling standard (26) with 12 alternating layers of Ni (53nm) and Cr (64nm) on Si. It was analyzed with a 10 kV O$_2^+$-beam and a sample potential of +4.5keV. Secondary ions were acquired using the 400µm contrast aperture (CD 1), the 750µm field aperture (FA2) and the 150µm image field setting resulting in a 60µm diameter optically gated area. AFM height and phase images of the sputter craters were acquired on a Dimension 3000 from Digital Instruments (see Figure 3-7). Crater depths were measured with a P-20 Long Scan Stylus profilometer from Tencor (27).

Due to the extreme roughness of the crater bottom obtained when the Cr/Ni multilayer sample was depth profiled without rotation (See AFM discussion below), the following normalization procedure was used to facilitate comparison of the two results. The crater obtained with rotation was measured via a stylus profilometer to obtain the depth scale for this sample. The first minimum of the depth profile obtained without rotation was aligned with the first minimum of the rotated depth profile and all subsequent data points were then plotted based on this normalization. Comparison of the depth profiles plotted in the above manner and presented in Figure 3-6 shows a dramatic
improvement in depth resolution when sample rotation were used. The FWHM of the Ni signal stays at a constant value of 62nm if sample rotation is used, while it almost doubles from 65 to 112nm without rotation.

AFM micrographs of the craters generated during these depth profiles are shown in Figure 3-7. Comparison of AFM measured crater bottom roughness resulting from the depth profiling of the sample without (Figure 3-7a) and with (Figure 3-7b) sample rotation indicates that the decay of the depth resolution of the non rotated sample may be due to the formation of roughness, presumably due to differential sputtering resulting from the polycrystalline nature of the metal layers. Comparison of the RMS roughness of crater bottoms indicated a factor of 30 decrease in crater bottom roughness from 60nm to 2nm produced with and without sample rotation respectively. The AFM phase images (Figures 3-7c, 3-7d), while not providing any quantifiable information, but highlight this difference in roughness. Figure 3-7c illustrates the preferential sputtering of the non rotated sample, which is almost certainly due to the grain structure in the polycrystalline films. These grains appear to have been reduced to circular hillocks of much lower dimension when sample rotation is used (Figure 3-7d). The circular nature of the hillocks are the likely result of more slowly sputtering region that have been sputtered from all directions (i.e. 360 degrees) showing the effectiveness of the use of sample rotation to reduce sputter induced roughness.
Figure 3-6: SIMS depth profile of a Ni/Cr-multi-layer structure with and without sample rotation
3.2.3 The Mass Spectrometer

The mass spectrometer of the CAMECA IMS 6F includes a magnetic sector that produces a magnetic field to separate the ions by mass. For a magnetic sector to function as a mass separation device, all ions entering the magnetic sector must have like kinetic energies. The magnetic sector, which functions as a momentum filter then functions as a mass spectrometer.

Since secondary ions leaving the sample surface always have some energy spread, which makes it necessary to sort the ions by energy using an electrostatic sector before
they enter the magnetic sector to be able to obtain high mass resolution. In the CAMECA IMS6F, mass separation is achieved by coupling a magnetic sector with an electrostatic sector through an electrostatic lens, the spectrometer lens, which cancels the energy dispersions produced by both sectors. The combination of the electrostatic sector and the spectrometer lens insures that ions with different initial energy will be focused to the same plane (cross over) after exiting the magnetic sector.

Ions entering the electrostatic sector with the same energy but on different trajectories will be focused onto the central ray by the electrostatic sector. The image points of the cross over formed by the electrostatic sector serves as object points for the spectrometer lens. The virtual image points formed by the spectrometer lens than serves as object points for the magnetic sector. The mass selection slit is placed at this plane. Trajectories and mass separation for ions which left the sample with the same energy but with different angles are shown in Figure 3-8 (28).
3.2.4 Secondary Ion Detection

The CAMECA IMS 6F has three secondary ion detectors: a microchannel plate/fluorescent screen combination; a Faraday cup and an electron multiplier.

The microchannel plate/fluorescent screen combination is used when the instrument is operated in the microscope mode. In this mode the sample is bombarded with either a broad or a finely focused beam rastered over the image field and each point.
on the sample can be regarded as a separate secondary ion emitting image point. The secondary ions comprising this image are accelerated and a series of electrostatic lenses is used to magnify the image of the sample. After energy and mass filtering, the image is focused by the projection lenses onto the microchannel plate. The microchannel plate consists of an array of hollow glass tubes (channels) with the inner surface covered with a conductive layer. When secondary ions strike the inner surface of the channels secondary ions are emitted. These secondary ions are accelerated in the channel and further collisions with the walls lead to electron multiplication. The factor of electron multiplication can be up to $10^6$, depending on the potential applied across the channels. Electrons leaving the channels are further accelerated onto a fluorescent screen resulting in photon emission. The image created on the fluorescent screen is detected by a CCD camera and displayed on a computer monitor.

The IMS-6F has two secondary ion counting detectors, a Faraday cup and an electron multiplier. Secondary ions are collected by the optical system of the instrument, mass filtered and focused onto the secondary ion counting detector. The Faraday cup is used for high secondary ion count rates between $1E5$ and $1E9$ cts/sec, while the electron multiplier can be used to detect count rates between $1E^{-1}$ and $5E5$ cts/sec, giving the instrument the possibility to detect secondary ions over a range of 10 orders of magnitude.

The Faraday cup is a hollow cylinder isolated from the instrument ground. Secondary ions entering the Faraday cup will hit its wall resulting in secondary electron emission. To prevent electrons from leaving the Faraday cup, a necessity for accurate counting, a repeller plate is placed in front of the Faraday cup with a small negative bias. The current resulting from the deposition of charge by the primary ions into the faraday cup is converted into a voltage using an electrometer circuit and the voltage is then converted by a voltage to frequency converter to a pulse rate proportional to current.

For secondary ion count rates below $5E5$ cts/sec, a high sensitivity electron multiplier counting system capable of counting single ion impacts is used. The electron multiplier of the CAMECA IMS 6F consists of 21 copper/beryllium dynodes. Secondary ions impacting on the first dynode induce secondary electron emission. The secondary electrons are successively accelerated through the further stages of the EM and electrons...
striking the dynodes of the EM induce the release of additional secondary electrons. A multiplication of about 1E8 is typically achieved. Electrons generated from each secondary ion striking the first dynode are multiplied by successive dynodes until the group of electrons leaving the last dynode is collected. This group of electrons collected by the electron multiplier collection electrode is measured as a pulse. The number of electrons in each pulse varies depending on the mass and velocity of the secondary ion impacting on the first dynode, the high voltage applied between the first and the last dynode and the age of the multiplier. The lowest amplitude pulses in the pulse height distribution, which usually do not result from ion impact events, are rejected by setting a discriminator threshold. In high resolution SIMS depth profiling low sample potentials are used in magnetic sector SIMS instruments, which produces secondary ions with lower velocity (kinetic energy) and secondary ions impact on the first dynode of the EM with a lower velocity. As a result a large amount of the ions impacting on the first dynode of the EM either create no pulses at all or low amplitude pulses, which are rejected by the EM discriminator threshold. This results in a reduction of ratio of detected pulses to the number of secondary ions impacting on the first dynode, which is called EM-conversion efficiency. Higher EM-conversion efficiency generally results in improved detection limits. Low EM-conversion efficiencies are a greater problem for higher masses due to the very low velocity of their secondary ions (29)(30), but there is a significant loss of sensitivity also for low Z elements at low sample or secondary ion accelerating voltage. A secondary ion post acceleration system for the IMS-6f that was developed to improve detection limits for low primary ion impact analysis was evaluated. A schematic of the post acceleration system is shown in Figure 3-9.
The secondary ion post acceleration system is designed to accelerate the secondary ions just prior to impact onto the electron multiplier first dynode to regain the conversion efficiency lost by lowering the secondary ion extraction energy. This method is preferable to simply increasing the electron multiplier voltage to increase gain, since increasing the voltage has been shown to radically decrease the useful life of the multiplier. The increased ion to electron conversion efficiency obtained by increasing the post acceleration voltage is not without cost since the noise of the EM signal also increases. Obtaining the optimum signal to noise level requires that the optimum conditions be determined so that an increase in conversion efficiency is achieved while maintaining an acceptable noise level. Figure 3-10 shows noise levels and $^{31}$P$^-$ secondary ion intensities (normalized to the $^{31}$P$^-$ secondary ion intensity measured without using post acceleration voltage) as a function of post acceleration voltage. These noise levels were obtained during depth profiling of an 8.2E18 atoms/cm$^3$ P bulk doped Si wafer using 1keV secondary ion accelerating voltage with the amplifier discriminator discrimination level set to -50mV. It can be seen in Figure 3-10 that, at post acceleration voltage settings below 4kV, the noise level is below 10 counts/min, a reasonable noise level for an EM. Above 4keV, the noise increased exponentially.
Attempts to operate at post acceleration voltages greater than 4kV with discriminator settings increased to reduce noise did not result in any improvement in EM conversion efficiency. Thus, for the IMS-6f used in this study and using 1keV sample accelerating voltage, the optimum operating conditions for the post acceleration system for P is between 3 and 4kV and a discriminator setting of -50mV. Under these conditions, a signal increase of around one order of magnitude can be achieved for 1keV $^{31}$P secondary ions while maintaining a low noise level and without damage to the electron multiplier.

![Graph showing noise and $^{31}$P secondary ion intensities vs. post acceleration potential](image)

**Figure 3-10:** Noise and $^{31}$P secondary ion intensities (normalized to the $^{31}$P secondary ion intensity measured without using post acceleration voltage) vs. post acceleration potential for mass 31 and a threshold of -50mV

### 3.3 Crater Depth and Topography

In SIMS depth profiling, sputter rates are traditionally calibrated by measuring the final crater depth with a stylus profilometer and obtaining the average sputter rate by dividing the crater depth by the final analysis time. The average sputter rate is then applied to the whole profile to convert the profile from intensity versus time to intensity
versus depth. This approach can give significant errors in depth calibration in the initial stages of a SIMS depth profiles, due to changes in sputter rates resulting from surface layers, primary ion beam implantation and formation of beam induced crater bottom roughness (31)(32). In this work crater depths larger than 10nm were measured employing a Tencor P-20 stylus profilometer. A Burleigh Horizon Optical Profilometer (OP) and a Digital Instruments DI-3000 Atomic Force Microscope were used to measure shallow craters. Optical profilometry is in general more suitable than AFM for the large areas involved in SIMS (>150µm²). The DI-3000 was also used to investigate beam induced crater bottom topography, which can influence sputter rates, ion yields and depth resolution.

3.3.1 Stylus Instruments

A stylus profilometer scans a diamond stylus of a few micron (2-10) diameter is scanned across a surface and vertical deflection of the stylus is measured. The Tencor P-20 uses a capacitance sensor to register the vertical movement of the tip (33) but other sensors like linear, variable differential transducers (LVDT) are commonly used. In the P-20 a change in capacitance is than converted into a variation in height. Accuracy of depth measurements is about 1nm for a flat and smooth sample. The measurement stage is referenced to an optical flat to ensure smooth and stable motion of the stage.

3.3.2 Atomic Force Microscopy

In SIMS depth profiling, sputter rate changes can occur due to surface layers, primary ion implantation and beam induced crater bottom roughness. Knowledge of these sputter rate changes is essential to establish an accurate depth scale. For high resolution ultra shallow depth profiling, sputter rate changes then occur in the initial few nanometers of the SIMS profile. The accuracy and precision provided by stylus depth profilometry for measurements below approximately 10nm is not sufficient for precise
analysis of these sputter rate changes. Atomic Force Microscopy (AFM) can provide this accuracy and precision.

A schematic of an AFM is shown in Figure 3-11. In AFM a sharp tip mounted on the free end of a cantilever is scanned across a sample using a piezoelectric tube scanner. Forces between the tip and the sample cause the tip and thus the cantilever to deflect. A laser beam is reflected of the end of the cantilever and sensed by a position sensitive photo detector to measure this deflection. The information is transferred to a computer, which calculates a topographic data map from the deflection data.

**Figure 3-11: Schematic of an Atomic Force Microscope**

AFM measurements can give reliable data of crater bottom roughness induced by the SIMS primary ion beam. For this roughness measurement a representative approximately 1µm² area of the crater bottom is imaged. Using AFM to measure the crater depths is very difficult using a traditional AFM, where a piezo electric tube scanner is used to scan the tip across the sample due to large size of SIMS crater sizes (typically 75 by 75µm or larger). The measurement problem stems from the fact that extension of the scanner in the x or y direction, which occurs when the tip is scanned across the sample, also leads to an unwanted movement of the tube (tip) in the z-direction (see Figure 3-12). This unwanted movement is referred to as cross coupling.
Cross coupling is most commonly corrected using the open-loop correction. However, this correction cannot achieve the Ångstrom accuracy required for investigating sputter rate changes in the initial part of SIMS depth profiles. Hence AFM scan sizes are limited for high z-resolution measurements and full SIMS craters usually cannot be accurately measured. Even partial measurements of SIMS craters are complicated because of the large beam tail often associated with SIMS beams used in ultra shallow depth profiling. However, AFM’s have been designed, (e.g. DI Dimension 3100/5100 with Metrology AFM Head) which show a much reduced cross coupling effect, but they are not widely available due to their large cost.

### 3.3.3 Optical Profilometry

Optical profilometry measures height differences between two points by interfering a monochromatic beam reflected of the sample with a reference beam of the same frequency that is reflected from a reference mirror within the microscope. Height changes are extracted by comparing the phase differences between the two beams at different points of the sample. Optical profilometry is a fast, non-contact analysis having a field of view suitable for SIMS crater depth measurement crater that produces accurate results with sub-nanometer height resolution if the optical properties of the sample do not change over the analyzed area. The drawback under which optical profilometry of SIMS crater suffers is that primary ion bombardment used in SIMS changes the optical
properties of the sample which leads to an unknown error in the measurement of height differences between an ion bombarded surface and a native sample surface. A schematic illustration of an optical interferometer is shown in Figure 3-13 (34).

Figure 3-13: Illustration of an Optical Profilometer

The Burleigh Horizon Optical Profilometer, the model used in this study, uses green light with a wavelength of 550nm and a 40nm FWHM, which is divided into a reference beam and a sample beam by a beam splitter. After the reference beam has been reflected from a reference mirror and the sample beam has been reflected from the sample surface, the two beams recombine (interfere) and travel to a CCD camera. Amplitude of the recombined beam will depend on the path difference between the reference beam and the
sample beam. The path difference between the two beams is influenced by surface topography, an interference image of the sample will be detected by the CCD camera.

Height resolution of the instrument is improved by employing a piezoelectric stepper to change the distance of the microscope head to the sample. After the first image is recorded, the microscope head is translated four times in steps of $\pi/2$ phase shift and an image is acquired at each step. A sin wave is fitted through the intensity data of corresponding pixels in the five images. Height differences between two pixels are calculated from the phase differences between two sin waves via:

$$h = \left( \frac{\phi}{2\pi} \right) \times \left( \frac{\lambda}{2} \right)$$

where $h$ is the height difference between two pixels, $\phi$ is the phase difference between sample beam and reference beam and $\lambda$ is the wavelength of the incident light. This formula assumes homogenous reflectivity across the analyzed area, which is not necessarily an accurate assumption for measuring the depth of SIMS crater. Primary ion implantation changes sample composition and structure that can influence reflectivity. A change in refractive index results in a phase shift not related to height difference which introduces an error into the measurement. The magnitude of the error due to the primary ion bombardment used in SIMS will be addressed in chapter 8.

Resolving power (lateral resolution) of a microscope using optical lenses like the Burleigh Horizon is given by Rayleigh as $d = 0.61\lambda/ NA$, where NA is the numerical aperture of the lens. The NA of the lenses used in this study was 0.3, which gives a lateral resolution of approximately 1µm. Depth resolution is about 1Å, comparable to AFM. Advantages of Optical Profilometry compared to AFM are shorter acquisition times and a larger field of view that is more suitable for measuring SIMS craters.
3.4 Samples used in this Study

The samples used in this study were chosen for their utility for studying of high depth resolution SIMS depth profiling techniques useful for the study of p/n-junctions having the junction depths that will be necessary for future MISFET (MOSFET) generations. Source drain extension (SDE) junction depths, which are shorter than source/drain junctions and hence require higher depth resolution in SIMS depth profiling, are projected by the Semiconductor Industry Association (SIA) Roadmap (1) and International Technology Roadmap for Semiconductors (ITRS) (2) to be between 11-19 µm for 0.05 µm MOSFET technology generation as shown in Figure 3-14.

![Figure 3-14: Illustration of a MOS Field Effect Transistor and decreasing SDE junction depth](image)

3.4.1 Low Energy Dopant Implants

The dopants used in today’s MISFET technology generation to form p/n junctions in Si, namely B as p-dopant and P and As as n-dopants are likely to remain the dopants of choice for future MISFET generations. For n-dopants, As seems to be the more likely choice to form ultra shallow junctions because of its lower diffusivity in Si and its higher mass compared to P, which aids ultra shallow ion implantation. However, P will still be
used as an n-dopant and has importance as a cross contaminant. A list of the ion implants used in this study is given in Table 3-1.

<table>
<thead>
<tr>
<th>Implant</th>
<th>Energy</th>
<th>Dose[atoms/cm²]</th>
<th>R_p [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>500eV</td>
<td>1E15</td>
<td>3.6</td>
</tr>
<tr>
<td>B</td>
<td>300eV</td>
<td>1E15</td>
<td>2.6</td>
</tr>
<tr>
<td>P</td>
<td>50keV</td>
<td>4.7E14</td>
<td>68.9</td>
</tr>
<tr>
<td>P</td>
<td>2keV</td>
<td>4E14</td>
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<td>3.4</td>
</tr>
<tr>
<td>P</td>
<td>500eV</td>
<td>1E15</td>
<td>2.3</td>
</tr>
<tr>
<td>As</td>
<td>500eV</td>
<td>1E15</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 3-1: Samples used in this study

3.4.2 Bulk Doped Standards

There is often a mismatch in doses of ultra shallow dopant implants measured by the ion implanter compared to the dose measured using SIMS, independent of the particular SIMS instrument or technique used. It is not clear whether the dose measured by SIMS or that measured by the implanter is the more correct dose, but a standard deviation of less than 10% for the dose measurement of a 500eV, 1E15 atom/cm² during a round robin study involving different SIMS instrument types, impact energies and conditions shows that the SIMS results are reproducible. Bulk doped standards calibrated using deep high energy implants can be used to obtain accurate relative sensitivity factors for conversion of counts/seconds into atoms/cm³ in SIMS for obtaining the implanted dose of ultra shallow implants.

Inaccuracy of dose calculation in ultra shallow implant dopant profiling is increased due to the larger amount of dopant which comes to rest within the transient zone (s. section 2.3.5). In the transient zone in Si, due to changes in ion yield resulting from the build up of implanted primary ions and the surface oxide, a single RSF does nor provide accurate results. Bulk doped standards can be used to investigate these RSF
changes, assuming that the impurity to be measured is constant from the surface into the bulk (described in Chapter 8)

3.4.3 Multiple Delta Doped Structures

In the last years several epitaxial growth techniques have been developed which are capable to produce near atomically sharp delta layers or interfaces. The best known of these techniques are molecular beam epitaxy (MBE) (35), chemical vapor deposition (CVD) (36), atomic layer epitaxy (ALE) (37) and laser ablation/deposition (LAD) (38). Near atomically sharp interfaces produced with these techniques are ideal for the investigation of depth resolution obtainable with SIMS. Delta layers for experimental studies in SIMS are almost exclusively made by MBE.

Delta doped layers are ideal samples for investigation of the influence of instrument parameters like primary ion, angle of incidence, etc., on depth resolution, as the leading and trailing edge slopes of the nearly atomically sharp features are only influenced by the SIMS measurement and not by concentration gradients in the sample. Multiple delta doped structures are also ideal samples to investigates sputter rate changes during SIMS depth profiling, because the distance between two deltas can be accurately determined by an independent technique such as TEM. An MBE grown B delta doped structure with the first 5 deltas spaced 5nm apart and the following 11 deltas spaced 15nm apart was used in this study for the investigation of sputter rate changes during SIMS depth profiling. A schematic of this structure is shown in Figure 3-15 along with an idealized SIMS profile of this structure.
Figure 3-15: Illustration of a B delta doped structure and a simulation of an ideal SIMS profile of this structure

3.5 References

12. M. V. Ardenne, Technik, 11, 65 (1956)
13. Duoplasmatron , Illustration in CAMECA IMS 6F manual
27. KLA-TENCOR, San Jose, CA
33. Tencor P-20 reference manual, 4-1
4 SIMS Depth Profiling of Low Energy B in Si Implants using Low Energy $O_2^+$ Ion Bombardment using a CAMECA IMS 6F

4.1 Introduction

B has been the p-dopant of choice for Si dating back to the earliest work on the formation of p/n-junctions (1). Originally B was mainly introduced into Si wafer by high temperature thermal diffusion using $B_2O_3$, $BBr_3$ or $BCl_3$, but this process has since been widely replaced by ion implantation. Advantages of ion implantation as compared to thermal diffusion include lower process temperature, resulting in reduced redistribution of previously introduced dopants, better ability to precisely control dopant dose, higher uniformity of dopant across the wafer surface and greater process cleanliness. A disadvantage of ion implantation is the large amount of lattice damage introduced by collisions of the implanted ions with target atoms. However, the original crystal lattice structure of Si can be relatively easily restored by annealing the Si wafer (1). The relatively low mass of B makes ultra shallow ion implantation challenging, but improved ion implanter technology and implantation of $BF_2$ instead of B has reduced minimum implantation energies down to a few hundred eV.

