

# **Optimisation of sample preparation and analysis conditions for Atom Probe Tomography characterisation of low concentration surface species**

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## **Abstract**

The practicalities for atom probe tomography (APT) analysis of near-surface chemistry, particularly the distribution of low concentration elements, are presented in detail. Specifically, the challenges of surface analysis using APT are described through the characterisation of near-surface implantation profiles of low concentration phosphorus into single crystal silicon. This material system was chosen to illustrate this surface specific approach as low concentration phosphorus has significant mass spectra overlaps with silicon species and the near surface location requires particular attention to Focussed Ion Beam specimen preparation and deposition of various capping layers. Required changes to standard sample preparation procedure are described and the effects of changes in APT analysis parameters are discussed with regards to this specific material system.

Implantation profiles of 14 kV phosphorus ions with a predicted peak concentration of 0.2 .at % were successfully analysed using APT using pulsed laser assisted evaporation. It is demonstrated that the most important factor in obtaining the most accurate implantation profile was to ensure all phosphorus mass peaks were as free of background noise as possible, with thermal tails from the Si<sup>2+</sup> ions obscuring the P<sup>2+</sup> ions being the major overlap in the mass spectrum. The false positive contribution to the phosphorus profiles from hydride species appears minimal at the capping layer/substrate interface. The initial capping layer selection of nickel was successful in allowing the analysis of the majority of the phosphorus profile but nickel and phosphorus mass spectra overlaps prevent optimum quantification of phosphorus at the surface.

## **Introduction**

As characterisation techniques have become more refined and interaction volumes have become smaller and more selective, it has become possible to measure surface regions at the nano-, and in some cases, atomic-scale. The ability to characterise at the atomic-scale and ultimately manipulate local surface chemistry is critical to a range of industrial research ranging from the synthesis of catalytic surfaces and nanoparticles [1] to the design of modern integrated semiconductor electronics such as fin-FETS [2]. For these devices it has been shown that variations in individual dopant positions can have a measurable effect on electronic parameters and hence a great deal of research has been carried out on attempting to accurately quantify dopant concentration and spatial distribution within nanoscale volumes[3]. As the direct measurement of dopants within nanoscale devices is extremely difficult and costly, fabrication stages are often guided through the use of simulations informed by characterisation of diffusion or ion implantation profiles into test materials

and structures. Modern devices require ultra-shallow diffusions and implants in order to continue the size reduction drive of Moore's Law and fabrication is increasingly confined to surface regions.

In the field of semiconductor research and industry, Secondary Ion Mass Spectroscopy (SIMS) is the current industry standard technique for obtaining depth profiles with nanometer scale resolution in the analysis direction [4]. For many applications, this is an extremely accurate technique for depth profiling to verify processing stages of deposition or implantation, as the chemical sensitivity of SIMS can be parts per billion [5]. However, SIMS data is gathered from a relatively large surface area, with average sputtered craters having diameters of hundreds of microns and depths of tens of microns. This can result in small variations in local chemistry or structure being blurred out or missed entirely, especially between regions of differing sputtering rates can blur otherwise sharp interfaces between phases. Surface analysis using SIMS is also prone to increased formation of hydride species and non-equilibrium sputtering at the start of analysis combined with known intermixing sputtering artefacts can lead to large variations in apparent concentration. Comparisons with known standard materials is an integral part of SIMS analysis and there can be significant variation in analyses between different facilities [6]. Due to the large sample area of SIMS it is not possible to analyse an isolate nanoscale region or device in isolation and so site specific nanoscale analysis is required.

Suitable characterisation tools include Transmission Electron Microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM), which can give atomic scale spatial resolution and qualitative nanoscale chemical resolution when combined with Energy-dispersive X-ray Spectroscopy (EDX) or Electron Energy Loss Spectroscopy (EELS) [7]). Using modern Focussed Ion Beam (FIB) for site specific specimen preparation, specific regions of semiconductor materials or devices can be selected for analysis in TEM and STEM [8].

In order to accurately and quantitatively measure local variations in structure and composition in the scale required by modern semiconductor electronics, a technique that can offer nanoscale spatial information in three dimensions with high chemical resolution is required. Atom Probe Tomography (APT) provides 3D atom-by-atom reconstructions of nanoscale volumes and has emerged as a highly effective technique, complementing the information from more established microscopies by providing unique quantitative analysis of local chemistry at near atomic-scale resolution [9].

In many instances, APT has been shown to have comparable chemical sensitivity with SIMS, sharper interface measurement in depth profiles and has the added bonus of increased spatial resolution in the plane of the sample [10] [11]. However, this is at the cost of greatly reduced maximum depth achievable within a single APT analysis and lower mass resolving power and chemical sensitivity due to the reduced volume being analysed.