The accepted method for the SIMS analysis of B distribution profiles employs an $O_2^+$ primary ion beam and extraction of positive secondary ions. The $O_2^+$ bombardment alters the Si sample surface by changing it into a more ionic state, which increases the positive ion yield of elements that possess electronegativities smaller than the electronegativity of O (2). In the case of high O surface concentration (>64 at.%), formation of the SiO$_2$ bandgap increases ion yields further by reducing the neutralization probability of ions leaving the surface in good agreement with the electron tunneling model (chapter 2.3.6) (2).

Low energy $O_2^+$ ion bombardment, a requirement for high depth resolution analysis of B, became available for the analysis of ultra shallow B implants with the introduction of the FLIG ion gun by ATOMIKA (3)(4) and the Accel/Decel (5) system by CAMECA. High depth resolution analysis of ultra shallow B implants is discussed in this section.
Sputter rate changes due to primary ion implantation and beam induced crater bottom roughness are evaluated employing a B delta doped structure with known distances between the thin doped delta regions.

### 4.2 Experimental Method

B analysis in Si was performed using an \( \text{O}_2^+ \) primary ion beam extracted from the duoplasmatron of the CAMECA IMS-6F (see instrument description in chapter 3). Low energy \( \text{O}_2^+ \) ion beams were produced using a duoplasmatron in combination with the Accel/Decel system from CAMECA which improves the efficiency of \( \text{O}_2^+ \) ion extraction by first extracting ions using a negative potential (instead of ground) followed by deceleration of the ions to ground to get the desired primary ion beam energy (4). Table 4-1 lists the primary ion impact energies, primary ion accelerating voltages and sample potential combinations used to acquire the B SIMS depth profiles in this chapter. Table 4-1 also lists primary ion normal impact energies, the normal impact energy per Cs or O atom and the primary ion beam angle of incidence. The angles of incidence were calculated using the formula derived by Meuris (6) which includes the IMS-6F primary ion column deflector voltages used for positioning the beam onto the primary column optical axis of the IMS-6F mass spectrometer.

<table>
<thead>
<tr>
<th></th>
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<td>45</td>
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<td>1.15</td>
<td>0.65</td>
<td>0.34</td>
<td>0.17</td>
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**Table 4-1: Experimental conditions used for B analysis in this work**
Secondary ions were collected from an area 60\(\mu\)m in diameter centered on a square raster. Raster edge dimensions ranged from 200 to 300 \(\mu\)m with the raster size chosen based on the primary ion beam diameter. Raster size was chosen to be at least three times the diameter of the primary ion beam to avoid signal contribution from the crater edges on the total collected secondary ion signal. If sample rotation was used, the sample was rotated at 20 rpm and secondary ions were extracted from an area 60\(\mu\)m in diameter (FA2) centered on a circular area of 250 to 350 \(\mu\)m in diameter depending on the raster size and primary beam diameter. A mass resolution of 300 \(M/\Delta M\), a 150\(\mu\)m image field and a 100\(\mu\)m contrast diaphragm (CD2) were used in all cases. Depth scales were established based on crater depths measured using a TENCOR P-20 stylus profilometer. AFM micrographs were acquired using a Digital Instrument DI-3000 atomic force microscope (AFM). The samples analyzed included a 500eV, 1E15 atoms/cm\(^2\) B implanted into (100) Si, a 300eV, 1E15 atoms/cm\(^2\) B implanted into pre-amorphized (100) Si, a 1.2E19 atoms/cm\(^3\) B bulk doped Si wafer and a B delta doped structure with the first five deltas spaced 5nm apart with the following 10 deltas spaced 15nm apart. A schematic of the B delta doped structure is shown in section 3.4.3.

All experiments performed employing the various experimental conditions involving \(O_2^+\) primary ion beams were done with and without the use of \(O_2\) flooding. Under \(O_2\) flooding conditions, the pressure in the sample chamber was adjusted using an \(O_2\) flood leak valve to maintain the sample chamber at a pressure at which the Si\(^+\) matrix signal saturated. At this saturation pressure, B\(^+\) sensitivity was also maximized. Measurements using \(O_2\) flooding below the saturation pressure lead to excessive crater bottom roughness (7). It was hypothesized that the heterogeneity of the altered oxide layer due to the mixture of Si oxidation states (Si\(^0\), Si\(^{+1}\), Si\(^{+2}\), Si\(^{+3}\), Si\(^{+4}\)) using these conditions provides seeding and growth for the formation of periodic ripple structures (8). To limit beam induced crater bottom roughness only \(O_2\) flooding with saturation pressure was used.

Samples were analyzed with and without sample rotation to study the possible influence of beam induced crater bottom roughening on the instantaneous removal rate and therefore depth calibration. For sample potentials below 3keV, secondary ion post acceleration was employed and optimized to achieve the best signal to noise ratio for
secondary ion detection (9). The immersion lens of the IMS-6F was operated in 
acceleration mode below sample biases of 2keV to reduce the effect of lens aberrations at 
low energy. Beam energies discussed in the sections below are total beam impact 
energies.

4.3 Results and Discussion

4.3.1 Crater Bottom Roughness Development and Profile Shifts Produced 
by Glancing Angle $O_2^+$ Ion Bombardment

The formation of crater bottom roughness under ion bombardment can severely 
limit the obtainable depth resolution in SIMS depth profiling, hampering the ability to 
separate closely spaced features and the ability to acquire accurate profile shapes of ultra 
shallow implants. In addition, roughening can cause changes in the sputter yields and 
alterations in ionization probabilities of sputtered particles (10). If constant sputter rates 
are applied for the depth calibration of ultra shallow profiles an erroneous depth scale 
will be obtained. If this depth scale is than used to generate an RSF from a standard 
sample for implant quantification, an erroneous RSF will be obtained. In this section the 
effect of keV and sub keV glancing angle $O_2^+$ ion bombardment (incidence angles 
between 45° and 56° and with and without the use of O$_2$ flooding) on crater bottom 
roughness, depth resolution and depth scale calibration will be investigated. Various 
means for minimization of beam induced crater bottom roughness including sample 
rotation and will be evaluated. The B delta doped structure (11) described in section 
3.4.3 was used for this investigation because the known distances between the deltas 
provides the information required for investigation of changes in erosion rates.

SIMS erosion rates are usually calculated based on crater depths measured using 
diamond stylus profilometry. The erosion rate calculated from crater depth 
measurements is assumed to be linear throughout the depth profile and used to convert 
the time scale of the acquisition into the depth scale of the depth profile. This will 
automatically put the final data point at the correct point of the depth scale, as it
corresponds to the physical position of the crater bottom. All depth versus concentration data points plotted on this depth scale before the final data point will only correspond to an actual physical position in the sample if the sputter rate is linear with time, i.e. the sputter rate did not change between the start and the end of the measurement. Changes in sputter rate will result in shifts of the concentration versus depth data away from the actual physical depth in the sample to an apparent depth. In SIMS depth profiling, two distinctively different sputter rates can often be observed: (1) a surface transient sputter rate where erosion rates are changing due to primary ion implantation, surface layers, surface contamination, sample surface amorphization or beam induced crater bottom roughening and (2) a bulk sputter rate which occurs after steady state sputtering conditions have been achieved. If the surface transient sputter rate is faster compared to the bulk erosion rate, data points along the whole profile will be shifted towards the surface as shown in Figure 4-1. A slower surface transient sputter rate compared to the bulk erosion rate depth will result in data points along the whole profile shifted to a greater depth as shown in Figure 4-2.

Figure 4-1: Difference in actual and apparent profile depth depending on depth calibration
Figure 4-2: Difference in actual and apparent profile depth depending on depth calibration

Figure 4-3 shows depth versus time for an arbitrary depth profile with faster surface and slower bulk sputter rate stopped after sputtering for two different times. Figure 4-3 shows that stopping a depth profile which has a non linear sputter rate at two different times results in two different average sputter rates which leads to different errors (profile shifts) in depth at different stages of the depth profile.
Differing depth (profile) shifts, depending on the final crater depth, and the different errors in depth measurement that result, severely limit the ability to compare depth profiles obtained using different instrument conditions or instrument types. To be able to compare depth shifts, alternative depth calibration techniques have been used, with the most common ones employing a depth calibration based on delta doped standards (12)(13). A well characterized delta doped standard offers features at certain known depths within the sample. The known depths of these features allows the determination of the steady state bulk sputter rate by dividing the depth separating two deltas by the sputter time which was needed to sputter from one to the other. Figure 4-4 shows the depth shift development if the steady state sputter rate is applied to the whole measurement. Using this depth calibration method, the depth shift increases from the surface until the steady state sputter rate is achieved, but stays constant from there on independent from the total analysis time.

Figure 4-3: Dependence between actual and apparent depth on final crater depth
This depth calibration method is used in this chapter to investigate the effect of keV and sub keV glancing angle $\text{O}_2^+$ bombardment (incidence angles between 45 and 56° and with and without the use of $\text{O}_2$ flooding) on profile shifts and sputter rate changes using the MBE grown B delta doped structure described in section 3-4 with the goal of finding conditions which give minimal amount of profile shift or highest depth scale accuracy. The samples used for this investigation are a 300eV B implant into (100) Si and the B delta doped sample described earlier. Figure 4-5 shows the original surface topography of the B delta doped sample, which had a RMS value of 0.14nm with no preferential orientation. It is not believed that the original surface roughness or even crystal structure has an influence on the final crater bottom topography at comparable depth (14)(15).
4.3.1.1 Influence of Angle of Incidence on Crater Bottom Roughness Development and Profile Shifts Produced by Glancing Angle O$_2^+$ Ion Bombardment

In this section the influence of variations in the primary ion angle of incidence on beam induced crater bottom roughness, profile shift and depth resolution will studied for glancing angle O$_2^+$ bombardment. In order to separate the effect of primary beam angle from other effects, the total O$_2^+$ primary ion impact energy was kept constant and all analysis are performed using O$_2$ flooding. O$_2$ flooding is a well known method for minimization of the surface transients in SIMS depth profiling making flooding very desirable for ultra shallow depth profiling. However, O$_2$ flooding has received very conflicting reviews in the SIMS community because of observed profile artifacts like ion yield changes and profile shifts which have been shown to increase in magnitude when O$_2$ flooding is used (9)(16). It will be shown in this study that beam energy/angle combinations exist that allow O$_2$ flooding to be successfully used for high depth resolution profiling of ultra shallow features.
AFM images of crater bottoms after depth profiling with 1keV O$_2^+$ ion beams under O$_2$ flooding conditions with saturation pressure and angles varying from 56 to 45 degrees from normal are displayed in Figure 4-6. 1keV, 56$^\circ$ O$_2^+$ caused a significant increase in beam induced crater bottom roughness from 0.15nm (RMS) before sputtering to 0.56nm RMS after sputtering. In addition a sputter induced periodic ripple structure can be observed which formed perpendicular to the incident beam. At 50$^\circ$ angle of incidence, a periodic ripple structure can be still observed, but there was no increase in RMS crater bottom roughness within the measurement error, indicating that smoothening due to ion beam induced surface diffusion is offsetting an increase in roughness due to angle and curvature depending sputtering (see chapter 2.3.2). If the angle of incidence is further reduced to 45$^\circ$, 0.14nm RMS random roughness is measured.

Figure 4-7 depicts the influence of an increase in crater bottom roughness on sputter rates as evidenced by profile shifts by showing SIMS depth profiles of the B delta doped structure analyzes with a 1keV O$_2^+$ beam and angles of incidence of 56 and 45 degrees. Depth scale was calibrated by applying the steady state sputter rate to the profile (see section 4.3.1). The steady state sputter rate was obtained by dividing the distance between the 5$^{th}$ and the 6$^{th}$ B delta to 14.7nm by the sputter time between these two deltas. The width between the 5$^{th}$ and the 6$^{th}$ B delta was determined by analyzing the B delta doped structure with a 500eV, 45$^\circ$ degree O$_2^+$ primary ion beam under O$_2$ flooding conditions to the 11$^{th}$ delta and measuring the crater depth, as these conditions have shown to produce minimal changes in sputter rate and a large depth minimizes the relative error in crater depth measurements. The shift of the depth of the 6$^{th}$ B delta towards the surface was reduced from 6.1nm (depth = 33.9nm) for the 56$^\circ$ angle if incidence data, compared to 1.4nm (depth = 38.6nm) for 50$^\circ$ angle of incidence, compared to the nominal value of 40nm (given by the grower of the structure). This apparent improvement in profile shift result from the improvement in crater bottom roughness obtained using less glancing angle of incidences 1keV O$_2^+$ primary ion beams. This analysis also shows that ripple formation as seen in figure 4-6 induced by the 1keV O$_2^+$, 50 degree ion beam does not necessarily result in large beam induced crater bottom roughness and thus profile shift as long as the ripple amplitude is limited.
Figure 4-6: 1 x 1 μm AFM micrographs of SIMS crater bottoms after profiling (100) Si with a 1keV O$_2^+$ primary ion beams while using O2 flooding and changing the angle of incidence from 56 to 50 to 45°.
4.3.1.2 Influence of O$_2$ Flooding on Crater Bottom Roughness Development and Profile Shifts Produced by Glancing Angle O$_2^+$ Ion Bombardment

Figure 4-8 shows six AFM micrographs of crater bottom roughness produced by O$_2^+$ primary ion beams with various angles of incidence and total impact energies. The left column shows crater bottoms after sputtering in UHV (~5E-10 torr) conditions while the right column depicts crater bottoms after sputtering the sample while flooding it with O$_2$ with a saturation pressure of approximately 5E-6 torr. In the first row, a significant increase in beam induced crater bottom roughness can be observed for 1keV, 56° O$_2^+$ primary ion beam bombardment under O$_2$ flooding conditions compared to depth profiling with the same primary ion beam conditions in UHV. In the second row, the impact energy is the same as in the first row while the angle of incidence has been changed from 56 to 50 degree. For both UHV and O$_2$ flooding, periodic ripple structures
can be observed in the crater bottom after 1keV O$_2^+$, 50 degree sputtering. Ripple wavelength is visibly shorter and beam induced crater bottom roughness is reduced (as indicated by the smaller RMS value of the crater bottom roughness), when flooding the sample surface with O$_2$ using 1keV O$_2^+$, 50 degree sputtering. For the last row of AFM micrographs, the angle of incidence was only slightly changed to 48° while the impact energy was cut in half to 500eV. Ripples are also formed within the sputtered crater under these primary ion beam conditions with and without O$_2$ flooding, although ripple wavelength is reduced when O$_2$ flooding is used. Ripple wavelength is correlated to the projected range ($R_p$) of the primary ion beam (17)(18).

Figures 4-9 and 4-10 exhibit how O$_2$ flooding can increase (at higher impact angles) or slightly decrease (at lower impact angles) the shift of the profile towards the surface by altering crater bottom topography. Depth calibration was performed by setting the depth between the 5$^{th}$ and the 6$^{th}$ delta to 14.7nm as described in section 4.3.1.1. A reduction in profile shift of 4.9nm is detected analyzing the B delta structure using a 1keV, 56° angle of incidence beam under UHV conditions instead of under O$_2$ flooding. Bombarding the surface of the B delta sample with a 500eV, 48° O$_2^+$ beam under O$_2$ flooding instead of under UHV conditions results in a small reduction in profile shift towards the surface when O$_2$ flooding is used. This smaller reduction in profile shift can be expected from the relatively small amount of change in crater bottom topography development under these conditions.
Figure 4-8: 1 x 1 μm AFM micrographs of SIMS crater bottoms after profiling (100) Si with a 1keV, 56°, 1keV, 50° and 500eV, 48° O₂⁺ primary ion beams with and without using O₂ flooding.
Figure 4-9: Depth profiles obtained from a B delta doped structure with a 1keV, 56° O$_2^+$ primary ion beam with and without using O$_2$ flooding

Figure 4-10: Depth profiles obtained from a B delta doped structure with a 500eV, 48° O$_2^+$ primary ion beam with and without using O$_2$ flooding
4.3.1.3 Sample Rotation – An Alternative to Reduce Beam Induced Crater Bottom Roughness and Profile Shifts

Several specific conditions that produce only minimal beam induced crater bottom roughness and profile shift with or without employing O$_2$ flooding have been reported in the chapters 4.3.1.1 and 4.3.1.2. In experiments, where ion beam impact conditions that do not produce roughness cannot be used or are not desired, sample rotation can be explored as an alternative way of minimizing ion beam induced crater bottom roughness. Sample rotation was originally employed by Zalar (19) for Auger electron spectroscopy sputter depth profiling and much of the work utilizing sample rotation can be traced back to his work. Later Cirlin, Stevie, van Berkum and Loesing (20)(21)(22)(23) showed how sample rotation can be effectively utilized for high depth resolution SIMS profiling, especially of polycrystalline metal and multi-layer samples. Figure 4-11 displays how sample rotation was effectively used to reduce beam induced crater bottom roughness for a 1keV, 56° O$_2^+$ beam under O$_2$ flooding conditions from 0.53nm RMS to 0.23nm RMS.

The depth profiles of the B delta doped structure displayed in Figure 4-12 were acquired using beam conditions given in Figure 4-11. Depth scales are calibrated by setting the width between the 5th and the 6th delta to 14.7nm and applying the steady state sputter rate to the whole profile.
Figure 4-11: 1 x 1 μm AFM micrographs of SIMS crater bottoms after profiling (100) Si with a 1keV, 56° O₂⁺ primary ion beam with and without sample rotation using O₂ flooding.
Figure 4-12: Depth profiles obtained from a B delta doped structure with a 1keV, 56° O$_2^+$ primary ion beam with and without sample rotation using O$_2$ flooding.

4.3.2 Influence of O$_2$ Flooding on Depth Resolution

Figures 4-9 and 4-10 also showed an improvement in depth resolution as measured by trailing edge decay length of the first delta layer when O$_2$ flooding is employed compared to measurements under UHV conditions. O$_2$ flooding and the conversion of the sample surface from SiO$_x$ to stochiometric SiO$_2$ seems to increase the instantaneous swelling of the surface under O$_2^+$ ion bombardment and dilutes the Si atomic densities, hence effectively reducing $R_p$ of the primary ion beam and ripple wavelength.

Improvement in depth resolution at the first delta is significantly smaller when the 500eV, 48° O$_2^+$ is used instead of the 1keV, 56° O$_2^+$ primary ion beam under O$_2$ flooding conditions. The lower $R_p$ of the 500eV, 48° O$_2^+$ compared to the 1keV, 56° O$_2^+$ yields a higher O surface concentration resulting in a surface composition which is closer to SiO$_2$. The near SiO$_2$ stochiometry of the surface obtained using 500eV O$_2^+$ reduces the amount...
of additional swelling which can be obtained by using O\textsubscript{2} flooding since the amount of conversion of the sample surface required to reach SiO\textsubscript{2} stoichiometry is reduced.

4.3.3 SIMS Analysis of Ultra Shallow B Implants in Si under Glancing Angle O\textsubscript{2}\textsuperscript{+} Ion Bombardment

In the previous section, the effect of beam induced crater bottom roughening and sputter rate changes produced by glancing angle O\textsubscript{2}\textsuperscript{+} ion bombardment and of the associated shifts of concentration over depth information were discussed. A B delta structure was used for this purpose because of the well defined B delta positions. SIMS depth profiling of implanted dopants suffers from the same kind of profile shifts as observed in the previous section for the B delta doped structure. As a result, junction depth analysis of ultra shallow dopant implants using SIMS, one of the primary applications of SIMS in semiconductor industry, can contain significant errors if conditions are used that produce significant profile shifts. The accuracy of SIMS depth profiles of ultra shallow B implants in terms of depth resolution and profile shape under glancing angle O\textsubscript{2}\textsuperscript{+} ion bombardment is investigated in this section. Analysis conditions, shown in sections 4.3.1.1, 4.3.1.2 and 4.3.1.3 to not produce significant profile shifts, were used in this section.

The quantification accuracy of SIMS ion implant dopant profiling will depend among other factors on the amount of dopant which came to rest in the transient zone of the SIMS depth profile. The transient zone (24) (see also chapter 8) is the depth in SIMS depth profiling over which ion and sputter yields are changing due to primary ion implantation, beam induced crater bottom roughness or matrix changes. Transient zone depth is defined as the distance from the surface at which a matrix signal, e.g. \textsuperscript{30}Si in Si samples, reaches 90 percent of its steady state value. Using a given set of SIMS conditions, the amount of dopant contained in the transient region increases as dopant implant energy is reduced. Quantification in the transient zone is challenging because relative sensitive factors, which are used to convert measured counts into concentration, and sputter rates can change rapidly. If the depth of the transient zone is reduced, ion
yield and sputter rate will stabilize more quickly and quantitative accuracy will be improved. Lower primary ion impact energies reduce the transient zone width by reducing the $R_p$ of the primary ions, reducing the SIMS primary ion dose it takes to achieve a constant, stable primary ion surface concentration and hence constant, stable ion yields. In samples with surface layers, such as SiO$_2$ on Si, the transient zone depth can be influenced by the thickness of the surface layer and not solely by the depth (dose) necessary to stabilize primary ion surface concentration since matrix changes influences secondary ion yields and atomic densities and hence influence secondary ion intensities (25). Matrix changes during SIMS depth profiling of samples on which a native surface oxide forms, can be minimized by flooding the sample with O$_2$, which minimizes transient zone depth. Positive ion yields are increased under O$_2$ flooding and it has been shown that analysis conditions exist were O$_2$ flooding in combination with O$_2^+$ primary ion bombardment does not increase beam induced crater bottom roughness and hence usage of these analysis conditions minimizes profile shifts (see sections 4.3.1.2).