Using methodologies adapted from FIB based TEM sample preparation it is now possible to select a specific nano-device and contain it entirely within a single APT analysis volume [2, 12]. APT has found significant application in the semiconductor industry where it can be shown that spatial variation in small numbers of atoms can have clearly measurable effects on the electronic properties of nanoelectronic devices [13, 14]. These devices typically use relatively large concentrations of dopants and multiple ion implantation stages are often used to place them with extreme accuracy. However, there are an increasing number of semiconductor applications where atomic scale characterisation of low concentration implantations would provide far greater insight [15] [16].

Therefore to explore the potential of APT to accurately measure distributions of low concentration, near surface species, this paper investigates the analysis of shallow phosphorus implants in silicon with peak concentrations approaching the limit of detection for modern atom probe systems. APT analyses of shallow implants into silicon have been previously carried out using various dopant species including boron and arsenic[17] [11, 18] for device applications and comparison with industry standard techniques such as SIMS.

Phosphorus donors in isotopically pure silicon-28 have shown great promise as quantum bits or 'qubits' [19, 20] [21] and if they can be precisely positioned using ion implantation, it would allow their fabrication to be up scaled to the required industrial levels for viable quantum computers[22]. In order for implantation models to be improved to allow deterministic implantation, high quality atomic scale characterisation of low concentration, near surface phosphorus profiles is required. It has been shown that phosphorus has a greater straggle distance in silicon than other typical silicon dopants and this is not easily taken into account using standard Stopping Range of Ions in Matter (SRIM) simulations[23]. These simulations are used extensively in standard semiconductor device fabrication but need to be further refined to take into account local crystallography [24] in determining low concentration implantation conditions for forming single atom electronic devices. TEM has also shown that the damage profiles caused by low energy phosphorus implantation into silicon does not match SRIM predictions [25].

There has been extensive characterisation of a range of low energy phosphorus implants using both SIMS and complementary Nuclear Reaction Analysis in an effort to quantify the implantation profile shape and concentrations [26]. Low energy phosphorus implantation profiles has been shown to be far more difficult to quantify using SIMS than those of other typical dopants such as boron or arsenic as phosphorus mass spectra readily overlap with silicon hydride species in single ion and compound ion peaks (the latter being harder to deconvolute) and this can lead to unacceptable levels of false positive phosphorus identification in the surface regions [26] [23]. There is also a great deal of noise in the measurement of phosphorus concentration measurements for surface analysis using SIMS despite relatively high concentrations[23] and this prevents the use of SIMS for accurate quantification of phosphorus for ion implantation for quantum devices.

In this study, the implantation of 14 kV phosphorus was selected for analysis. Each 14 kV phosphorus ion impact into silicon causes the minimum number of detectable electron/hole pairs that are used to confirm that an ion has been implanted into the active regions of pre-fabricated nanoscale devices used for quantum manipulation[22, 27]. The range and straggle of the 14 kV phosphorus ions is also sufficient for the majority of ions to be close enough to the surface that they can be used as viable qubits. For the case of APT analysis of low concentration, near surface implantation of phosphorus, there are a number of decisions pertaining to experimental design that must be considered in order to: ensure that the surface region is undamaged during sample preparation, maximise yield of viable sample, reduce sample preparation time in order to maximise number of datasets and ensure that phosphorus mass spectra peaks are clear enough to give usable data to give a clear and accurate implantation profile.