Analysis conditions which minimize profile shift under O$_2$ flooding (listed in Table 4-2) were used to acquire SIMS depth profiles of ultra shallow B implants. A 500eV, 1E15 atoms/cm$^3$ and a 300eV, 1E15 atoms/cm$^3$ B implants into (100) Si with $R_p$’s of 3.6 and 2.5nm respectively, were investigated.

<table>
<thead>
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<th>Primary Ion</th>
<th>Impact Energy [keV]</th>
<th>Incident Angle [degree]</th>
<th>O$_2$ Flooding</th>
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</tbody>
</table>

Table 4-2: Experimental conditions (see section 4.1 for complete description of conditions)

Figure 4-13 shows SIMS depth profiles of the 500eV, 1E15 atoms/cm$^3$ B implant obtained using a 1keV, 56° O$_2^+$ primary ion beam ($R_p$= 1.9nm), O$_2$ flooding and sample rotation and using a 500eV, 48° ($R_p$= 1.4nm) O$_2^+$ primary ion beam, O$_2$ flooding but no
sample rotation. Results obtained from the 500eV B implant with the two selected analysis conditions displayed in Figure 4-14 are very comparable. Profile shape and decay length are only slightly improved with the lower energy O$_2^+$ ion beam, indicating that an accurate profile has been obtained using either set of conditions. The higher SIMS primary ion beam does not significantly add distortions on to the 500eV B implant profile, but appears to be slightly shifted towards the surface. The similar profile shapes obtained with the two different beam conditions confirm the assumption that a SIMS primary ion beam having an R$_p$ 0.5 times or less the R$_p$ of a B implant does not considerably change the obtained depth profile of an ion implant (26).

![Graph of depth profiles](image)

**Figure 4-13:** 500eV, 1E15 atoms/cm$^2$ B implant into (100) Si analyzed with 500eV, 48° and 1keV O$_2^+$, 56° under O$_2$ flooding conditions. Sample rotation was used for the 1keV O$_2^+$, 56° to reduce beam induced crater bottom roughness.

Figure 4-14 shows SIMS depth profiles of a 300eV, 1E15 atoms/cm$^3$ B ion implant into (100) Si (R$_p$= 2.5nm) analyzed using 1keV O$_2^+$, 56°, O$_2$ flood and sample
rotation and 500eV O\textsubscript{2}\textsuperscript{+}, 48°, O\textsubscript{2} flooding with R\textsubscript{p}'s of 1.9 and 1.4nm respectively. All analyses were performed under O\textsubscript{2} flooding conditions. Comparison of the two depth profiles shows that using lower energy primary ion beam provides a better representation of the physical dopant distribution in the sample based on their decay lengths. Decay length obtained using 500eV or 1keV O\textsubscript{2}\textsuperscript{+} primary ion beams as measured at the trailing edge of the implant were 1.0nm and 1.4nm for the 500eV, 48° and 1keV, 50° O\textsubscript{2}\textsuperscript{+} primary ion beams respectively. It is probable that the 500eV, 48° O\textsubscript{2}\textsuperscript{+} primary ion beam with a R\textsubscript{p} of 0.56 times projected range of the 300eV B implant does not result in atomic mixing that significantly alters the profile shape of the analyzed implant, but even lower primary ion beam impact energies are necessary to verify that assumption.

Impact energies below 500eV for O\textsubscript{2}\textsuperscript{+} bombardment are not practical on a CAMECA IMS 6F, but impact energies as low as 150eV have been reported on a ATOMIKA 4500, a quadrupole type SIMS instrument (3) and impact energies of 250eV will be available on the next generation CAMECA magnetic sector SIMS (27). Beam induced crater bottom roughening and profile shift will have to be investigated for these ultra low energy O\textsubscript{2}\textsuperscript{+} primary ion beams but, assuming that conditions can be found under which the crater bottom remains relatively flat, accurate analysis of ultra shallow B implants with implantation energies below 300eV appears to be possible. The availability of 150-250eV O\textsubscript{2}\textsuperscript{+} should allow accurate SIMS analysis of the shallow B implants required for future generations MOSFET.
4.4 Summary

Results reported in this chapter demonstrate the importance of the effect of beam induced crater bottom roughness on sputter rate. Reduction in crater bottom roughness was shown to reduce the shift in the apparent depth of layers analyzed in the delta layer sample analyzed. These profile shifts have to be minimized for more accurate depth scale calibration of SIMS profiles. It was shown that for minimum shifts, beam induced crater bottom roughness and primary ion impact energies have to be minimized to minimize changes in sputter rate. Data was presented which showed that beam induced crater bottom roughness under glancing angle $O_2^+$ primary ion bombardment can be minimized by careful selection of primary ion angle of incidence and by using sample rotation. The use of $O_2$ flooding during glancing angle $O_2^+$ primary ion bombardment
can either increase or decrease crater bottom roughness depending on primary ion energy and angle. If the primary ion angle of incidence is kept below 50° for 1keV and 500eV O$_2^+$ SIMS analysis of ion implants in Si, O$_2$ flooding can be used to improve measurement sensitivity, decrease transient zone width and improve depth resolution for low energy glancing angle O$_2^+$ analysis of ultra shallow ion implants.

4.5 References

11. 15 layer B delta doped structure grown by Prof. E. H. C. Parker at the University of Warwick
5 SIMS Depth Profiling of Low Energy P Implants in Si using Low Energy $O_2^+$ and Cs$^+$ Ion Bombardment on a CAMECA IMS 6F

5.1 Introduction

The next generation of very large scale integrated (VLSI) and ultra large scale integrated (ULSI) devices will contain device features on the order of 0.10 $\mu$m. These devices will require metal-oxide-semiconductor sources and drains that are less than 33nm deep, which are classified as ultra shallow junctions (1). P will almost certainly continue to be widely used as an n-dopant in Si, even though its use for forming ultra shallow junctions is difficult due to its high diffusivity. If SIMS is to provide meaningful quantitative in depth analysis of ultra shallow P in Si, $^{30}$Si$^1$H mass interference must be eliminated, primary ion impact energy must be minimized (2) to minimize primary ion beam mixing, and detection limit and thus sensitivity must be maximized. Currently the accepted method for analyzing P in Si with SIMS is using Cs$^+$ primary ion bombardment and extraction of negative secondary ions (3). Unfortunately, the combination of the negative bias on the sample (required in the IMS-6f for efficient secondary ion extraction) and the positive polarity of the Cs$^+$ ions results in the primary ions being accelerated toward the sample, resulting in high impact energies. As an alternative to the use of Cs$^+$ primary ions for the analysis of ultra shallow P, an O$_2^+$ primary ion beam can be employed along with positive sample bias to extract positive P secondary ions (4)(5). Because the polarity of the O$_2^+$ primary ions and the sample bias for extracting P$^+$ are the same, primary ions are repelled from the sample and impact energies are reduced resulting in a condition favorable for high depth resolution analysis. Although the reduction in P secondary ion yield obtained using O$_2^+$ versus Cs$^+$ primary ion bombardment is about one order of magnitude, some of the loss of P$^+$ ion yield can be recovered through the use of O$_2$ flooding. In anticipation of the use of P for ultra shallow junctions, aspects of the optimization of SIMS for ultra shallow depth profiling of P in Si
using Cs\(^+\) and O\(_2\)\(^+\) primary ions are studied in this chapter. Topics discussed include profile decay length, sputter induced roughness and the ion yield transient (6).

In order to gain further insight with respect to the changes in decay length versus energy observed, SEM (secondary electron Microscopy) and AFM (Atomic Force Microscopy) micrographs of the SIMS depth profile sputter crater bottoms were acquired and correlated with primary ion impact energy. Depth profiles of bulk doped P in Si samples were also acquired for each primary ion impact energy to gain information on the ion yield transients i.e. changes in the ion yields of P and Si resulting from both the appreciable fraction of the analyzed depth made up of the surface native oxide and also resulting from the depth required for the primary ion yield enhancing Cs\(^+\) or O\(_2\)\(^+\) to reach a constant level.

### 5.2 Details of Experimental Method

Table 5-1 lists the type of primary ion and the primary ion beam accelerating voltage/secondary ion (or sample) accelerating voltage combinations used to achieve the primary ion impact energies discussed below. Table 5-1 also lists the primary ion impact energy normal to the sample surface and the approximate angle of impact of the primary ions. The angles of incidence were calculated using the formula derived by Meuris (7), which includes the deflector voltages used for positioning the beam onto the optical axis of the IMS-6f mass spectrometer.
Table 5-1: Experimental conditions used for P analysis in this chapter

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<td>5</td>
<td>-4.5</td>
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<tr>
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<td>-2</td>
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<tr>
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<td>5</td>
<td>3</td>
<td>-2</td>
<td>4.5</td>
<td>23</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>3</td>
<td>2</td>
<td>-1</td>
<td>2.8</td>
<td>24</td>
</tr>
<tr>
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<td>23</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>1.6</td>
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<td>-0.6</td>
<td>1.5</td>
<td>24</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>1.0</td>
<td>2.5</td>
<td>1.5</td>
<td>0.64</td>
<td>50</td>
</tr>
<tr>
<td>O₂⁺</td>
<td>0.5</td>
<td>1.15</td>
<td>0.65</td>
<td>0.34</td>
<td>47</td>
</tr>
</tbody>
</table>

For the P depth profiles acquired using 9.5, 7.0, 5.0 and 3.0keV Cs⁺ (8) primary ion impact energies, the IMS-6f primary column and the immersion lens were operated in the most commonly used crossover and deceleration modes respectively. Profiles recorded with 2.5 and 1.6 keV impact energies Cs⁺ were acquired with the primary column and the immersion lens operated in the collimated and acceleration modes respectively, resulting in improved primary beam density at a given current and minimized chromatic aberrations of secondary ions resulting from operation of the immersion lens at higher potentials.

Low energy O₂⁺ ion beams were produced using a duoplasmatron in combination with a Accel/Decel system, described in more detail in section 3.2.1, which improves O₂⁺ ion extraction efficiency by first extracting the ions using a negative potential (instead of ground) followed by deceleration of the ions to ground to get the desired primary ion beam energy. In conjunction with O₂⁺ primary ion beams, O₂ flooding was used. The O₂ pressure in the sample chamber was adjusted using an O₂ flood leak valve to maintain the sample chamber pressure at which the maximum the ³⁰Si⁺ secondary ion matrix signal was obtained. At this pressure, P⁺ sensitivity was maximized and the transient zone width was minimized.
Secondary ion post acceleration was employed and optimized to achieve the best signal to noise ratio for secondary ion detection (3). The immersion lens was operated in acceleration mode for sample biases at or below 2kV to reduce the effect of lens aberrations at low energy. Beam energies discussed in this chapter are total beam impact energies.

Secondary ions were collected from an area 60µm in diameter centered on a square raster. Raster edge dimensions ranged from 180 to 300µm (raster size chosen based on the primary ion beam diameter). If sample rotation was used, the sample was rotated at 20 rpm and secondary ions were extracted from an area 60µm in diameter centered on a circular area of 250 to 350 µm in diameter depending on the raster size and primary beam diameter. A mass resolution of 4000 M/ΔM, a 150µm image field and a 400µm contrast diaphragm (CD1) were used in all cases. Depth scales were established based on crater depth measurements using a TENCOR P-20 stylus profilometer. AFM micrographs were acquired using a Digital Instrument DI-3000 atomic force microscope, SEM images were acquired using a Hitachi S-3200N environmental SEM. The samples analyzed were a 2keV, 7°, 4E14 atoms/cm² P implanted into (100) Si, a 1keV, a 1.1E14 atoms/cm² P implanted into (100) Si, a 500eV, 7°, 1E15 atoms/cm² P implanted into pre-amorphized (100) Si and a 8.2E18 atoms/cm³ bulk doped P wafer.

In order to obtain an accurate RSF (Relative Sensitivity Factor) for quantitative measurement of P in Si for the ultra shallow depth profiles acquired at the various primary ion impact energies, a selected piece of the bulk doped wafer was standardized versus a high energy P implant in Si. An RSF was obtained from a 50keV P in (100) Si sample (4.7e14 atoms/cm² P at zero degrees) acquired at 9.5keV Cs⁺ primary ion impact energy. A selected piece of the bulk doped P in Si wafer was then depth profiled using the 9.5keV Cs⁺ primary ion impact energy until a constant level of P had been achieved. The concentration of this constant level of P was then determined using this RSF. For subsequent analyses at lower primary ion impact energies, the constant level of P obtained from this selected piece of bulk doped P in Si was used to calculate the P RSF’s for those energies. The 1keV P in Si implant was analyzed with and without sample rotation under 2.5kev Cs⁺ bombardment to investigate the effect of beam induced crater bottom roughness on profile decay length.
5.3 Results and Discussion

5.3.1 Ion Beam Induced Crater Bottom Topography Changes under Low Energy Cs Bombardment

SEM micrographs of the bottoms of the SIMS depth profiles craters, shown in Figure 5-1, clearly indicate that sputter induced roughness increased significantly with decreasing $\text{Cs}^+$ primary ion impact energy. The magnitude of sputter induced roughness created by the range of impact energies was evaluated by scanning 20 by 20 $\mu$m sections of the center of the sputter craters using AFM. An example topographic image of the data obtained from the sputter crater created using 2.5keV $\text{Cs}^+$ is presented in Figure 5-2 to illustrate the magnitude and morphology of the induced roughness. The RMS roughness values, determined over the full range of primary ion impact energies used, are plotted in Figure 5-3. It can be seen that roughness increases linearly as impact energy decreases. The cause of the roughness is likely to be connected to random roughness created under near normal incidence ion bombardment, as ripple structure formation has not been observed under normal and near normal incidence $\text{Cs}^+$ bombardment (3).
Figure 5-1: 6µm by 6µm SEM micrographs of SIMS craters sputtered with 9.5 (a), 5 (b), 2.5 (c) and 1.6keV (d) total Cs⁺ primary ion impact energy
Figure 5-2: 20µm by 20µm AFM topography image (height scale = 20nm) of SIMS craters sputtered with 2.5keV, 24° Cs⁺ primary ion impact energy

Figure 5-3: Sputter crater RMS roughness vs. Cs⁺ primary ion impact energy
5.3.2 Artifacts in SIMS Depth Profiles of Ultra Shallow P in Si Profiles under Glancing Angle $O_2^+$ Ion Bombardment

Artifacts in SIMS depth profiling such as profile shift and near surface ion yield changes which occur under low energy glancing angle $O_2^+$ bombardment have been discussed in detail in chapter 4 for the analysis of ultra shallow B profiles. Because of the dilute concentrations generally used in semiconductor doping, the type of dopant has not been observed to influence these artifacts. Experimental conditions used in this chapter were chosen with regard to minimizing profile shift and transient zone width in accordance with the results presented in chapter 4.

5.3.3 Decay Length of Ultra Shallow P in Si Ion Implants analyzed using Low Energy Cs Beams

Figure 5-4 shows depth profiles of the 2keV, 4E14 and the 1keV 1.1E14 atoms/cm$^3$ P implants in Si, acquired using 1.6, 2.5, 5.0 and 7.0keV and 2.5, 5.0and 7keV Cs$^+$ primary ion impact energies respectively. Profiles recorded with 9.5 and 3.0 keV impact energy are not shown in Figure 5-4 to improve readability. The 1keV P in Si implant was not analyzed with 1.6keV impact energy because of dramatically reduced source lifetime due to source clogging detected during the analysis of the 2keV P implant. Therefore while a profile obtained with a 1.6keV Cs$^+$ primary ion beam is shown in Figure 5-4, the lowest practical obtainable impact energy on the CAMECA IMS 6F for Cs$^+$ primary ions appears to be 2.5keV.

As lower primary ion impact energies are used, a clear improvement in the depth profile trailing edge decay length is seen (See Figure 5-4 and Table 5-2). Profile shape did not visibly improve with the use of lower impact energies and still seems to be largely influenced by near surface ion yield changes and by ion beam mixing. Comparison of the projected ranges ($R_p$) of the 1 and 2keV, $7^o$ P implants (3.4 and 5.3nm) respectively with the $R_p$ of the 2.5keV, $24^o$ Cs primary ion beam (5.4nm) shows that for both implants the $R_p$ of the primary ion beam is beyond the $R_p$ of the implant to be analyzed. The deep, in comparison with the P implant, $R_p$ of the Cs$^+$ beam thus causes significant mixing of
sample constituents within the region of the sample containing the peak of the P implants.

The degree of this mixing negates the possibility of obtaining a good profile shape using these bombardment conditions.

Figure 5-4: Depth profiles obtained from a) 2keV, $4 \times 10^{14}$ atoms/cm$^2$ and b) 1keV, $1.1 \times 10^{14}$ P implant into (100) Si analyzed with Cs$^+$ primary ion beams with impact energies between 7.0 and 1.6keV

<table>
<thead>
<tr>
<th>Cs Ion Beam Impact Energy [keV]</th>
<th>Decay Length (2keV P in Si) [nm]</th>
<th>Decay Length (1keV P in Si) [nm]</th>
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<tbody>
<tr>
<td>1.6</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>2.5</td>
<td>4.6</td>
<td>2.8</td>
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<td>3.0</td>
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<tr>
<td>5.0</td>
<td>6.4</td>
<td>4.4</td>
</tr>
<tr>
<td>7.0</td>
<td>7.9</td>
<td>5.5</td>
</tr>
<tr>
<td>9.5</td>
<td>8.8</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 5-2: Primary ion beam conditions and decay length for a 1 and 2keV P implant into (100) Si
Figure 5-5 shows profiles obtained from the 1keV P in Si implant, obtained with 2.5keV Cs$^+$ ion bombardment with and without using sample rotation. Decay length, obtained with and without sample rotation, remained constant within the measurement accuracy at 2.8nm. This indicates that while roughness can have an influence on trailing edge decay length, it does not appear to be a major contributing factor for 2.5keV Cs$^+$ ion bombardment. Using this Cs beam energy and angle of impact, decay length seems to be dominated by collision cascade mixing.

![Figure 5-5](image)

**Figure 5-5:** Depth profiles obtained from a 1keV, 1.1 E14 P implant into (100) Si analyzed with a 2.5keV Cs$^+$ primary ion beam with and without sample rotation

5.3.4 **Ion Yield Transients under Cs$^+$ and O$_2^+$ Primary Ion Bombardment**

What appears to be an indication of the interface between the native oxide and bulk Si can be seen as a change in the slope of the profiles shown in figure 5-5 at approximately 1.8nm or just after the peak in the P$^+$ secondary ion intensity. As can be
seen in Figure 5-6 and Table 5-3, the depth covered by the ion yield transient, defined as the depth at which the $^{30}\text{Si}$ matrix signal reaches 90% of its equilibrium level, decreased from 8.6 to 1.9nm when going from 9.5 to 2.5keV impact energy. This decreasing trend in transient depth with decreasing Cs$^+$ impact energy did not continue (within the measurement accuracy) upon further reduction of the impact energy from 2.5 to 1.6keV. However, the Si secondary ion intensity of the ion yield transient does increase faster in the first nanometer when 1.6keV Cs$^+$ is used, giving an indication that the transient width is defined by the native oxide thickness and not by primary ion surface concentration for low Cs$^+$ primary ion energies.

<table>
<thead>
<tr>
<th>Primary Ion</th>
<th>Ion Beam Impact Energy and Angle</th>
<th>Ion Yield Transient Zone Depth [nm]</th>
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<tbody>
<tr>
<td>Cs$^+$</td>
<td>1.6 keV, 24°</td>
<td>1.9</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>2.5 keV, 23°</td>
<td>1.8</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>3.0 keV, 24°</td>
<td>3.4</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>5.0 keV, 23°</td>
<td>6.1</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>7.0 keV, 25°</td>
<td>7.6</td>
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<td>8.6</td>
</tr>
<tr>
<td>O$_2^+$</td>
<td>1.0 keV, 50°</td>
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</tr>
<tr>
<td>O$_2^+$</td>
<td>0.5 keV, 47°</td>
<td>0.3</td>
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</tbody>
</table>

Table 5-3: Primary ion beam conditions and transient zone width
5.3.5 Low Energy O$_2^+$ Ion Bombardment as an Alternative to Cs$^+$ for SIMS

Depth Profiling of Low Energy P in Si Implants on a CAMECA IMS 6F

Figures 5-7 a) and b) show P depth profiles of the 1keV, 1.1E14 atoms/cm$^3$ and the 500eV, 1E15 atoms/cm$^3$ P ion implants into (100) Si obtained using 1keV, 50° and a 500eV, 47° O$_2^+$ primary ion beam. O$_2$ flooding was used during the acquisition of all profiles. In both cases, the use of the lower impact energy primary beams yields obvious improvement in the profile shape. However, the classic implant profile shape is only evident for the 1keV P implant analyzed with the 500eV, 47° O$_2^+$ primary ion beam. This improved profile shape is believed to result from the fact that only in the case of the 500eV, 47° O$_2^+$ primary ion beam is the $R_p$ of 1.4nm less than half of the 3.4nm $R_p$ of the 1keV P implant. Since the $R_p$ of the 500eV P implant is about 1.9nm, the 1.4nm $R_p$ of the 500eV, 47° O$_2^+$primary ion beam is still too large to provide an undistorted profile shape for the 500eV implant although the best decay length obtained in this study was obtained for the 500eV P implant profiled using a 500eV, 47° O$_2^+$ primary ion beam (See
Table 5-4). In addition, the 500eV, 47° O2+ primary ion beam with O2 flooding also produced the narrowest ion yield transient, approximately 3Å. While a reduction in transient zone width aids in near surface quantification, it has been shown that ion and/or partial sputter yield changes of impurity (dopant) species can extend over 10’s of nanometers even if a small transient zone width of the matrix signal has been established (9).

![Figure 5-7: a) P depth profiles of a 1keV, 1.1E14 atoms/cm³ P implant into (100) Si obtained with 1keV, 50° and 500eV, 47° O2+ primary ion beams under the use of O2 flooding b) P depth profiles of a 500eV, 1E15 atoms/cm³ P implant into (100) Si obtained with 1keV, 50° and 500eV, 47° O2+ primary ion beams under the use of O2 flooding](image)

Figures 5-8 a) and b) show a comparison of the 1keV and the 500eV P implants analyzed with 500eV, 47° O2+ using positive secondary ion extraction and with 2.5keV, 24° Cs+ primary ion beams using negative secondary ion extraction. Table 5-4 list transient zone width, decay length and detection limits obtained under the various conditions. Table 5-4 also list useful yields, sputter yields and sputter rates. For both P implants investigated,
the 500eV, $47^\circ$ O$_2^+$ primary ion bombardment produces significantly improved profile shape and decay length as compared to the profiles obtained using 2.5keV Cs$^+$. However, use of 500eV O$_2^+$ resulted in a reduction of the P detection limit by about one order of magnitude. Instead of simply comparing detection limits, a better understanding of analysis sensitivity can be gained comparing useful yields, which are independent of primary ion beam current and raster size. P useful yield is defined here as the ratio of the amount of sputtered P within the optical gated area divided by the amount of detected P ions. While useful yields are independent of primary ion beam current and raster size, they are dependant on instrument transmission, which is the ratio of ions reaching the ion counting detector to ions sputter from the sample. Useful yields also depend on detector counting efficiency, which is the ratio of ions reaching the detector to ions counted by the detector. A better value for comparison of the depth profiling conditions with respect to P detection sensitivity can be obtained if the influence of instrument transmission and detector conversion efficiency on the measured useful yields is reduced. Counting efficiency of the electron multiplier, the ion detector used under all conditions for counting sputtered P ions, is kept almost constant due to the use of secondary ion post acceleration (see section 3.2.4) and hence does not significantly influence useful yields. To reduce the influence of instrument transmission on useful yields with regard to instrument transmission efficiency which is linearly dependent on sample potential for the IMS-6F, useful yields were normalized to the sample potential of the various conditions used. Normalized useful yields, shown in Table 5-4, are about a factor of four to six lower for 1 and 500eV O$_2^+$ bombardment respectively compared to 2.5keV Cs$^+$ bombardment indicating that O$_2^+$ bombardment, positive ion extraction and O$_2$ flooding results in a less than 1 order of magnitude loss in sensitivity compared to Cs$^+$ bombardment and negative secondary ion extraction for the analysis of ultra shallow P.
Figure 5-8: a) P depth profiles of a 1keV, 1E14 atoms/cm³ P implant into (100) Si obtained with 500eV, 47° O₂⁺ (+ox. flood) and 2.5keV, 24° Cs⁺

b) P depth profiles of a 500eV, 1E15 atoms/cm³ P implant into (100) Si obtained with 500eV, 47° O₂⁺ (+ox. flood) and 2.5keV, 24° Cs⁺

<table>
<thead>
<tr>
<th></th>
<th>500eV, 47° O₂⁺, ox. flood</th>
<th>1keV, 50° O₂⁺, ox. flood</th>
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<td>Transient zone width</td>
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<tr>
<td>(90%⁻³⁰Si⁻ signal)</td>
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<tr>
<td>Decay Length (1/e)</td>
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<td>[atoms/cm³]</td>
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<td></td>
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<tr>
<td>Useful Yield</td>
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<td>(normalized for Sample HV)</td>
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<tr>
<td>Sputter Yield</td>
<td>0.4</td>
<td>0.5</td>
<td>1.3</td>
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Table 5-4: Transient zone width and decay length (1/e) for 1keV, 50° and 500eV, 47° O₂⁺ ion bombardment under the use of O₂ flooding and 2.5keV Cs⁺, 24° ion bombardment
5.4 Summary

AFM and SEM images have been presented which show the increase in random roughness as the impact energy of a near normal Cs⁺ primary ion beam is reduced from 9.5 to 1.6keV. This Cs primary ion beam generated roughness does not appear to limit obtainable depth resolution for the lowest practical obtainable Cs⁺ impact energies of 2.5keV on the CAMECA IMS 6F. It was shown that 2.5keV Cs⁺ primary ion bombardment causes atomic mixing in silicon samples to a degree which does not allow accurate analysis of the profile shape of ultra shallow P implants in Si. However it was also shown that transient zone width and decay length can be significantly improved by lowering impact energies. Cs⁺ primary ion impact energies below 2.5keV under negative secondary ion extraction are not practically obtainable on the CAMECA IMS 6F due to acceleration of the positive Cs⁺ ion towards the negatively biased sample and source limitations. O₂⁺ primary ion bombardment and positive secondary ion extraction is an attractive alternative to Cs⁺ primary ion bombardment and negative secondary ion extraction for ultra shallow depth profiling of P. Low energy O₂⁺ primary ion bombardment provides a significant improvement in depth resolution with a less than one order of magnitude loss in sensitivity.

5.5 References


6 Negative Cluster Ion Bombardment: An Alternative for SIMS Depth Profiling of Low Energy Implants of n-Dopants

6.1 Introduction

Junction depths for source drain extensions structures for the 0.1 μm MOSFET (MISFET) generation is predicted to be between 19-33 nm(1)(2). This continuing reduction in device geometries and thus junction depths requires continuing development of SIMS ultra shallow junction depth profiling techniques if SIMS is to continue to provide the precision and accuracy required for continuing device development and process monitoring. While As is currently the n dopant of choice for ultra shallow junction formation in Si, P will almost certainly continue to be widely used as an n-dopant in Si.

For meaningful determination of P dopant concentration in Si using SIMS, the $^{30}\text{Si}^{1}\text{H}$ mass interference has to be eliminated from the secondary ion intensity measured at mass 31. Elimination of this interference requires a mass resolution of $M/\Delta M$ of 4000 (10% valley definition) which can readily be achieved using magnetic sector SIMS instruments such as the CAMECA IMS 6F. It is well known that use of Cs$^{+}$ primary ions lowers the surface work function of Si, which enhances P negative ion yield and provides the best detection limits for P in Si. It is also well known that lower primary ion beam energies reduce primary ion beam induced mixing of sample constituents, which results in improved depth resolution (3). Unfortunately, the combination of the negative bias on the sample (required in the IMS-6f for efficient negative secondary ion extraction) and the positive polarity of the Cs$^{+}$ ions results in the Cs$^{+}$ ions being accelerated toward the sample resulting in high Cs$^{+}$ impact energies (4). If it were possible to produce a negative primary ion that lowers surface work function to increase negative ion yield in a manner commensurate with practical SIMS analysis, impact energies could be reduced. Impact energies could be further reduced if primary cluster ions are used, where each atom in a primary ion cluster only carries energy according to its mass fraction in the cluster (e.g. in a 1keV Cs$_{10}$ cluster ion each Cs atom would have an energy of only
0.1keV), with the cluster breaking up into its constituents upon impact on the sample surface.

In SIMS sputter depth profiling, cluster ions have been mainly used for the analysis of ultrashallow B implants in Si and promising results were shown in regard to transient zone width and trailing edge decay length (a measure for depth resolution) using SF$_5^+$ primary cluster ions (5)(6). Other positive primary cluster ions that were used in SIMS depth profiling are CF$_3^+$ (7), NO$_2^+$ (8) and O$_3^+$ (9). Various positive cluster ions have also been successfully used for organic surface characterization and imaging providing significant enhancements in secondary ion yield compared to O$_2^+$ or Cs$^+$ ion bombardment (10)(11)(12)(13).

Negative (cluster) primary ions, with the exception of O$^-$ for measurements on insulators for charge compensation, have not been widely used in SIMS depth profiling, but have been investigated for the use in accelerators and accelerator physics. The promise of lower impact energies using negative (cluster) primary ions with negative sample potentials in magnetic sector SIMS and the need for high depth resolution analysis of ultra shallow n-dopants has sparked the interest in negative ion sources for the use in SIMS depth profiling. Peabody Scientific developed the PSX-120 Sputter Negative Ion Source for negative (cluster) ion production with the CAMECA IMS 6F to give researchers the possibility to investigate high depth resolution analysis of ultra shallow n-dopants with magnetic sector SIMS. Its use for profiling of ultra shallow P implants will be evaluated in this chapter.

6.2 Details of Experimental Method

Negative primary ions were produced using the PSX-120 Sputter Negative Ion Source (see schematic in Figure 3-3). For source operation, Cs is heated to a temperature of about 200°C, which produces a gaseous Cs flow into the source that is directed onto a 1100°C tantalum ionizer, which is located in the center of the source. Upon contact with the ionizer, Cs becomes thermally ionized (14). Positive Cs$^+$ ions are accelerated toward
the negatively biased source target were they cause sputtering. Negative ions from the
target sputter process are extracted from the source. Any vacuum compatible material
can be used as a source target. Details of target investigations are presented in section
6.3.1. In addition to the source potential, the ionizer can be negatively biased in order to
control target impact energy regulation and for beam focusing. An einzel lens after the
source provides improved ion extraction efficiency.

Initially a variety of target materials were investigated with respect to their possible
use in high depth resolution analysis of ultra shallow n-dopants. Target materials
investigated include cesium iodine (CsI), cesium sulfate (Cs₂SO₄), Si (Si), graphite (C),
and various high melting point organic compounds. Results are discussed in chapter 6-3.

From these results and data presented by Gillen (15), CsC₆⁻ cluster ions (16) were
chosen for investigation of low energy glancing angle depth profiling of ultra shallow P
implants. Depth profiling results using CsC₆⁻ were compared with O₂⁺ and Cs⁺ as
primary ions for P depth profiling. In the cases were O₂ flooding was used to optimize P
ion yield and transient zone width, pressure in the sample chamber was adjusted using the
O₂ flood leak valve to maintain the sample chamber pressure at which the maximum the
³⁰Si⁺ matrix signal occurred. Experimental conditions are listed in Table 6-1.

P⁻ secondary ions were collected from area 60 µm in diameter (FA2) centered on
a square raster of 300µm width (as required by the primary beam diameter). The 150 µm
image field, 400 µm contrast aperture (CD1) and a mass resolution of 4000 m/Δm were
used. In the cases were sample rotation was employed, the sample was rotated at a speed
of 20rpm and secondary ions were extracted from a area 60µm diameter centered on a
circular area with a diameter between 350 and 450 µm as required by the primary beam
diameter. Depth scales and etch rates were established by measuring the final crater
depths using a Tencor P20 profilometer. Because source stability over a 20-minute
period was often not better than 4 percent, linear sputter rate corrections were applied to
the P depth profiles based on initial and final current.

The samples analyzed were a 1keV, 1.1e14 atoms/cm² P implanted into (100) Si,
500eV, 1E15 atoms/cm² P implanted into pre-amorphized (100) Si, a 8.4E18 atoms/cm³
bulk doped P wafer and the B delta structure described in section 3.4.3.
Table 6-1: Experimental conditions with energies in kV (keV)

<table>
<thead>
<tr>
<th>Primary Ion</th>
<th>Source Potential</th>
<th>Sample Potential</th>
<th>Total Impact Energy</th>
<th>Normal Impact Energy</th>
<th>Normal Impact Energies per Atom</th>
<th>Angle of Incidence [Degrees]</th>
<th>Rp (TRIM) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsC6-</td>
<td>-6.8</td>
<td>-3.0</td>
<td>3.8</td>
<td>2.87</td>
<td>1.86 (Cs)</td>
<td>41</td>
<td>4.4</td>
</tr>
<tr>
<td>CsC6-</td>
<td>-6.8</td>
<td>-3.9</td>
<td>2.9</td>
<td>1.94</td>
<td>1.26 (Cs)</td>
<td>48</td>
<td>3.5</td>
</tr>
<tr>
<td>CsC6</td>
<td>-6.8</td>
<td>-4.25</td>
<td>2.55</td>
<td>1.57</td>
<td>1.02 (Cs)</td>
<td>52</td>
<td>2.9</td>
</tr>
<tr>
<td>CsC6-</td>
<td>-6.8</td>
<td>-4.5</td>
<td>2.3</td>
<td>1.32</td>
<td>0.86 (Cs)</td>
<td>55</td>
<td>2.7</td>
</tr>
<tr>
<td>CsC6</td>
<td>-5</td>
<td>-2.4</td>
<td>2.6</td>
<td>1.93</td>
<td>1.25 (Cs)</td>
<td>42</td>
<td>3.6</td>
</tr>
<tr>
<td>CsC6-</td>
<td>-4</td>
<td>-2.25</td>
<td>1.75</td>
<td>1.19</td>
<td>0.77 (Cs)</td>
<td>47</td>
<td>2.8</td>
</tr>
<tr>
<td>O2+</td>
<td>2.5</td>
<td>1.5</td>
<td>1.0</td>
<td>0.64</td>
<td>0.32 (O)</td>
<td>50</td>
<td>2.1</td>
</tr>
<tr>
<td>O2+</td>
<td>1.15</td>
<td>0.65</td>
<td>0.5</td>
<td>0.34</td>
<td>0.17 (O)</td>
<td>47</td>
<td>1.4</td>
</tr>
<tr>
<td>Cs+</td>
<td>1.5</td>
<td>-1.0</td>
<td>2.5</td>
<td>2.30</td>
<td>2.30 (Cs)</td>
<td>23</td>
<td>5.4</td>
</tr>
</tbody>
</table>

6.3 Results and Discussion

6.3.1 Investigation of Source Target Materials for Sputter Negative Ion Sources with Respect to High Resolution SIMS Depth Profiling of Ultra Shallow N-dopants

Assuming the electron tunneling ion yield model presented in section 2.3.6 is valid, negative secondary ion yields in SIMS vary exponentially with the surface work function of the sample and the electron affinity of the analyzed element. In SIMS sputter depth profiling Cs+ primary ions are typically used to reduce the work function of Si samples and hence increase negative ion yield. Other elements that have lower elemental work functions than Si and hence are likely to reduce the work function of Si include alkali and alkali earth elements. Also some refractory and rare earth elements have lower work functions than Si. If negative primary ions containing alkali or alkali earth elements are to be used for SIMS sputter depth profiling they have to be able to be produced with currents in excess of 10nA and with beam diameters less than 100 µm. The same physics that governs secondary ion yield in SIMS also governs primary ion formation in a negative sputter ion source. With negative ion yield depending
exponentially on electron affinity, larger primary ion currents can be expected from source targets that have a high electron affinity. Thus, in order to produce large primary ion currents, source sputter targets should consist of element(s) with high electron affinity and the target surface must have a low work function. In this section, sputter targets of various compositions are evaluated for negative primary ion production using the PSX-120 sputter negative ion source.

Targets investigated were cesium iodide (CsI), cesium sulfate (Cs$_2$SO$_4$), silicon (Si), graphite (C), and various high melting point organic compounds.

CsI and Cs$_2$SO$_4$ were used with the idea that Cs forms stable negative ion cluster with halide/group VI elements of a large magnitude. CsI$^-$ is often used in mass spectrometers for calibration and Cs$_2$SO$_4$ was chosen because the single positive charged Cs$^+$-ion and the two times negatively charged S$^{2-}$ ion might form a stable CsS$^-$ cluster with high intensity. Although the presence of I or S on surfaces generally increases the surface work function, it was thought possible that the presence of Cs may compensate for and perhaps overwhelm this increase. In this case, an increase in P$^-$ ion yield would be obtained. To obtain mass spectra of CsI and Cs$_2$SO$_4$, powders of each compound were compacted into source target holders and bombarded with 4.8keV Cs$^+$ (within the source). Negative ions were extracted from the source and mass separated by varying the field strength of the primary beam magnetic sector of the IMS-6F. In the initial set of experiments, only low, unstable primary ion intensities could be obtained from these compounds, apparently due to charging of these salts of under Cs$^+$ ion bombardment. Mixing the salts in a 1:1 volume percent ratio with graphite powder resulted in a more stable source output. Mass spectra of CsI and Cs$_2$SO$_4$ are shown in Figures 6-1 and 6-2.

C$^-$, C$_2^-$, Cu$^-$ and I$^-$ primary ions were observed from the CsI/C target with intensities larger than 1nA, but use of these primary ions did not give a measurable increase in negative secondary ion yield for P and Si. These elements have higher work functions compared to Si and hence do not reduce the surface work function of Si. Similar results were found for the Cs$_2$SO$_4$/graphite target. Either primary ion yields for formation of Cs$_x$X$_y$ (X=Halogen) clusters are low or the source target sputtering during which the process is too violent to allow Cs$_x$X$_y$ cluster formation close to the surface or sputtering of Cs$_x$X$_y$ clusters directly from the surface.
Another problem with cesium containing salt target materials results from the target sputtering process becoming self-sustaining, which means that neutral Cs sputtered from the salt targets are positively ionized at the tantalum ionizer and accelerated back towards the target, a process also called self ionization. The additional Cs supplied to the source target by the self ionization process increases the source target Cs surface concentration to levels at which extraction of Cs$_x$X$_y$ clusters from the source becomes unstable. Reducing the source Cs reservoir temperature reduces the amount of Cs supplied to the source and target and can compensate for the additional amount of Cs supplied to the target by the self-ionization process. However a stable Cs concentration at the target surface and hence stable Cs$_x$X$_y^-$ is difficult to achieve. For targets on which sputtering became self sustaining, it is also difficult to achieve stable current for a newly inserted targets, since the target sputtering does not become self sustaining until Cs coming from the target reduces the amount of Cs needed from the reservoir. Source stability can often not be achieved for over one hour.
Figure 6-1: Mass spectra of primary ions obtained from a CsI/C source sputter target that was bombarded by a 4.8keV Cs\(^+\) ion beam within the PSX-120 sputter negative ion source obtained by sweeping the primary beam mass filter.

Figure 6-2: Mass spectra of primary ions obtained from a Cs\(_2\)SO\(_4\)/C source sputter target that was bombarded by a 4.8keV Cs\(^+\) ion beam within the PSX-120 sputter negative ion source obtained by sweeping the primary beam mass filter.
Source targets in the section above were investigated with the goal of finding a Cs containing negative primary ion cluster that can be used for depth profiling of n-dopants in Si. One problem with the use of these primary ions, as well as with the commonly used Cs\(^+\) and O\(_2^+\) primary ions, for depth profiling is that the sample surface concentration and associated secondary ion and sputter yields changes due to primary ion implantation. The region over which these changes occur is known as transient zone, as described in chapter 2. If a primary ion can be used which does not change sample composition, a reduction in transient zone width and an improvement in near surface characterization might be possible to achieve. For Si samples a reduction in transient zone width could therefore theoretically be achieved if Si primary ions are used. To test this theory a small piece of a Si wafer was compacted into a target holder for the PSX-120 and used to produce Si primary ions. A mass spectra from this target, using a extraction high voltage of 6.8kV, was obtained by sweeping the primary beam magnet over its range is shown in Figure 6-3. The maximum $^{28}\text{Si}$ current obtained was approximately 100nA. A beam diameter of 80µm was achieved with at a current of 5nA and used to analyze a Si wafer with a dopant concentration of less than 1E15 atoms/cm\(^3\). Sample bias was 3.9kV, resulting in a primary beam impact energy of 2.9keV and a 50 degree angle of incidence. The observed transient zone width under these condition was significantly larger compared to the values obtained using 2.5keV, 23° Cs\(^+\) or 1keV, 45° O\(_2^+\) primary ions. Other theoretical explanations for the extended transient zone width if not caused by the native oxide may be beam induced crater bottom roughness or the isotopic enrichment of $^{28}\text{Si}$ in the sample.
Figure 6-3: Mass spectra of primary ions obtained from a Si source sputter target that was bombarded by a 4.8keV Cs\(^+\) ion beam within the PSX-120 sputter negative ion source obtained by sweeping the primary beam mass filter

Graphite targets were first used by Gillen (12) in a PSX-120 ion source. He showed that it is possible to extract CsC\(_6\)^- currents from graphite rod targets with current in access of 50nA and showed strong ion yield enhancements for the analysis of organics. A mass spectra from a graphite target that was bombarded by a 4.8keV Cs\(^+\) ion beam within the PSX-120 sputter negative ion source, using a source extraction potential of 6.8keV, was obtained by sweeping the primary beam magnet over its range. This spectra is shown in Figure 6-4. The preferential formation of C\(_{2n}\)^- compared to C\(_n\)^- is displayed in the chart as well as the higher ion yield of CsC\(_6\)^- compared to CsC\(_4\)^- and CsC\(_2\)^-. Analysis of a Si wafer bulk doped with 8.2E18 atoms/cm\(^3\) P with CsC\(_6\)^- gave an ion yield improvement for P of a factor of about 40 compared to Si primary ion bombardment. Based on the above, CsC\(_6\) showed the most promise as a Cs containing negative primary cluster ion. The remainder of this chapter contains a detailed discussion of issues regarding the use of CsC\(_6\).
Figure 6-4: Mass spectra obtained by sweeping the primary beam mass filter from a graphite rod source sputter target that was bombarded by a 4.8keV Cs\(^+\) ion beam within the PSX-120 sputter negative ion source.

Figure 6-5a and 6-5b show mass spectra centered on mass 205 acquired by scanning the primary beam mass filter. Mass selection aperture sizes of 750µm (mass resolving power of 1) and 100µm (MSRP of 3) were used for 6-5a and 6-5b respectively. The two peaks visible in Figure 6-5b indicate that the mass 205 CsC\(_6\)^− signal has a significant contribution of what might be TaC\(_2\), which could be the result of sputtering of the tantalum ionizer in the source. The signal of the second peak decreased with source usage time, perhaps as a result of increasing Cs and C coverage on the ionizer.
Figure 6-5: Primary ion current as a function of primary ion mass with low and high primary ion mass resolution

The C\textsubscript{2}\textsuperscript{-} primary ion current versus source target impact energy obtained with the ionizer set at 30\% of the total extraction potential is shown in Figure 6-6. Extracted C\textsubscript{2}\textsuperscript{-} primary ion current increased until saturating at a target impact energy of about 5keV. Impact energies above 5keV lead to extensive sputtering of the target, high leakage current due to secondary electron emission and short target lifetime. Therefore target impact energies above 5keV should be avoided.
Figure 6-6: Maximum $C_2^-$ current extracted from the PSX-120 negative sputter ion source versus target impact energy

Figure 6-7a and 6-7b show characteristic changes of the detected $^{28}\text{Si}^-$ secondary ion matrix signal during 3.9keV, 50° CsC$_6^-$ sputtering of (100) Si wafers. During steady state conditions, i.e. constant ion and sputter yields have been established, changes in the detected secondary ion intensity of matrix signal are directly proportional to fluctuations in primary ion beam current. In Figure 6-7a, two typical $^{28}\text{Si}^-$ secondary ion signals acquired during different depth profile acquisitions using 3.9keV, 50° CsC$_6^-$ are shown. Sudden changes in $^{28}\text{Si}^-$ secondary ion current are seen during both acquisitions. During the acquisition shown in the lower curve in Figure 6-7a, changes in $^{28}\text{Si}^-$ secondary ion current are of short duration and the measured $^{28}\text{Si}^-$ signal returns quickly to a value comparable to the intensity before the signal drop occurred. During the other depth profile acquisition, a stable $^{28}\text{Si}^-$ secondary ion current intensity of lower magnitude than the $^{28}\text{Si}^-$ secondary ion intensity before the signal change is established. These changes in detected $^{28}\text{Si}^-$ secondary ion current indicate rapid CsC$_6^-$ primary ion current changes, which means rapid changes in sputter rate. Rapid changes in sputter rate are usually unacceptable in SIMS sputter depth profiling, since an accurate scale can only be established with great difficulty. Pores in the graphite rods used as the source target material for producing CsC$_6^-$ primary ions apparently cause the signal drops, as compacting the graphite rods with a mechanical press greatly reduced the rate with which
the signal drops occurred. However, even with a compressed graphite target source stability is often not better than 10% over 20 minutes over the first 10 hours of source operation as shown in Figure 6-7b. After this time, the stability of the primary ion current extracted from the source becomes continuously worse due to extraction problems from the hole sputtered into the carbon target. Once this hole is formed, a target exchange is required. A picture of a graphite target after approximately 12 hours of 4.8keV Cs$^+$ bombardment (−2kV on the ionizer and −6.8kV on the target) within the PSX-120 Sputter Negative Ion Source is shown in Figure 6-8. The depth of the sputter hole shown in the figure is several millimeters.

Figure 6-7: Si$^-$ secondary ion matrix signals acquired during 3.9keV, 50$^\circ$ CsC$_6^-$ depth profiling of (100) Si wafers as a measure for CsC$_6^-$ primary ion current stability
Reducing target impact energy by increasing ionizer bias and hence reducing the potential difference between source ionizer and source target can increase target lifetime while keeping extraction potential constant at the expense of reduced source output. Target lifetime might possibly be increased without a loss in source output by rotating the source target in an eccentric or elliptical fashion, which would increase the target area and extend the time required for formation of deep sputter hole in the target. The formation of a deep source target sputter hole and the related extraction problems could also be avoided with a carbon containing target that would provide a renewable (flat) surface. Theoretically, a target material could be used which would melt under the ion beam and have sufficiently high enough capillary forces to stay within the target holder resulting in a renewable source target. The temperature of the target holder measured by removing the source target rises to at least 70°C under 4.8keV Cs⁺ ion bombardment.

Table 6-2 lists several high boiling point organic compounds that might melt in the target holder, but keep a low vapor pressure in the liquid phase. Table 6-2 also lists boiling points of these compounds when introduced to the source vacuum of about 1E-6torr, calculated using the Clausius-Clapeyron equation. It can be seen that the boiling point of all investigated compounds is now close to or under 70°C. The compounds with boiling points larger than 65°C at 5E-6torr were compacted into target holders, introduced into the PSX-120 sputter negative ion source and bombarded with 4.8keV Cs⁺. No significant CsC₆⁻ current was extracted from any of the investigated compounds. Instead of being
present in the liquid phase in the target holder, the used organic compounds either melted and evaporated quickly or sublimed, indicating a higher target temperature than 70°C. It is also possible that the capillary forces between the molten organic and the target holder were not strong enough to hold the molten organic inside the holder.

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Melting Point [°C]</th>
<th>Boiling Point (1 atm) [°C]</th>
<th>Boiling Point (5E-6 torr) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tripheylmethane</td>
<td>93</td>
<td>358</td>
<td>101</td>
</tr>
<tr>
<td>Octacosane</td>
<td>62</td>
<td>440</td>
<td>66</td>
</tr>
<tr>
<td>Glutaric Acid</td>
<td>98</td>
<td>200</td>
<td>14</td>
</tr>
<tr>
<td>Heptadecanol</td>
<td>54</td>
<td>308</td>
<td>-23</td>
</tr>
<tr>
<td>Glycerin (Glycerol)</td>
<td>20</td>
<td>290</td>
<td>-12</td>
</tr>
</tbody>
</table>

Table 6-2: Examples for high boiling point organic compounds

If beam energies below 5keV are desired, it is advantageous to reduce source ionizer potential to zero. This increases the potential difference between source ionizer and target. As a result the target is sputtered with more energetic Cs⁺ ions in the source, more material is sputtered from the target and a higher source output is achieved compared to settings with a biased ionizer. Reducing the ionizer and extraction potentials of the source however also yields a less efficient extraction of primary ions from the source and the source body becomes quickly contaminated with Cs, which increases the source leakage current. This makes it necessary to clean the source approximately every three days if extraction potentials at or below 5keV are used. Figure 6-9 shows pictures of the source extraction plate after cleaning and after 3 days of low energy CsC₆⁻ extraction. A large build up of contamination is seen in Figure 6-9b, which is detrimental to source performance.
6.3.2 Ion Beam Induced Crater Bottom Topography Changes and Profile Shift under Molecular Ion Bombardment

Ion beam induced surface topography changes have been studied by a large number of researchers for a variety of single element primary ions / matrix combinations (17)(18)(19)(20), but the effect of cluster ion bombardment on surface topography has not been widely studied. If primary cluster ions in general and CsC$_6^-$ in particular are to be used as an alternative for primary ions in SIMS sputter depth profiling, beam induced crater bottom topography changes have to be investigated and conditions found where surface topography is minimized to reduce sputter rate changes and improve depth scale accuracy. In this section, the effect of the use of CsC$_6^-$ primary cluster ions on sputter crater bottom topography was studied over a range of impact angles and energies (see Table 6-3). The range of energies and angles investigated were chosen to be relevant to high depth resolution profiling and were limited by source performance constraints.
Table 6-3: Experimental conditions with energies in keV

<table>
<thead>
<tr>
<th>Primary Ion</th>
<th>Impact Energy</th>
<th>Angle of Incidence [Degrees]</th>
<th>Normal Impact Energy</th>
<th>Normal Impact Energies per Cs Atom</th>
<th>Normal Impact Energies per C Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsC$_6^-$</td>
<td>3.8</td>
<td>41</td>
<td>2.87</td>
<td>1.86</td>
<td>0.17</td>
</tr>
<tr>
<td>CsC$_6^-$</td>
<td>2.9</td>
<td>48</td>
<td>1.94</td>
<td>1.26</td>
<td>0.11</td>
</tr>
<tr>
<td>CsC$_6^-$</td>
<td>2.55</td>
<td>52</td>
<td>1.57</td>
<td>1.02</td>
<td>0.09</td>
</tr>
<tr>
<td>CsC$_6^-$</td>
<td>2.3</td>
<td>55</td>
<td>1.32</td>
<td>0.86</td>
<td>0.08</td>
</tr>
<tr>
<td>CsC$_6^-$</td>
<td>2.6</td>
<td>42</td>
<td>1.93</td>
<td>1.25</td>
<td>0.11</td>
</tr>
<tr>
<td>CsC$_6^-$</td>
<td>1.75</td>
<td>47</td>
<td>1.19</td>
<td>0.77</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Figure 6-10 shows AFM micrographs of crater bottoms created by CsC$_6^-$ sputtering using the conditions listed in Table 6-3 on the B delta doped sample described earlier (crater depths ranged from 40 to 50 nm). An AFM micrograph of an unsputtered area of the same sample is shown for comparison. Independent of impact energy and angle, periodic ripple structures were formed on the crater bottom with the ripple orientation being perpendicular to the primary ion beam. While ripple structures are observed under all beam conditions used, differences in ripple wavelength (spacing) and magnitude are observed.
Figure 6-10: AFM micrographs of (100) after CsC₆ sputtering over a range of energies and angles: a) unsputtered, RMS = 0.15nm; b) 3.8keV, 41⁰, RMS = 0.16nm; c) 2.9keV, 48⁰, RMS-0.59nm; d) 2.3keV, 55⁰, RMS = 1.21nm; e) 2.6keV, 42⁰ RMS = 0.44nm; f) 1.75keV, 47⁰, RMS = 1.41nm

Researchers who have investigated beam induced topography changes using single atomic primary ions and who have observed periodic ripple structures often found either a linear dependence of ripple wavelength on total beam energy (21)(22) or on the
To determine if either of these dependences exist for CsC₆ sputtering of Si, plots of ripple wavelength versus total primary ion beam impact energy and versus effective impact energy \( (E_{\text{eff}} = E_p \cdot \cos \theta) \), a value proportional to projected range (25)(26), were made of the carbon component of the CsC₆⁻ molecule (see Figure 6-11). Values of ripple wavelength and RMS surface roughness for the different conditions are given in Table 6-4. The carbon component of the CsC₆⁻ molecule was chosen for plotting ripple wavelength versus total and effective beam energy as experiments by Gillen comparing Cs⁺ and CsC₆⁻ sputtering with the same angle of incidence and partial Cs energy component showed ripple structure formation in the crater bottom after CsC₆⁻ sputtering, but not after Cs⁺ sputtering. This is likely due to the lower \( R_p \) values of the carbon atoms compared to the Cs atom in the molecule and it appears that surface topography changes are induced by the element in the cluster that is placed closer to the surface.

A roughly linear decrease in ripple wavelength with decrease in total impact energy is observed, but a somewhat better correlation appears to be achieved when ripple wavelength is plotted versus normal impact energy, a value approximately proportional to projected range. It is interesting to note that both conditions with a 48° angle of incidence produced the same ripple wavelength, even though projected range was considerably different. This might indicate a possible crystallographic influence on ripple wavelength, even though the sample is amorphized after ion bombardment of a relatively low dose. Because of sample amorphization, effects of crystallographic orientation are widely believed to have no or only limited influence on beam induced topography. This was confirmed by experiments which showed that ripple orientation and beam induced crater bottom is independent of crystallographic orientation by bombarding (100), (110) and (111) Si with 6-8keV inert gas primary ion beams (27). However, in recent investigations an influence of crystallographic orientation on transition depth, which is the depth sputtered before ripple structures are formed, was observed (28). Figure 6-12 displays RMS values of the crater bottoms shown in Figure 6-10 as a function of effective impact energy. An exponential increase in RMS roughness is observed with a decrease in effective impact energy. If the RMS roughness
value for the highest effective impact energy which is essentially unchanged from the original surface topography, is excluded, a linear trendline can be established as well.

Table 6-4: Ripple wavelength and RMS roughness values for listed impact energies and angles

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CsC₆⁻</td>
<td>3.8</td>
<td>41</td>
<td>0.22</td>
<td>0.17</td>
<td>56±6</td>
<td>0.16</td>
</tr>
<tr>
<td>CsC₆⁺</td>
<td>2.9</td>
<td>48</td>
<td>0.17</td>
<td>0.11</td>
<td>36±4</td>
<td>0.59</td>
</tr>
<tr>
<td>CsC₆⁺</td>
<td>2.55</td>
<td>52</td>
<td>0.15</td>
<td>0.09</td>
<td>31±3</td>
<td>0.85</td>
</tr>
<tr>
<td>CsC₆⁺</td>
<td>2.3</td>
<td>55</td>
<td>0.13</td>
<td>0.08</td>
<td>27±3</td>
<td>1.21</td>
</tr>
<tr>
<td>CsC₆⁺</td>
<td>2.6</td>
<td>42</td>
<td>0.15</td>
<td>0.11</td>
<td>40±4</td>
<td>0.44</td>
</tr>
<tr>
<td>CsC₆⁺</td>
<td>1.75</td>
<td>47</td>
<td>0.10</td>
<td>0.07</td>
<td>36±4</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Figure 6-11: Ripple wavelength as a function of a) total carbon impact energy and b) effective carbon impact energy. Both impact energies are calculated according to the mass fraction of carbon atoms in the CsC₆⁻ primary cluster ion.
In mono-atomic glancing angle primary ion bombardment an increase in
topography and/or ripples is often not observed for some sputtered depth. Instead an
equilibrium condition exists were roughness stays essentially constant. This equilibrium
condition can last for several microns before it becomes unstable and an increase in
roughness is observed. The depth at which roughness starts to increase is described as
roughening onset \( (29)(30)(31) \). This depth was reported to decreases linearly with a
decrease in effective energy \( (E_p \cdot \cos (\theta)) \). To investigate the depth of the roughening
onset for \( \text{CsC}_6^- \) bombardment onto Si, a series of craters having depths between 2 and a
70nm were sputtered into a \((100)\) Si wafer. Figure 6-13 shows AFM micrographs of the
most shallow of these crater bottoms with depth between 3 and 5nm, after sputtering with
2.55keV, 52°; 2.9keV, 48° and 3.8keV, 41° \( \text{CsC}_6^- \) primary ions. 2D Fast Fourier
transformations of the AFM images are shown Figure 6-13 to reveal if periodic features
(ripples) have formed within the crater bottom. Preferential orientation of crater bottom
topography in the direction orthogonal to the primary ion beam (beam in \( x \)-direction) is
visible in the AFM images of the crater formed by 2.55keV, 52° and 2.9keV, 48° \( \text{CsC}_6^- \)
sputtering and confirmed by the Fourier transformations. For the 3.8keV impact energy
(lowest angle with respect to normal), a preferential orientation is not easily recognizable
in the AFM image, but the extension of the Fourier transformation of the AFM data in the
\( x \)-direction shows that even for this energy and angle periodic ripple structures

Figure 6-12: RMS roughness of crater bottoms shown in Figure 6-10 as a function of
effective carbon impact energies
orthogonal to the primary ion beam start to form very close to the surface. The changes in sputter and ion yield resulting from a roughening onset that is either directly on the original surface or very close to it clearly can affect both the depth and concentration calibration for a depth profile.
Figure 6-13: AFM images and associated Fourier transformations of crater bottoms with depth between 3 and 5nm created with a) 3.8keV 41°, b) 2.9keV 48° and c) 2.55keV 52° CsC₆⁻ primary ion bombardment
6.3.3 SIMS Depth Profiling of Low Energy P in Si Implants using CsC$_6^-$ Primary Ions and Comparison with O$_2^+$ and Cs$^+$ Primary Ion Beams

Low energy O$_2^+$ primary ion beam bombardment of ultra shallow P implants provides a significantly improved depth resolution compared to Cs$^+$ depth profiling, but also results in loss of sensitivity due to a lower ion yield of P containing secondary ions compared to Cs$^+$ primary ion bombardment as shown in chapters 4 and 5. In an attempt to combine the benefits of higher sensitivity for P obtained with Cs$^+$ primary ions with the better depth resolution obtained under glancing angle O$_2^+$ bombardment, CsC$_6^-$ primary ion beams and negative secondary ion extraction were used to analyze a 500eV, 1E15 atoms/cm$^2$ and a 1keV, 1.1E14 atoms/cm$^2$ P implants into Si as described in section 6.2. CsC$_6^-$ impact energy was 2.9keV with an angle of incidence of 48$^\circ$, as these conditions in combination with sample rotation minimize primary ion beam induced crater bottom roughness and allow consistent source operation.

O$_2$ flooding was used in an effort to maximize secondary ion yield when using CsC$_6^-$ primary ion bombardment. An increase of P$^-$ secondary ion yield of approximately one half order of magnitude was obtained at a sample chamber pressure of about 1E-6 torr. Higher O$_2$ pressures resulted in a decrease in P$^-$ and Si$^-$ ion yield. Careful adjustment of the O$_2$ pressure was necessary to obtain a stable P$^-$/Si$^-$ ratio. Figures 6-14 a and b show a comparison of the 1keV and the 500eV P implants analyzed with 500eV, 47$^\circ$ and 1keV, 50$^\circ$ O$_2^+$ using positive secondary ion extraction and with 2.5keV, 24$^\circ$ Cs$^+$ and 2.9keV, 48$^\circ$ CsC$_6^-$ primary ion beams using negative secondary ion extraction.

In Figure 6-14a it can be seen that CsC$_6^-$ primary ion bombardment gives a significant improvement in decay length compared to 2.5keV, 24$^\circ$ Cs$^+$ ion bombardment for the 1keV P implant while providing a detection limit of about 1E17 atoms/cm$^3$. The 500eV, 47$^\circ$ O$_2^+$ primary ion bombardment gives a small improvement in decay length and profile shape compared to the CsC$_6^-$ bombardment, but there is a loss of sensitivity of about one order of magnitude. 1keV, 50$^\circ$ O$_2^+$ primary ion bombardment gives a decay length identical within the experimental accuracy to the one obtained with 2.9keV CsC$_6^-$ ion bombardment and a slightly worse detection limit. The identical decay length under 2.9keV, 48$^\circ$ and CsC$_6^-$ 1keV, 50$^\circ$ O$_2^+$ ion bombardment is rather remarkable considering the almost identical angle of incidence, the about three times higher total impact energy.
and the larger projected range of the Cs component in 2.9keV, 48° CsC₆⁻ (Rₚ = 3.5 nm) compared to the O component in 1keV, 50° O₂⁻ (Rₚ = 2.1 nm). This result shows an even larger potential for the use of cluster ion bombardment for ultra shallow depth profiling than what could have been expected based on mass fractional energy of Cs in the CsC₆⁻ cluster. An explanation for this unexpected result might be related to the large amount of carbon deposited at the surface by the low energy carbon component of the CsC₆⁻ cluster.

1keV, 50° and 500eV, 47° O₂⁺ primary ion bombardment gave worse detection limits compared to 2.9keV CsC₆⁻ ion bombardment with the experimental conditions used, but detection limits are influenced by sputter rate, instrument transmission and detector counting efficiency (see equation 1). Also sputter rate is depending on sputter yield, primary ion current and bombarded area (see equation 2).

\[ I^\pm \propto v_s TD \]  
(1)

\[ v_s \propto Y I_p A \]  
(2)

with \( I^\pm \) being detected secondary ions, \( v_s \) = sputter rate, \( Y \) = sputter yield, \( A \) = bombarded area, \( I_p \) = primary ion current, \( T \) = instrument transmission, \( D \) = detector conversion efficiency

In contrast, useful yields are not influenced by sputter rates and the normalized useful yields (see chapter 5) shown in Table 6-5 are also roughly independent of instrument transmission. Secondary ion post acceleration used for the measurement reduces variation in detector conversion efficiency. From these normalized yield values it can be seen that the conditions used to produce 2.9keV, 48° CsC₆⁻ give an improvement in normalized useful yield of about 20% compared to 1keV, 50° O₂⁺ ion bombardment and about a factor of 2 higher normalized useful yield compared to 500eV, 47° O₂⁺ ion bombardment. Normalized useful yields show that the improvement in useful yield using CsC₆⁻ is largely due to an improved instrument transmission, which was partly offset by a lower sputtering rate. Sputter yield is significantly higher using CsC₆⁻ compared to the measurements done using O₂⁺ and Cs⁺ primary ion bombardment, indicating that higher sputter rates and lower detection limits might be obtainable using CsC₆⁻ primary ions if source design can be improved to provide higher beam densities. High sputter rates with
high depth resolution are difficult to obtain in SIMS, since sputter yields and beam
densities are generally reduced for lower impact energies. The higher sputter yields using
\( \text{CsC}_6^- \) instead of \( \text{O}_2^+ \) or \( \text{Cs}^+ \) primary ions may provide an advantage for measurements
where high depth resolution is required over an extended depth.

For the 500eV P implant, the 500eV, 47° \( \text{O}_2^+ \) primary ion bombardment produces
significantly improved profile shape and decay length as compared to the profiles
obtained using 1keV\( \text{O}_2^+ \), \( \text{CsC}_6^- \) and \( \text{Cs}^+ \), but detection limit is significantly reduced.
Again, the 1keV, 50° \( \text{O}_2^+ \) primary ion beam provides a result similar to 2.9keV \( \text{CsC}_6^- \) ion
bombardment. Comparison of the results presented in Figure 6-14 shows that negative
cluster ion bombardment can provide improvement for SIMS analysis of ultra shallow n-
dopants, but beam stability, source operation and the source lifetime between cleaning
have to be significantly improved for the sputter negative ion sources to be useful for
routine, practical SIMS analysis.

<table>
<thead>
<tr>
<th></th>
<th>500eV ( \text{O}_2^+ ), 47° ox. flood</th>
<th>1keV ( \text{O}_2^+ ), 50°, ox. flood</th>
<th>2.9keV ( \text{CsC}_6^- ), 48°, ox.flood</th>
<th>2.5keV ( \text{Cs}^+ ), 24°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transient zone width (90%-30% Si- signal)</td>
<td>0.3nm</td>
<td>0.6nm</td>
<td>2.4nm</td>
<td>1.8nm</td>
</tr>
<tr>
<td>Decay Length (1/e) 1keV P implant</td>
<td>2.0nm</td>
<td>2.3nm</td>
<td>2.2nm</td>
<td>2.8nm</td>
</tr>
<tr>
<td>Decay Length (1/e) 500eV P implant</td>
<td>1.6nm</td>
<td>2.0nm</td>
<td>2.1nm</td>
<td>2.8nm</td>
</tr>
<tr>
<td>Detection Limit [atoms/cm(^3)]</td>
<td>2E18</td>
<td>2E17</td>
<td>1E17</td>
<td>8E16</td>
</tr>
<tr>
<td>Useful Yield</td>
<td>9.0E-6</td>
<td>4.4E-5</td>
<td>9.8E-5</td>
<td>7.8E-5</td>
</tr>
<tr>
<td>Useful Yield (normalized for Sample HV)</td>
<td>1.3E-5</td>
<td>2.1E-5</td>
<td>2.5E-5</td>
<td>7.8E-5</td>
</tr>
<tr>
<td>Sputter Yield</td>
<td>0.4</td>
<td>0.5</td>
<td>4.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Sputter Rate [A/sec]</td>
<td>0.23</td>
<td>0.42</td>
<td>0.28</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Table 6-5: Transient zone width, decay length (1/e), detection limits, useful and
sputter yields for 1keV, 50° and 500eV, 47° \( \text{O}_2^+ \) under the use of \( \text{O}_2 \) flooding, 2.5keV
\( \text{Cs}^+ \), 24° and 2.9keV, 48° \( \text{CsC}_6^- \) ion bombardment
6.3.4 Comparison of SIMS Depth Profiling of Low Energy As Implants in Si using CsC\textsubscript{6}\textsuperscript{-} Primary Ions versus O\textsubscript{2}\textsuperscript{+} and Cs\textsuperscript{+} Primary Ion Beams

SIMS depth profiling of B has been under intense development in the SIMS community in recent years (32)(33)(34), but very little work has been reported concerning the investigation of ultra shallow As profiles using SIMS. For determining As profiles in Si by SIMS, AsSi\textsuperscript{-} is usually detected because of its high ion yield. Si\textsuperscript{2-} is often used as a reference matrix ion, since it has a similar energy distribution to that of AsSi\textsuperscript{-} resulting in improved reproducibility for quantification of As concentration. This improved reproducibility results from the fact that small changes in sample alignment can lead to differences in extraction field. These differences in extraction field have differing

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Figure 6-14: a) P depth profiles of a 1keV, 1.1E14 atoms/cm\textsuperscript{3} into (100) Si obtained with 500eV, 47\textdegree{} and 1keV, 50\textdegree{} O\textsubscript{2}\textsuperscript{+} (+ox. flood), 2.5keV, 24\textdegree{} Cs\textsuperscript{+} and 2.9keV, 48d CsC\textsubscript{6}\textsuperscript{-} (+ox. flood and sample rotation)

b) P depth profiles of a 500eV, 1E15 atoms/cm\textsuperscript{3} into (100) Si obtained with 500eV, 47\textdegree{} and 1keV, 50\textdegree{} O\textsubscript{2}\textsuperscript{+} (+ox. flood), 2.5keV, 24\textdegree{} Cs\textsuperscript{+} and 2.9keV, 48d CsC\textsubscript{6}\textsuperscript{-} (+ox. flood and sample rotation)
effects on ions having different energy distributions, which can lead to differences in detected useful yields of the respective ions. However, recent investigations by Tomita et al. (35) have shown, that Si$^{2-}$ ion yields are suppressed in the native SiO$_2$ layer on Si. For ultra shallow As implants, like the 500eV As into (100) Si ion implant investigated in this study, the peak of the implant is inside the native SiO$_2$. This, together with the suppressed Si$^{2-}$ ion yield in the native SiO$_2$ layer on Si, can lead to an overestimation of calculated As dose of up to 40%. Using Si instead of Si$^{2-}$ has shown to give an improved calculated dose for ultra shallow As implants (35) and Si was used as a reference ion in this investigation.

Figure 6-15 shows SIMS depth profiles of the 500eV, 1E15 atoms/cm$^3$ As implant into Si (100) implant, analyzed using 2.5keV, 23° Cs and 2.9keV CsC$_6^-$, 48° primary ion beams with negative ion extraction and using 1.0keV, 60° O$_2^+$ primary ions with O$_2$ flooding and with positive ion extraction. A significant improvement in depth resolution, indicated by a smaller decay length, is seen comparing the depth profiles obtained using 1keV O$_2^+$ compared to 2.5keV Cs$^+$, but the best results were obtained using 2.9keV CsC$_6^-$ primary ion bombardment. The improvement in depth resolution using 2.9keV, 48° CsC$_6$ instead of 1keV, 56° O$_2^+$ is in contrast to the similar decay length found for high-resolution depth profiling of ultra shallow P using comparable primary ion beam conditions. The increase in decay length for O$_2^+$ ion bombardment indicates that As segregates at the SiO$_x$/Si interface during high depth resolution analysis of ultra shallow As implants with O$_2^+$ primary ion beams. The SiO$_x$/Si interface forms continuously during depth profiling with O$_2^+$ primary ions, and is continuously pushed deeper into the sample, which also pushes the As deeper into the sample (36)(37)(38)(39). Direct evidence for this phenomenon has been obtained from Rutherford backscattering (RBS) analysis of an O$_2^+$ bombarded Si substrate implanted with As, were a large pileup of As was observed at the interface (32). Similar segregation of other elements like Sb and Ge in Si during O$_2^+$ sputtering or O$_2$ flooding has been reported (40).
Figure 6-15: As depth profiles of a 500eV, $1 \times 10^{15}$ atoms/cm$^3$ into (100) Si obtained with 1keV, 50° O$_2^+$ (+ox. flood), 2.5keV, 24° Cs$^+$ and 2.9keV, 48d CsC$_6^-$ (+ sample rotation)

6.4 Summary

The results reported here demonstrate the advantages that can be obtained by using a combination of glancing angle and cluster ion bombardment for high depth resolution profiling of shallow n-dopant implants. It has been shown that an improvement in P and limit with no apparent loss in depth resolution can be achieved by using a 2.9keV, 50° CsC$_6^-$ ion beam and negative secondary ion extraction compared to a 1keV, 50° O$_2^+$ primary ion beam. When P depth profiling results obtained using CsC$_6^-$ are compared with the result obtained using Cs$^+$ primary ion bombardment, a significant improvement in depth resolution using CsC$_6^-$ was obtained, with only a limited loss in sensitivity. For the analysis of ultra shallow As CsC$_6^-$ ion bombardment provided the highest depth resolution of all primary beam conditions used with only a minimal loss in sensitivity compared to Cs$^+$ primary ion bombardment. The loss in sensitivity during CsC$_6^-$
compared to Cs$^+$ ion bombardment could be avoided if CsC$_6^-$ primary ion beam densities are improved to allow smaller raster sizes and faster sputter rates. It also has been shown that CsC$_6^-$ sputter yields are significantly higher compared to O$_2^+$ and Cs$^+$ primary ion bombardment under the conditions used, indicating the possibility of the use CsC$_6^-$ for extended high depth resolution depth profile measurements. For practical applications of the PSX-120 sputter negative ion source for generation of CsC$_6^-$ primary ion production, significant improvements in source stability, ease of source operation and target lifetime are required. These improvements must be made if CsC$_6^-$ or other primary ions produced using sputter negative ion sources are to be seriously considered as an alternative for routine high depth resolution sputter depth profiling.

6.5 References


7 Comparison of Secondary Ion Mass Spectrometry Depth Profiling of Low Energy P and As Implants in Si on Magnetic Sector and Quadrupole Instruments

7.1 Introduction

Analysis of ultra shallow P or As profiles in Si requires a relatively high mass resolution of $M/\Delta M = 4000$ to resolve $^{31}\text{P}$ from its $^{30}\text{SiH}$ or $^{75}\text{As}$ from its $^{29}\text{Si}^{30}\text{Si}^{16}\text{O}$ interference to be able to reliably achieve the precision and accuracy required for the analysis of materials for current and future MOSFET generations. This mass resolution can be easily achieved with current magnetic sector SIMS instruments like the CAMECA IMS 6F used in this study. SIMS instruments equipped with quadrupole mass spectrometers are generally not able to resolve the mass interferences important for P and As depth profiling. In the case of quadrupole based instruments, measurements in UHV and extended sample pumping times in the instrument chamber (usually over night) can be used to reduce mass interferences related to elements present in the instruments analysis chamber vacuum. High doping concentration used in ultra-shallow implant doping also reduces the relative influence of mass interference on the total detected signal.

N-dopants like As and P exhibit higher negative ion yields under Cs$^+$ ion bombardment compared to their positive ion yields under O$_2^+$ bombardment, but negative ion detection in magnetic sector SIMS requires a negative sample potential in the IMS-6f. As discussed in chapter 5, this negative sample potential attracts and thus accelerates the usually used Cs$^+$ primary ions, increasing its impact energy and thus limiting the capabilities for low impact energy Cs$^+$ analysis of n-dopants using the IMS-6f. In Quadrupole instruments, the sample is not biased in which case the Cs impact energy is that of the primary beam energy alone. The lowest Cs$^+$ impact energies are currently available on quadrupole instruments since column development is currently more advanced in some quadrupole instruments allowing lower impact energies for Cs$^+$ and O$_2^+$ down to 150eV (1). An ATOMIKA 4500 quadrupole and a CAMECA IMS 6F
magnetic sector SIMS are compared in this study with respect to their capabilities for ultrashallow depth profiling of P and As using Cs\(^+\), O\(_2\)\(^+\) and CsC\(_6\)\(^-\) primary ions.

### 7.2 Details of Experimental Method

Table 7-1 lists the type of primary ion, primary ion impact energy and impact angle used with the two SIMS instruments, an ATOMIKA 4500 quadrupole SIMS and a CAMECA IMS 6F magnetic sector SIMS.

Quadrupole SIMS analyses were performed by J. Hunter using an ATOMIKA 4500 (2) instrument, equipped with FLIG (Floating Ion Gun) ion guns that can produce low energy O\(_2\)\(^+\) and Cs\(^+\) primary ion beams with energies down to 150eV. In this work, O\(_2\)\(^+\) bombardment analyses were performed using a 500eV ion beam at normal incidence. Positive secondary ions were extracted during O\(_2\)\(^+\) depth profiling. A 500eV, 60\(^\circ\) Cs\(^+\) primary ion beam and negative secondary ion extraction was used for analyses employing Cs\(^+\) primary ions.

Magnetic sector SIMS analyses were performed using a CAMECA IMS 6F. O\(_2\)\(^+\) ion bombardment analyses using the IMS 6-F were performed using a 500eV, 48\(^\circ\) O\(_2\)\(^+\) and a 1keV, 56\(^\circ\) O\(_2\)\(^+\) primary ion bombardment and extraction of positive secondary ions. During the analyses, the sample was flooded with O\(_2\) until the \(^{30}\)Si secondary ion signal stabilized to minimize transient zone width and maximize sensitivity (see chapter 4). Sample rotation with a speed of 20 rpm was used during 1keV, 56\(^\circ\) O\(_2\)\(^+\) primary ion beam bombardment to minimize beam induced crater bottom roughness.

Cs\(^+\) bombardment analyses on the CAMECA IMS 6-F were done with a 2.5keV, 23\(^\circ\) Cs\(^+\) primary ion beam. A 2.9 keV, 48\(^\circ\) CsC\(_6\)\(^-\) primary ion beam, produced using a Peabody PSX-120 sputter negative ion source, in conjunction with a sample rotation speed of 20rpm was used for the analyses employing CsC\(_6\)\(^-\) primary ions. Negative secondary ions were extracted form the sample under both Cs\(^+\) and CsC\(_6\)\(^-\) primary ion bombardment. O\(_2\) flooding was used with CsC\(_6\)\(^-\) for ultra shallow P analysis, but not during analysis of As implants, since the continuous formation of a SiO\(_2\) surface layer is known to cause As segregation.
Secondary ions were extracted on the IMS 6-F through a circular optical gated area 60µm in diameter centered on an area being at least three times the primary ion beam diameter, while a variable electronic gating was used on the ATOMIKA 4500. Samples were analyzed with a mass resolution of M/ΔM of 4000 with the IMS 6F to resolve $^{30}\text{SiH}$ from $^{31}\text{P}$ and $^{29}\text{Si}^{28}\text{Si}^{16}\text{O}$ from $^{75}\text{As}$. These mass interferences cannot be resolved during analyses using the ATOMIKA 4500 quadrupole based instrument, but samples were pumped overnight to reduce the magnitude of the interfering signals. As and P depth profiles were quantified using bulk doped P (see chapter 5) and bulk doped As (1.5E19 atoms/cm$^3$) wafer respectively. Quantification of the bulk doped samples was done using RSF’s obtained from 50keV As and 50keV P ion implants, which are not significantly influenced by surface transient effects. Sputter rates were determined by measuring crater depths with Tencor stylus profilometers.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Primary Ion</th>
<th>Impact Energy [keV]</th>
<th>Impact Angle [degree]</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMS-6F</td>
<td>$\text{O}_2^+$</td>
<td>1keV</td>
<td>56</td>
</tr>
<tr>
<td>IMS-6F</td>
<td>$\text{O}_2^+$</td>
<td>500eV</td>
<td>47</td>
</tr>
<tr>
<td>IMS-6F</td>
<td>Cs$^+$</td>
<td>3keV</td>
<td>23</td>
</tr>
<tr>
<td>IMS-6F</td>
<td>Cs$^+$</td>
<td>2.5keV</td>
<td>24</td>
</tr>
<tr>
<td>IMS-6F</td>
<td>CsC$_6^-$</td>
<td>2.9keV</td>
<td>48</td>
</tr>
<tr>
<td>ATOMIKA 4500</td>
<td>$\text{O}_2^+$</td>
<td>500eV</td>
<td>0</td>
</tr>
<tr>
<td>ATOMIKA 4500</td>
<td>$\text{O}_2^+$</td>
<td>250eV</td>
<td>0</td>
</tr>
<tr>
<td>ATOMIKA 4500</td>
<td>Cs$^+$</td>
<td>500eV</td>
<td>60</td>
</tr>
</tbody>
</table>

Table 7-1: Experimental conditions used for P and As analysis in this chapter
7.3 Results and Discussion

7.3.1 Analysis of Ultra Shallow P in Si Implants

Figure 7-1 shows P depth profiles obtained from a 500eV, 1E15 atoms/cm$^2$ P ion implant into (100) Si, analyzed using the conditions described above using Cs$^+$ and O$_2^+$ primary ion beams with the quadrupole based ATOMIKA 4500 and the magnetic sector based CAMECA IMS-6F type instruments.

The best depth resolution as indicated by a decay length (1/e) of 1.0nm was achieved using a 250eV O$_2^+$ primary ion beam at normal incidence on the ATOMIKA 4500, but profile shape in the initial part of the profile appears to be less distorted when the P implant was analyzed with 500eV, 48$^\circ$ O$_2^+$, O$_2$ flooding and high mass resolution on the IMS-6F. A decay length of 1.6nm was obtained using the 500eV O$_2^+$ ion beam at 48$^\circ$ obtained on the IMS-6F.

The profile obtained with 500eV Cs$^+$ at 60$^\circ$ on the ATOMIKA 4500 has a larger decay length of 1.8nm and a profile shape that appears somewhat distorted compared to the profile obtained using the 500eV O$_2^+$ ion beam at 48$^\circ$ obtained on the IMS-6F. It also seems to be shifted towards the surface, which could be the result of crater bottom roughening under the glancing angle Cs$^+$ ion beam associated changes in sputter rate.

Cs$^+$ impact energies lower than 500eV are obtainable on the ATOMIKA, but are generally not used, due to unstable secondary ion signals under these conditions. The unstable secondary ion signals are believed to be the result of an increased Cs surface concentration on the bombarded sample, resulting from the reduced projected range of low energy Cs$^+$ primary ions and low sputter yields. For high Cs surface concentrations the surface work function of the sample, which exponentially influences secondary ion yields (see chapter 2), increases after it decreased for low Cs surface concentrations in the initial stages of the depth profile, which overall gives unstable signals over the depth investigated in ultra shallow depth profiling.

For both instruments the best depth resolution, as indicated by smallest decay length, for analysis of P ion implants is achieved using O$_2^+$ (see Figure 7-1b) compared to
Cs⁺ or CsC₆⁻ primary ions. If detection limit and not depth resolution is the primary concern in an analysis, Cs⁺ primary ions give the best results, while CsC₆⁻ or medium energy O₂⁺ ion bombardment can provide a good compromise between depth resolution and sensitivity.

Figure 7-1: SIMS depth profiling of a 500eV, 1E15 atoms/cm² P implant into (100) Si. a) Comparison of profiles obtained using 3keV, 24° Cs⁺, 500eV, 47° O₂⁺ and 2.9keV CsC₆⁻ on a CAMECA IMS 6F, with profiles obtained using 500eV, 60° Cs⁺ and 250eV, 0° O₂⁺ on an ATOMIKA 4500 b) Profiles obtained using 500eV, 47° O₂⁺ on a CAMECA IMS 6F and 250eV, 0° O₂⁺ on an ATOMIKA 4500

For easier comparison with respect to depth resolution of Cs⁺, O₂⁺ or CsC₆⁻ beams having differing impact energies and/or angles, the concept of an effective energy (E_{eff}) was introduced by Hunter et al. (3) with

\[ E_{eff} = E_t \cdot \cos(\theta) \]  \hspace{1cm} (1)

and

\[ E_t = E_{primary} - E_{sample} \]  \hspace{1cm} (2)

where \( E_t \) = total impact energy, \( E_{primary} \) is the primary ion beam energy and \( E_{sample} \) is the sample potential.
$E_{\text{eff}}$ is not equal to the normal component of the total impact energy $E_{\text{in}}$, which was shown by Meuris et al. to be $E_{\text{in}} \cos^2 \theta$, but $E_{\text{eff}}$ is frequently used in the literature (4)(5)(6)(7) and is believed to be a good parameter for assessing depth resolution in SIMS sputter depth profiling. If equation 1 holds true, the same depth resolution can be achieved using a 60 degree beam with double the impact energy of an ion beam impacting at normal incidence angle. This would be advantageous since use of higher primary beam energies gives advantages with regard to beam focusing, maximum primary ion current and sputter yield.

Figure 7-2 shows a comparison of profiles obtained from a 500eV, 1E15 atoms/cm$^2$ P implant into (100) Si using 500eV, 47$^o$ O$_2^+$ on a CAMECA IMS 6F and profiles obtained using 500eV, 47$^o$ O$_2^+$ and 500eV, 60$^o$ O$_2^+$ on an ATOMIKA 4500. These primary ions all have the same total impact energy, but different effective energies. The concept of using an effective energy as a value to compare primary ions with different energies and angle with respect to depth resolution seems to be confirmed by comparing data presented in Figure 7-2. 500eV, 0$^o$ O$_2^+$ and 500eV, 60$^o$ Cs$^+$ primary ion beams have the same effective energy of 250eV/atom and give essentially the same decay length. However, 500eV, 47$^o$ O$_2^+$ ($E_{\text{eff}} = 170$eV/atom) primary ion bombardment which should produce a smaller decay length, gives a similar decay length with a significantly smaller $E_{\text{eff}}$. In addition Wittmaack did not observe a decay length variation for Si and B in Si for 5-10keV O$_2^+$ as the angle of incidence was varied between 0 and 70$^o$ (8), indicating that the effective energy should be used with extreme care when comparing depth resolution. A potential explanation for the similar decay lengths produced by glancing and normal O$_2^+$ bombardment with the same beam energy may be the swelling of the sample due to bombardment induced oxidation of Si. Primary ion energy is transferred partly to O atoms that were previously implanted into the sample by the primary ion beam energy that would otherwise be consumed for the relocation of Si in the sample. After sputtering of previous implanted O atoms the history of all energy transfers that have happened among these O atoms in the sample will be lost.
Figure 7-2: SIMS depth profiling of a 500eV, 1E15 atoms/cm² P implant into (100) Si. Comparison of profiles obtained using 500eV, 47° O₂⁺ on a CAMECA IMS 6F, with profiles obtained using 500eV, 47° O₂⁺ and 500eV, 60° O₂⁺ on an ATOMIKA 4500.

7.3.2 Analysis of Ultra Shallow As in Si Implants

Figure 7-3 shows As depth profiles obtained from a 500eV, 1E15 atoms/cm² As ion implanted into preamorphized (100) Si, analyzed using the conditions described with the quadrupole based ATOMIKA and the magnetic sector based CAMECA type instruments. In contrast to the analysis of P, the best depth resolution for the analysis of As is obtained with 500eV Cs⁺ on the ATOMIKA 4500 and with 2.9keV CsC₆⁻ on the CAMECA IMS-6F, with decay length of 0.9 and 1.8nm for the 500eV As implant respectively. The increase in decay length for O₂⁺ bombardment with both instruments and with different impact energies and angles indicates that As segregates at the SiOₓ/Si interface for high depth resolution analysis of ultra shallow As implants. The SiOₓ/Si interface forms continuously during depth profiling with O₂⁺ primary ions, and is...
continuously pushed deeper into the sample, which also pushes the As deeper into the sample \((9)(10)(11)(12)\). Direct evidence for this phenomenon has been obtained from Rutherford backscattering (RBS) analysis of an \(O_2^+\) bombarded Si substrate implanted with As, were a large pileup of As was observed at the interface \((12)\). Figure 7-3 also shows that while \(2.9\text{keV, }48^\circ\text{CsC}_6^-\) provided a significant improvement in depth resolution compared to \(2.5\text{keV, }23^\circ\text{Cs}^+\) for depth profiling of ultra shallow depth profiles using the IMS 6F, lower impact energies such as the \(500\text{eV Cs}^+\) ion beam used on the ATOMIKA are necessary to achieve the “true” shape of the \(500\text{eV As implant,}.,\)

![Graph](image.png)

Figure 7-3: SIMS depth profiling of a \(500\text{eV, }1E15\text{ atoms/cm}^2\) As implant into preamorphized (100) Si. Comparison of profiles obtained using \(3\text{keV, }24^\circ\text{Cs}^+,\ 1\text{keV, }50^\circ\text{O}_2^+\) and \(2.9\text{keV CsC}_6^-\) on a CAMECA IMS 6F, with profiles obtained using \(500\text{eV, }60^\circ\text{Cs}^+\) and \(500, 0^\circ\text{O}_2^+\) on an ATOMIKA 4500
7.4 Summary

Results presented in this chapter demonstrate the ability of SIMS sputter depth profiling to accurately analyze ultra shallow n-dopants with high depth resolution. A comparison between two state of the art instruments, the magnetic sector based CAMECA IMS 6F and the quadrupole based ATOMIKA 4500 for analysis of 500eV P and As implants into preamorphized Si was presented. For depth profiling of ultra shallow P and As in Si the lower impact energies which can be obtained on the ATOMIKA were found to provide a significant improvement in depth resolution, but samples had to be pumped in the analysis chamber for extended times to avoid mass interferences to the P and As secondary ion signals. After pumping, these mass interferences did not significantly limit the ability of the ATOMIKA 4500 to analyze P and As. As segregated to the SiO$_2$/Si interface during O$_2^+$ sputter depth profiling limited the obtainable depth resolution using O$_2^+$ ion bombardment. Low energy Cs$^+$ bombardment gave significantly better results compared to O$_2^+$ for high depth resolution analysis of As on the ATOMIKA. CsC$_6^-$ provided the best depth resolution for As analysis on the CAMECA system, a significant improvement as compared to the use of Cs$^+$ ion bombardment of similar impact energy. This shows that cluster ion bombardment can be used to increase depth resolution in SIMS sputter depth profiling. Best results for the analysis of ultra shallow P implants with regard to profile shape and depth resolution were obtained on both instruments using low energy O$_2^+$ primary ion beams, likely due to the lower impact energies per atom in O$_2^+$ compared to Cs$^+$.

7.5 References

8. K. Wittmaack, in SIMS XII proceedings, eds. A. Benninghoven, P.Bertrand,
10. F.Schulte and M.Maier in Secondary Ion Mass Spectrometry, SIMS V. edited by
    B 39, 1567 (1984)
8 Methods to Improve Analysis Accuracy of Secondary Ion Mass Spectrometry in the Transient Zone

8.1 Introduction

In SIMS, quantification of impurities in samples is most often based on the RSF approach. One assumption in the RSF approach is that, assuming a constant primary beam current, a change in measured secondary ion intensity corresponds directly to a change in concentration. For depth calibration, the assumptions is made that a linear sputter can be applied to the whole profile, with the linear sputter rate obtained from final crater depth measurements. Neither of these assumptions is valid during the initial part of the SIMS depth profile, the transient zone, where ion and sputter yields are changing, due to effects described in detail below. In this chapter, ion and sputter yields in the transient zone are investigated and a model is presented and applied with the aim of improving the quantification of ultrashallow SIMS depth profiles.

Reactive primary ion species like Cs$^+$ and O$_2^+$ are used to in SIMS sputter depth profiling to increase secondary ion yields and thus to enhance detection sensitivity. Secondary ion yields can change over several orders of magnitude as a function of the surface concentration of primary ions incorporated into the sample. As a result, a change in measured secondary ion intensity of an impurity is only directly proportional to a change in the concentration of the impurity when a constant concentration of the reactive primary ion is present in the sample, which is an essential assumption for the RSF approach used in quantifying SIMS depth profiles (1)(2). During the initial part of the profile, primary ion concentration builds up in the sample and ion yields can vary greatly. Another factor influencing ion yields in the transient zone or the top few nanometer of a SIMS depth profile are surface layers such as SiO$_2$ on Si. Different matrixes such as Si and SiO$_2$ can have vastly different secondary ion yields, which is commonly described as matrix effect (1)(2). Surface contamination can also influences ion yields, but this problem can largely be avoided with appropriate sample handling. The complex nature of ion yield changes in the transient zone and oxide led some scientists to the conclusion
that reliable quantification in this transient zone is impossible (3)(4). Although the
factors influencing ion yields in the transient zone are complex, it will be shown below
that study of the ion yield changes in a SIMS depth profile can lead to an improved
understanding of the processes occurring in the transient zone and that methods can be
developed to increase analysis accuracy. For ultra shallow implant depth profiling an
improved quantification in the transient zone is especially important, since a larger
portion of the total implanted impurity dose will come to rest within the transient zone as
would be the case for higher implantation energies. In this chapter, a correction
procedure based on bulk-doped standards to quantify secondary ion yields is discussed
and applied to ultra shallow depth profiles with the goal of improving quantitative ultra
shallow SIMS depth profiling.

While an ion yield transient correction procedure that produces a more accurate
measurement of concentration is desirable, it is equally important to minimize the depth
over which the correction procedure must be applied. This is most effectively done by
reducing primary ion impact energies, which minimizes the depth necessary to achieve a
constant primary ion concentration at the sample surface, i.e. minimizes the transient
region depth. Under O₂⁺ bombardment of Si, O₂ flooding can be employed to reduce the
effect of the O rich native SiO₂ on secondary ion yields to further reduce the transient
zone width. O₂ flooding under the proper conditions results in a continuously fully
oxidized surface throughout the analysis, largely eliminating matrix and ion yield
changes between the SiO₂ surface and the Si bulk. Total surface oxidation can also be
obtained with low energy normal incidence bombardment or low energy glancing angle
O₂⁺ ion bombardment.

Although low pressure O₂ flooding during depth profiling using Cs⁺ primary ions
and negative secondary ion extraction can give a small improvement in ion yields,
flooding during Cs⁺ primary ion bombardment has been shown to be to unstable for
practical use. Hence for similar impact energies Cs⁺ bombardment usually produces a
wider transient zone width compared to O₂⁺ ion bombardment used with O₂ flooding.
With Cs⁺ bombardment still being widely used to produce high negative ion yields or
because the use of O₂⁺ bombardment causes impurity segregation, it is important to
reduce quantitative inaccuracy resulting from ion yield transients for Cs⁺ ion
bombardment in order to improve the dose accuracy determination of ultra shallow dopant implants.

In addition to changes in secondary ion yields in the initial stages of a depth profiles, sputter rate is affected by the increasing concentration of the primary ion species, the presence of the surface layers and structural changes in the sample. High accuracy quantitative depth profiling of ultra shallow junctions requires calibration of sputtered depths over the first few nanometers, i.e. throughout the transient zone. To calibrate sputtered depth in the transient zone, the rapidly changing sputter rates within the transient zone have to be measured as a function of depth (primary ion dose). Sputter rate changes can be calculated by measuring crater depth at different stages of a depth profile and dividing the difference in depth between two points by the time (dose) that was necessary to sputter from one depth to another. If sputter rate changes are to be measured within the transient zone, which has a total depth of only a few nanometers, crater depth has to be measured with sub-nanometer accuracy. While AFM can provide the depth resolution to measure these very shallow craters, the lateral dimensions of most SIMS craters are beyond the practical x,y scan limits of most current available AFM technology. Even if the SIMS craters are of a size suitable for AFM, the data acquisition times required to acquire AFM topography images of craters are prohibitive. Optical profilometry (OP), which measures sample topography by measuring the phase shift of light reflected from differing sample heights using optical interferometry, is capable of making non-contact height measurement of an entire sputter crater and its immediate surroundings with approximately 0.2nm height resolution in just a few seconds. Based on the above capabilities, optical profilometry may provide a practical and rapid method of measuring SIMS craters including very shallow craters such as those resulting from the depth profiling of ultra shallow junctions. To investigate of the possible utilization of OP for shallow SIMS crater measurement, Si samples were exposed to Cs+ doses ranging from a dose sufficiently low to result in no measurable alteration of surface topography to a dose sufficient to sputter an approximately 25nm deep crater. Sputter rate variations measured using OP are compared to values obtained using T-DYN, a Monte-Carlo program that simulates ion-solid interactions and sputtering and that continuously updates atom positions in the sample (6)(7)(8)(9). Issues involving correction of the OP
measurements for errors resulting from the alteration of the optical characteristics of the Si surface by the Cs$^+$ ion beam will also be discussed.

### 8.2 Details of Experimental Method

A CAMECA IMS 6F was used to profile a (100) Si wafer bulk doped with 8.2E18 atoms/cm$^2$ P and a 1keV, 1.1E14 atoms/cm$^2$ P implant into (100) Si with 3keV Cs$^+$ and 2.9kev CsC$_6^-$ primary ions at impact angles of 24 and 48 degree respectively. Negative secondary ions were collected from an area 60μm in diameter centered on the bombarded area. For Cs$^+$ ion bombardment, a square raster with a side dimension of 200μm was used. Sample rotation was employed during CsC$_6^-$ depth profiling to minimize beam induced crater bottom roughness. In this case, the sample was rotated at 20 rpm and secondary ions were extracted from an area 60μm (FA2) in diameter centered on a circular area of 350 μm in diameter. A mass resolution of 4000 M/ΔM, a 150μm image field and a 400μm contrast diaphragm (CD1) were used in all cases. The energy slit was centered on the Si secondary ion energy distribution and one half turn open.

The 3keV Cs$^+$ beam was also used to create two series of craters with increasing dose on two Si (100) wafers. For the first dose series a (100) Si wafer was exposed with doses ranging from approximately 3.5E14 atoms/cm$^2$ to approximately 6.9E16 at/cm$^2$. A Cs$^+$ beam current of 25pA as measured by the IMS-6f primary Faraday cup was rastered over a 15μm by 15μm area for varying times to produce this dose series. Raster size was chosen so that the rastered area was amenable to practical AFM measurement. Exposure times of not less than 5 seconds were used to insure that precise dose increments were obtained. After exposure to the Cs$^+$ beam, the topography of the areas of the samples exposed to the Cs$^+$ beam was then measured both optically using a Burleigh Horizon Non Contact Optical Profilometer and with contact mode atomic force microscopy (AFM) using a Burleigh Vista AFM.

The second dose series was done by rastering the Cs$^+$ primary ion beam over a 200 by 200 μm area, a size often used in SIMS depth profiling on a (100). Each 200 by 200μm crater was centered on a 500 by 500 μm area on the Si wafer, which were marked before
the ion bombardment by fiducially marks and measured optically using a Burleigh Horizon Non Contact Optical Profilometer. Each area was measured again optically after exposure to Cs\(^+\) bombardment. Changes in topography (crater depth) were obtained by subtracting the OP images obtained from the same area before and after ion beam exposure to reduce the effect of initial sample topography on crater depth measurements. For this exposure series, the primary ion dose being varied from 1E14 atoms/cm\(^2\) to 1E17 atoms/cm\(^2\) by using beam current of 0.4, 5 and 10nA and variable exposure times.

8.3 Results and Discussion

8.3.1 Quantification inside the Transient Zone

Even if the lowest practical primary ion impact energies for Cs\(^+\) and CsC\(_6\) bombardment on the IMS-6F are used, it is clear from the discussion above that the ion yield transient resulting from both the appreciable fraction of the analyzed depth made up of the surface native oxide and also from the depth required for the primary ion yield enhancing Cs\(^+\) to reach a constant level will have a significant effect on the ability to quantify ultra shallow ion implants, especially in the near surface region. In order to improve the quantitative accuracy, an ion yield transient correction method developed previously (10) and described below was applied to the 3keV Cs\(^+\) and 2.9keV CsC\(_6\) primary ion impact data.

The ion yield transient correction procedure relies on the following assumptions: [1] the bulk doped sample to be used to determine the shape of the ion yield transient has the same oxide thickness as the sample to be quantified; and [2] the P to Si atom ratio remains constant throughout the bulk doped sample including within the native oxide. If these assumptions are valid, an ion yield transient correction function can be generated in the following manner:

1) A bulk doped sample and the sample to be quantified are depth profiled under identical instrumental conditions;
2) The ion yield transients obtained from the bulk doped P sample (See Figures 8-1 and 8-2) for P and Si are then rationed $^{31}\text{P}/^{28}\text{Si}$ in Figures 8-1 and 8-2) and this ratio in normalized to its steady state value (Bulk Corr. Function in Figures 8-1 and 8-2);

3) Before application to the data to be quantified, the correction function is smoothed to reduce variations due to noise and extrapolated if necessary to generate sufficient data points to allow point by point rationing of the data to be quantified;

4) The P depth profile intensity versus depth data obtained from the P implanted sample is then divided by the correction function.

Using both CsC$_6^-$ and Cs$^+$ primary ion beams, an initially higher P$^-$ intensity is measured compared to the steady state values, indicating an increased ion yield of P in the native SiO$_2$. The bulk correction function is consistently above 1 in the initial stages of the depth profiles, indicating an over estimation of P due to the transient zone. It is also interesting that the Si$^-$ signal stabilizes significantly faster than the P$^-$ signal, an effect which is also seen for SiO$^-$ and Si$_2^-$ secondary ions compared to Si.

![Figure 8-1: Si$^-$ and P$^-$ ion yield transients, P$^-$/Si$^-$ ratio and normalized correction factor for a 2.9keV CsC$_6^-$ primary ion beam impacting on a P bulk doped Si wafer](image-url)
Figure 8-2: Si⁻ and P⁺ ion yield transient, P/Si⁺ ratio and normalized correction factor for a 3.0keV Cs⁺ primary ion beam impacting on a P bulk doped Si wafer

Figure 8-3 presents SIMS depth profiles of a 1keV P implant into (100) Si acquired using 3keV Cs⁺ (a) and 2.9keV CsC₆⁻ (b) primary ion impact energy before and after application of the ion yield transient correction function. Both the corrected and uncorrected P depth profiles were then quantified using an RSF determined from the P concentration in the bulk doped P sample. The P level in the bulk doped wafer had been previously quantified versus a 50keV P implant. Use of the bulk doped sample has the advantage of not requiring that a depth profile of a deep implant such as the 50keV P implant be acquired as the standard, since, at the primary ion beam currents necessary to achieve the proper depth resolution for a 1keV P implant, the acquisition time of the 50keV depth profile would be prohibitively long.

The ion yield transient correction procedure adjusts the data points over the first 10nm of the profile in what appears to be the correct direction i.e. reducing the surface P concentration to more realistic appearing levels. Calculation of the P dose of the ion yield transient corrected and the uncorrected depth profiles for the 1.1keV, 1.1E14 atoms/cm² P implant (dose given by the implanter) gave 9.8E13 (corrected) and 1.6e14 (uncorrected) atoms/cm² for the 2.9keV CsC₆⁻ primary ion beam and 1.3E14 (corrected) and 3.0E14 (uncorrected) atoms/cm² for the 3.0keV Cs⁺ primary ion beam. While it is obvious that the corrected dose for both primary ion beams is much closer to the
implanted dose (12% (Cs⁺) and 18% (CsC₆⁻) error for the corrected versus 45% (Cs⁺) and 200% (CsC₆⁻) error), there is insufficient data to truly characterize the efficacy of the correction. After the correction procedure is applied to the profiles, both corrected profiles show more realistic appearing concentration level close to the surface and a significant reduction in slope change after about 2nm. This coupled with the apparently more accurate calculated dose indicates that the ion yield correction does provide significant improvement. Profile shape does not appear to have the shape characteristics of an implant even after correction, which is likely a result of atomic mixing due to the relatively high impact energies and not due changes in ion yield.

Figure 8-3: SIMS depth profiles of a 1keV, 1.1E14 atoms/cm² P implant into (100) Si analyzed a) with 2.9keV CsC₆⁻ and b) 3keV Cs⁺ before and after applying bulk correction
8.3.2 Depth Calibration in the Transient Zone

8.3.2.1 OP Evaluation and Comparison of OP with AFM on Experimental Sized Craters

Depth calibration in the initial stages of a SIMS depth profile, the transient zone, is complicated as a result of sputter yield (removal rate) changes due to incorporation of primary ions and surface layers like SiO$_2$ on Si which lead both to surface composition changes and structural changes near the sample surface. Measurement of these sputter rate changes is complicated by the shallow nature (nanometers) over which they occur combined with the relatively large analysis areas (10000’s of $\mu$m$^2$) commonly used in SIMS depth profiling. Optical profilometry can provide the fields of view (up to 2 x 2 mm) and the depth resolution (sub-nanometer) necessary to investigate sputter rate changes in SIMS depth profiling. The Burleigh Horizon optical profilometer used in this study measures sample topography over a chosen field of view (250$\mu$m x 250$\mu$m and 500 x 500$\mu$m field of views used in this work, 480 x 480 pixels) based on phase shift of the incident ($\lambda$=550nm, green) light reflected from the sample surface. However, since height (depth) measured by the optical profilometer is directly related to the phase shift of the light reflected from the sample surface, any change of the relative refractive index across the measured surface will induce an additional phase shift which will result in a change in the apparent depth.

The following simplifying assumptions were made as to the effect of changes in the complex refractive indices occurring during the initial stages of sputtering on the optical profilometer depth measurement: 1) The native oxide film and its subsequent removal has negligible effect on the refractive index and 2) For Cs in Si, all significant changes in the complex refractive index have occurred at a Cs dose (estimated to be <1E14) significantly less than that producing significant sputtering (> 1 monolayer). Assumption 2 implies that the increase in Cs concentration that occurs over the sputtered depth necessary to reach the maximum equilibrium level of implanted Cs concentration has
negligible effect on the complex refractive index. Further assumptions were made concerning swelling of the sample resulting from ion beam bombardment: 3) Initially the crater swells to a maximum level due to the larger volume occupied by implanted Cs compared to removed Si, 4) There is always a region surrounding the sputtered area, subsequently referred to as the crater lip, that is always swollen to the maximum level. As sputtering continues and the crater deepens, this lip, which is maintained by the Cs$^+$ ion beam tails, moves out from the edge of the crater and broadens as sputtering progresses. If these assumptions are valid, the optical profilometer should be a viable tool for measuring changes in Cs$^+$ primary ion sputter rate from the onset of significant sputtering until the equilibrium concentration of Cs has been reached, a range of depths over which standard stylus profilometry measurements are difficult to impossible.

AFM is an accepted method for nano- and subnanometer height measurements. However AFM measurement times are prohibitively long and most AFM instruments use single tube piezoelectric scanners, which introduce an increasing error in height measurements with increasing scan size. 15 x 15 µm SIMS craters formed by Cs$^+$ ion bombardment, which are of an appropriate size to be measured using both AFM and OP, are compared to determine if OP can provide accurate depth measurements for SIMS craters. Figure 8-4 presents examples of AFM and OP topographical images illustrating the type of data obtained from these techniques. The crater lip can be observed in both images.

![AFM and OP topographical micrographs of crater edges after 1.4 E16 atoms/cm$^3$, 3keV Cs sputtering illustrating the data provided by these respective instruments (X, Y and Z axes are all in nm)](image-url)
Immediately after Cs\(^+\) primary ions begin impacting onto the Si surface, sputtering will start due to the transfer of momentum of the Cs\(^+\) primary ions to atoms of the target. This transfer of momentum can happen either by direct collisions or at the result of a collision cascade (see chapter 2). Assuming that sputtering occurs immediately after the start of Cs\(^+\) ion bombardment, swelling of the crater has to happen due to a larger amount of Cs atoms implanted into the sample compared to the number of Si (and O) atoms removed and/or as a result of the larger size of Cs atoms compared to Si atoms. This also means that sputtering has already occurred during the swelling of the crater. After the swelling has reached a maximum height, the sputter crater forms in the center of the swollen area (high primary ion dose area) while lips are formed at the edge of the swollen area (low dose area). Measuring crater depths with respect to the top of the crater lip instead of the surface of the substrate will thus give more accurate, while still not correct, crater depth measurements. Listed in Table 8-1 and plotted in Figure 8-5 are lip to crater bottom depth measurements obtained over a range of doses for both AFM and OP along with the differences between the AFM and optical measurements when available. In comparing the AFM and the OP measurements, the OP systematically gives a crater depths which averages about 1nm (0.8 to 1.3nm) greater than AFM over the range for which data was obtained. The constant \(\Delta Z\) between AFM and OP measurements can be used for correction of the OP depth measurement, since the AFM, a more physical measure, is believed to be closest to the truth. This correction can be applied for larger depths greater than the maximum crater depth in this study, since at a Cs dose of 7E16 the equilibrium concentration of Cs has been reached and the native oxide has long been removed. For Cs doses less than 2.8E15, the relationship between the AFM and OP measured depths could not be determined, as the depth for these doses were too shallow for AFM depth measurements with a 25 x 25\(\mu\)m large scan size.
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<th>OP Depth [nm]</th>
<th>ΔZ [nm]</th>
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<td>-</td>
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</tr>
</tbody>
</table>

Table 8-1: Measured depths versus sputter time and dose; offset between AFM and OP measurements (ΔZ) for 3keV, 24° Cs⁺ bombardment

![Figure 8-5: AFM and OP sputtered depth measured from crater lip to crater bottom](image)

Since the goal of the work presented in this chapter was to identify a crater depth measurement technique with the sensitivity, accuracy and ease of use to allow
determination of sputter rate in the earliest stages of SIMS depth profiling (0 to 20nm), sputter rate changes between the dose increments were calculated and plotted in Figure 8-6. The agreement between the AFM and OP sputter rate changes is quite good over the range of doses for which both types of data exist.

![Figure 8-6: Change in sputter rate with dose as measured using AFM and OP for 3keV, 24° Cs⁺ primary ion bombardment](image)

**8.3.2.2 Evaluation of OP for “Real Life” SIMS Crater**

The 15 x 15µm crater size and 25pA beam current used to investigate the accuracy of OP by comparing crater depth measurements obtained using AFM and OP are not practical crater sizes for depth profiling of ultra shallow implants. Use of 25pA, a beam current required for the fine focusing of the beam required to produce well formed 25 x 25 µm craters would required prohibitively long profile times and result in very low secondary ion sensitivity. Figure 8-7 shows OP depth measurements acquired from 200 x 200 µm SIMS sputter crater, profiled using 3keV Cs⁺ with a dose range of 1E14 to 1E17 atoms/cm². Maximum crater depth of 38.6 nm was achieved after sputtering for 640 seconds with a 3keV, 10nA Cs⁺ primary ion beam. Crater depths were measured in respect to crater lips, which had a height of about 0.5nm. These lip heights were smaller
than the average crater lip height of about 1nm observed for the 15 x 15 µm craters. Lip height was measured with respect to the average surface height of the bombarded area before and after the analysis, which is necessary to account for changes in initial surface roughness over a 4E4µm² large area. This procedure was not done for the 15 x 15 µm craters and might explain the difference in observed lip height. Crater depth appears to increase linearly with dose, but variations can be seen for Cs doses below 5E16 atoms/cm² or a depth of approximately 20nm, a depth which far exceeds commonly observed transient zone width of 3-4nm for 3keV, 24° Cs⁺ sputtering. To improve the visualization of the deviations from the linear sputter rate, the difference in depth between applying a linear sputter rate and the actual sputter depth for a given dose, Δdepth, is shown in Figure 8-8. A 4th order polynomial approximation for depth difference up to a dose of 5E16 atoms/cm² is also shown in figure 8-8. This fit smoothes out what is probably noise variations and generates a function which could than be applied as a sputter rate correction for depth profile acquisition acquired under identical instrument conditions. The initially negative Δdepth values indicate a smaller than average removal rate in the early stages of 3keV Cs, 24° Cs⁺ depth profiling. A negative Δdepth means that if the average removal rate would be applied to the whole profile, the profile would be shifted into the bulk. Δdepth values increase quickly after approximately 4E15 atoms/cm² Cs⁺ ion bombardment and a maximum Δdepth value of about 0.9nm is obtained after exposing the sample to a dose of roughly 3E16 atoms/cm², which means that the profile would be shifted by 0.85nm towards the surface if a average sputter rate is applied. However, the shallow depth and the not well defined peaks of the shallow P and As implants used in this study do not allow an accurate test of the profile shifts predicted from the OP-data and T-DYN simulation (see section 8.3.2.3). A multiple P or As delta doped structure with delta spacings similar to the spacings used for the B delta doped structure described in section 3.4.3 (first 5 deltas spaced 5nm apart) would be a suitable sample for applying a depth scale correction (based e.g. on the 4th order polynomial function shown in figure 8-8) and for the investigation in how far initial variations in sputter rate can be corrected.
Figure 8-7: Crater depth obtained using OP from SIMS craters after 5E14 to 1E17 atoms/cm$^2$ 3keV, 24° Cs$^+$ ion bombardment.

Figure 8-8: Difference between depth as determined by OP and applying a constant sputter rate for calibration. A fourth order polynomial approximation is shown for the Cs dose range of 5E14 and 5E16 atoms/cm$^2$.
8.3.2.3 Comparison of OP with T-DYN Simulations

T-DYN (6)(7)(8)(9) simulates sputtering and primary ion implantation during dynamic SIMS sputter depth profiling by using Monte Carlo calculations based on the TRIM (11). The T-DYN program calculates trajectories of primary ions and sample atoms set into motion in the collision cascade initiated by the primary ions, continuously updating atom positions in the sample. Although T-DYN simulations may be useful for validating the OP measurements, low energy stopping powers are not included in the latest T-DYM version.

Correction of depth scales in the transient zone, the area of the SIMS profile were sputter and ion yields are changing, will require that instantaneous sputter rates are known as a function of primary ion dose or sputtered depth. Figure 8-9 shows instantaneous sputter rates, defined here as a change in sputtered depth per 1E15 atoms/cm$^2$ Cs$^+$ primary ion dose, calculated from the OP data shown in Figure 8-7, along with a T-DYN simulation and crater depth as calculated by measuring final crater depth and assuming a linear sputter rate versus primary ion dose. Agreement between OP-data and T-DYN simulation is not unreasonable after the wafer has been exposed to a Cs dose of approximately 2E16 atoms/cm$^2$ with OP showing an additional peak in instantaneous sputter rate at a dose of approximately 7E15 atoms/cm$^2$.

The peaks in instantaneous sputter rate seen in the OP data and the T-DYN simulation at a dose of approximately 2E16 atoms/cm$^2$ are separated by about 30% difference in dose, with the peak observed in the OP measurements being at a lower dose. This difference may be the result of errors in low energy stopping powers used in the T-DYN simulation. Figure 8-10 shows the steady state cesium concentration versus depth in a Si sample after 3.0 and 14.5keV Cs$^+$ sputter depth profiling, obtained using SIMS sputter depth profiling with a 500eV O$_2^+$ ion beam of the bottom of the crater formed by the 3.0 and 14.5keV Cs$^+$ bombardments. Figure 8-10 also shows T-DYN simulations of the steady state cesium concentration distribution versus depth in a Si sample after 3.0 and 14.5keV Cs$^+$ ion bombardment of Si. Comparing the cesium concentration versus depth obtained by low energy oxygen SIMS analysis of the 3.0 and 14.5 keV Cs bombarded samples with the apparent cesium concentration versus depth shown by the T-
DYN simulation for 3.0 and 14.5 keV Cs$^+$ ion bombardment it can be seen that both T-DYN simulations are shifted towards the bulk, but that this shift is significantly larger for 3.0keV compared to 14.5keV Cs$^+$ bombardment. This increase in shift towards the bulk in the T-DYN simulation of 3.0keV compared to 14.5keV Cs$^+$ bombardment of Si indicates an increase in an apparent underestimation of nuclear and/or electronic stopping powers in the T-DYN simulations as the energy of the Cs ion beam is reduced. An underestimation of nuclear and/or electronic stopping powers means that cesium ions penetrate deeper into the sample and hence deposit less energy close to the surface, which would result in lower sputter rates (see chapter 2) which could explain the difference in peak position in instantaneous sputter rates between OP data and T-DYN-simulation at a dose of about 2E16 atoms/cm$^2$.

An explanation for the initially higher instantaneous sputter rates observed with OP (the first peak in the OP data in figure 8-9) compared to the T-DYN simulation could be errors in the OP measurements due to changes in the refractive index of the surface due to the enrichment of the surface with Cs or the fact that T-DYN simulations do not take any crystallographic changes into account. Also for O$_2^+$ ion bombardment of Si, surface sputter rates of up to 8 times higher than the bulk sputter rate have been observed (12), a further indication that surface sputter rates are higher than bulk sputter rates. Detailed investigation focusing on sputtering changes in the top two nanometers employing long-range AFM scanners that do not have the artifacts associated with single tube piezo scanners will be necessary to clarify this problem.

It is also interesting to note that non-linear changes in sputter rate occur in Figure 8-9 in both the experimental data and in the simulation. This may indicate that these subtle sputter rate changes really exist and are not due to statistical noise in the data. Based on both OP and T-DYN-data, sputter rates apparently do not become stable for 3keV, 24° Cs$^+$ sputtering of Si until a crater depth of approximately 15nm has been reached, as determined by measuring the depth until the instantaneous sputter rate reaches 90% of its steady state value. This depth of 15nm is much larger than the transient zone depth of 3.4nm for 3keV, 24° Cs$^+$ sputtering of Si, with transient zone depth determined by measuring the depth until the $^{30}$Si secondary ion signal reaches 90% of its maximum value. This demonstrates that sputter rate changes can still go on well
after a matrix signal has long reached a stable level. This fact was already suspected due to changes in the B signal over 10’s of nm observed when analyzing B bulk doped Si wafers with O$_2^+$ primary ion bombardment (13).

Figure 8-9: Instantaneous sputter rates determined from OP data and T-DYN simulations as a function of Cs$^+$ primary ion dose (left y-scale). Depth as measured by OP is shown as a function of Cs$^+$ primary ion dose for comparison (right y-scale)

Figure 8-10: SIMS depth profiles obtained from 14.5 and 3.0keV, 1E17 atoms/cm$^2$ Cs$^+$ implants and profiles simulated using T-DYN for comparison
8.4 Summary

Results reported in this chapter demonstrate how a correction procedure based on bulk doped standards can be used to decrease the influence of ion yield changes in the transient zone on the measured signals, resulting in an apparent improvement in both profile shape and in integrated dose for high resolution profiling of ultra shallow dopant implants. Dose calculation and profile shape depend also on an accurate sputter rate calibration. It was shown that optical profilometry can be used to obtain instantaneous sputter rates in the top view nanometers of a depth profile with short analysis time and a field of view suitable for measuring SIMS craters. Initial crater swelling and lip height formation was observed during depth profiling of Si with 3keV Cs\(^+\) with OP and AFM. It appears that the maximum lip height is a better reference point for crater depth measurements and that more accurate crater depth measurements can be obtained this way, as compared to taking the original sample surface as a reference point for crater depth measurements, as sputtering starts concurrently with ion bombardment. Results acquired with OP were in reasonably good agreement with data obtained using AFM and T-DYN simulations.

8.5 References

9 Conclusions and Future Work

9.1 The Contribution

Ultra shallow dopant implants have been used to study the relationship between atomic mixing induced by energetic primary ions and achievable depth resolution in Secondary Ion Mass Spectrometry. Limitations which atomic mixing imposes on SIMS sputter depth profiling analyses of low energy n-dopants implants with respect to accurate determination of dopant versus depth distribution using magnetic SIMS with positive Cs\(^+\) primary ions and a negative sample potential have been shown. An alternative to SIMS depth profiling of P using Cs\(^+\) primary ions and negative secondary ion extraction has been presented using commonly available O\(_2\)^+ primary ions and positive secondary ion extraction in a magnetic sector SIMS. Using low energy O\(_2\)^+ primary ion beams will allow accurate profile shape determination of ultra shallow B and P implants, with a limited loss in P detection limit if O\(_2\) flooding is used. Negative cluster ion bombardment was investigated for ultra shallow n-dopant profiling and promising results were shown especially for As analysis using magnetic sector SIMS. Problems associated with sputter ion sources were discussed. The importance of investigating and controlling beam induced crater bottom roughness to avoid apparent shifts in depth of analyzed dopant profiles away from their actual physical position was highlighted and possibilities shown how to avoid excessive beam induced crater bottom roughness. Methods to improve quantification and profile accuracy SIMS depth profiles of ultra shallow dopant implants have been shown by investigating and applying correction procedures for ion and sputter yield changes in the initial stages of sputter depth profiling.

9.2 Beam induced Crater Bottom Roughness and Profile Shift

Depth calibration in SIMS sputter depth profiling is most often done by applying a linear sputter rate calculated from a crater depth measurement to entire depth profile. It has been demonstrated that severe errors in depth calibration can occur if this depth
calibration method is used for ultra shallow SIMS depth profiling when primary ion beam conditions are used that create excessive crater bottom roughness. Sample rotation reduces beam induced crater bottom roughness and profile shift, but is only available on a very limited number of instruments. It has been shown that combinations of primary beam energies and angles of incidence exist for low energy $O_2^+$ ion beams that generate minimal crater bottom roughness and thus produce in minimal beam induced profile shift. The use of $O_2$ flooding during glancing angle SIMS depth profiling using $O_2^+$ primary ions can increase or decrease crater bottom roughness, depending on beam conditions. Thus $O_2$ flooding should only be used for routine analysis after beam induced crater bottom roughness has been investigated under the identical conditions to be used for the SIMS depth profile analyses. Periodic ripple structure formation under $CsC_6$ cluster ion bombardment appeared to be correlated to the low energy C component in the cluster, limiting the possible use of glancing angle cluster ion bombardment if sample rotation is not available to minimize beam induced crater bottom roughness.

9.3 Analysis of Ultra Shallow Dopants using SIMS

Investigation of ultra shallow implant profiles in Si has shown that artifacts often neglected in SIMS sputter depth profiling like atomic mixing, the transient zone or profile shifts are critical for the accuracy of ultra shallow depth profiling. Minimizing primary ion impact energy on the sample either by lowering the primary ion beam energy or by increasing or decreasing the potential on the sample depending on the sample polarity with respect to the primary ion polarity, glancing angle bombardment or using cluster ions effectively reduces atomic mixing and improves depth resolution. Reducing normal impact energies with glancing ion instead of normal or near normal $O_2^+$ ion bombardment appears to have only a very limited effect on decay length measurements. Decay lengths $(1/e)$ of 0.8nm for B and 1.6nm for P were achieved using low energy $O_2^+$ ion bombardment, while the best results with a decay length of 1.8nm for As depth profiling using the CAMECA IMS 6F were achieved using $CsC_6^-$ primary ions. The use of $CsC_6^-$ improved depth resolution compared to $Cs^+$ ion bombardment for ultra shallow P and As
analysis using the CAMECA IMS 6F, which shows the possible improvements that can be achieved in SIMS sputter depth profiling with cluster ion bombardment. Further development of negative ion sources will be necessary to enable the SIMS community to fully utilize negative primary ions for sputter depth profiling. An ATOMIKA 4500 quadrupole SIMS using impact energies as low as 250eV was able to produce lower decay length values for P and As compared to the lowest impact energies achievable on a IMS 6F. Transient zone width was reduced with lower primary ion impact energies as well as by using O_2 flooding during O_2^+ primary ion bombardment. The smallest transient zone width achieved was 0.3nm for 500eV, 48° O_2^+ ion bombardment of Si while using O_2 flooding.

9.4 Quantification within the Transient Zone

Large errors were found for integrated dose calculations of ultra shallow dopant implants analyzed with SIMS, when a significant portion of the implant is in SIMS depth profile transient zone. Integrated dose calculations were improved by applying a correction procedure based on bulk doped standards. Sputter rate changes during the initial part of a SIMS depth profile were studied using AFM and OP. OP was established as a fast and easy way to measure ultra shallow SIMS crater in Si using Cs^+ primary ions with an error of about 1nm due to changes in the refractive index of the sample. T-DYN simulation provided further insight with sputter rate behavior during the initial stages of SIMS depth profiles.
9.5 Recommendations for Future Work

9.5.1 Beam Induced Crater Bottom Roughness

In this study it was shown that cluster ion bombardment results in an improvement in depth resolution compared to atomic primary ion bombardment. It was also shown that glancing angle CsC\textsubscript{6} primary ion bombardment of Si causes ripple formation and changes in sputter rate, which were postulated to be related to the low energy carbon component of the CsC\textsubscript{6} molecule, as the R\textsubscript{p} of carbon is less than the R\textsubscript{p} of Cs and hence carbon is placed closer to the surface. That carbon causes the ripple formation in Si during CsC\textsubscript{6} sputtering was also indicated by measurements performed by G. Gillen, but closer investigation is necessary to confirm the results. Cs bombardment with the same energy and angle as the Cs component in the CsC\textsubscript{6} cluster could show if the component in a cluster which is placed closer to the surface (smaller R\textsubscript{p}) is responsible for beam induced crater bottom roughness. In the IMS-6F this could be done by using Cs\textsuperscript{+} and positive sample potential and CsC\textsubscript{6}\textsuperscript{-} and negative sample potential. Information obtained from these measurements would be valuable for roughness formation under cluster ion bombardment in general, which is receiving increasing attention in the SIMS community.

9.5.2 Profile Shifts in SIMS Depth Profiles

In this work OP, AFM and T-DYN were used to obtain instantaneous sputter rates and a possible correction function for 3keV, 24° Cs\textsuperscript{+} sputtering. While the measurements showed in general good agreement with each other, the correction function needs to be applied to an appropriate sample to investigate if or how much the correction function minimizes profile shifts in SIMS profiles obtained with 3keV, 24° Cs\textsuperscript{+} primary ion bombardment. An ideal sample would be a P or As delta layer with delta spacing of approximately 5nm.
It would be also useful to investigate the accuracy of OP for measuring shallow crater depths and instantaneous sputter rates for low energy \(O_2^+\) and \(CsC_6\), as the next generation CAMECA type instruments (SC ULTRA and IMS-WF) will have OP instruments available inside in the sample chamber for in situ crater measurements during ion bombardment. This would be especially interesting for low energy \(O_2^+\) bombardment as the formation of a \(SiO_2\) and the related changes in optical properties of the surface might introduce a significant error in the depth measurement. The B delta doped structure used in this work could be used for developing a correction procedure for the possible errors of OP measurements during \(O_2^+\) depth profiling.

### 9.5.3 Ultra Shallow P in Si Analysis

In this work it was shown that for ultra shallow SIMS depth profiling of P in Si current state of the art \(CsC_6^-\) profiling can achieve results with respect to depth resolution and P sensitivity comparable to \(O_2^+\) depth profiling of P in Si, with \(CsC_6^-\) impact energies being significantly higher. Reliable \(CsC_6^-\) extraction with extraction potentials lower than used in this work will only be possible if extraction efficiency is improved. This might be possible to achieve by using different source sputter target geometries. Two target geometries are shown in figure 9-1. While the thin target elevated from the rest of the holder could avoid the formation of a deep sputter crater could avoid the loss of extraction efficiency with time during ion bombardment, a conical shaped target could improve initial extraction efficiency.

![Figure 9-1: Sputter Target Geometries for PSX-120 Sputter Negative Ion Source](image)

a) elevated target b) conical target
While different target geometries could increase extraction efficiency, measuring the molecular PC\textsuperscript{-} secondary ion instead of atomic P\textsuperscript{-} could increase P detection sensitivity. However, for reliable measurements using PC\textsuperscript{-} secondary ions will require a stable C\textsuperscript{-} signal, with C being implanted into the sample by the primary CsC\textsubscript{6}\textsuperscript{-} ions. A stable C\textsuperscript{-} signal was not observed in this work, but also not thoroughly investigated. Preliminary measurements showed that if a stable C\textsuperscript{-} signal can be obtained, P detection limits could be reduced by more than one order of magnitude using PC\textsuperscript{-} instead of P\textsuperscript{+}. 