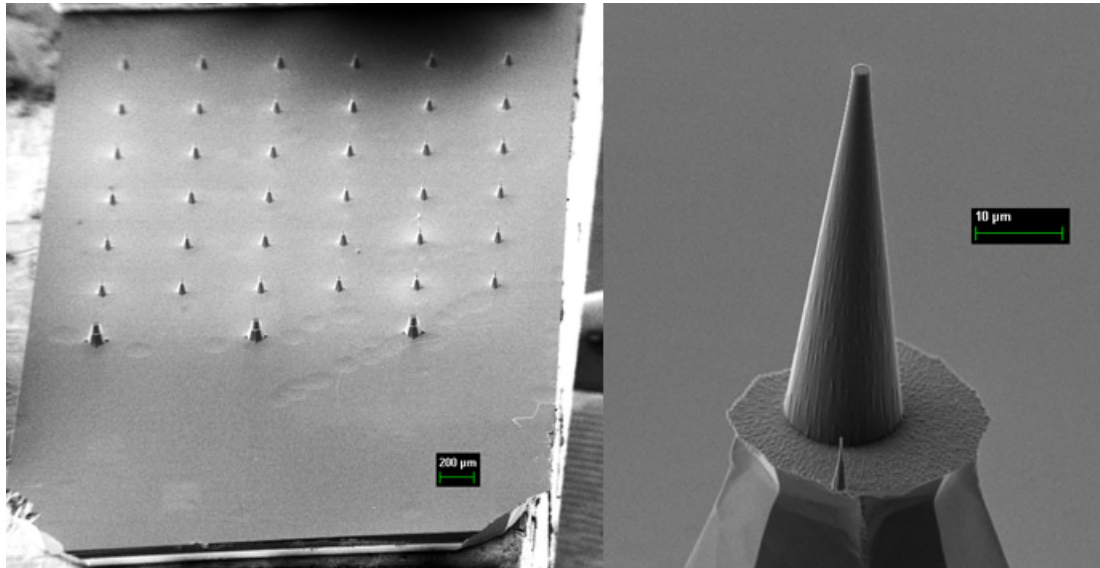
## **Methodology**

### *Substrate selection*

To create a functioning quantum devices using a half spin  $^{31}\text{P}$  atom requires implantation into isotopically pure  $^{28}\text{Si}$  to remove the spin interaction of the half spin  $^{29}\text{Si}$  isotope, this silicon is undoped and therefore is less conductive than typical silicon used for electronic devices. As APT analysis of electrically insulating materials is known to result in more fractures and reduced data quality, implantation into more electrically conductive silicon substrates was deemed to be a suitably analogous material system for initial experiments while improving the likely yield of samples successfully characterised.

In order to investigate the potential for reducing costly FIB-based sample preparation time, implantation was carried out directly into a commercially available flat topped silicon micro-post arrays. These arrays of 36 posts, with post diameters of  $2\text{ }\mu\text{m}$ , are designed to be used as a platform for APT samples made using FIB liftout and are therefore made of highly conductive silicon with a resistivity less than  $0.1\text{ }\Omega\text{cm}$ . By implanting directly into pre-fabricated posts and then sharpening them to the required APT sample size and shape, the equipment and operator expertise required can be greatly reduced compared to that required for a standard FIB liftout preparation. A Scanning Electron Microscopy (SEM) secondary electron micrograph of both the array and a flat top post can be found in figure 1. Pre-sharpened versions of these posts are used as supports for the analysis of directly deposited materials or multilayer systems and have been shown to viable for this purpose [28] [29].

As the planar straggle [22] of the implantation of the  $14\text{ kV}$  phosphorus ions is over two orders of magnitude greater than the diameter of the flat top micro post, the implantation into the top of the post should be analogous to a larger, planar surface apart from those regions immediately adjacent to the post edge. Therefore this approach is likely suitable for APT analysis of low energy implants where the implantation profile peak is within a typical APT analysis depth of a few hundred nm. In the first step, the sample was dipped in a dilute HF to etch away any excess oxide from the micropost fabrication process and allow implantation through a regrown surface oxide of approximately  $2\text{ nm}$ .



*Figure 1 – SEM micrograph of silicon micro post array (left) and silicon flat top post (right)*

### *Deposition of Capping Layers*

In order to preserve the surface regions of the sample during standard FIB based sample preparation, a capping layer is required. The selection of a capping material is application-specific but there are a number of important general requirements for the material used [30, 31] of which adhesion to substrate, minimal mass spectra overlaps with species of interest in the substrate and minimal evaporation field differences between capping layer and substrate materials are the most important.

Standard FIB-based sample preparation for APT using liftout requires the deposition of a carbon, tungsten or platinum protective layers using a Gas Injection System (GIS) via e-beam or FIB cracking of a carbon-based precursor gas prior to bulk milling of trenches. These are usually deposited through a Gas Injection System (GIS) via e-beam or FIB cracking of a carbon-based precursor gas. However these are not suitable for a capping material for APT analysis of near surface regions of silicon as they are not uniformly dense, have a significantly higher evaporation field requirement compared to silicon, and also cause FIB damage of the surface during deposition [9]. This requires them to be removed entirely during final tip polishing and it is extremely difficult to remove the entirety of this layer without removing the implanted surface regions.

There are a variety of materials suitable for depositing onto silicon for APT analysis [32]. As the primary consideration is of adhesion and protection of the surface from FIB damage during sample preparation, nickel was selected as the initial capping material, in line with previous attempts at using capping layers on silicon [18, 33]. Higher-quality layers can be deposited prior to FIB preparation utilising processes such as sputter coating, thermal evaporation, atomic layer deposition or electrochemical deposition. Thermal evaporation was selected as the method of depositing nickel onto the silicon samples as this gives a thin, uniform layer. These were dipped into HF to remove the surface oxide and ~100nm of nickel was evaporated onto it using high purity nickel wire (99.99+ %)

and an alumina coated tungsten thermal evaporation boat. Evaporation was carried out at a base pressure of approximately  $10^{-6}$  torr to ensure minimal contamination of the deposited material and the samples were physically shielded during initial evaporation to prevent the deposition of impure nickel and oxides.

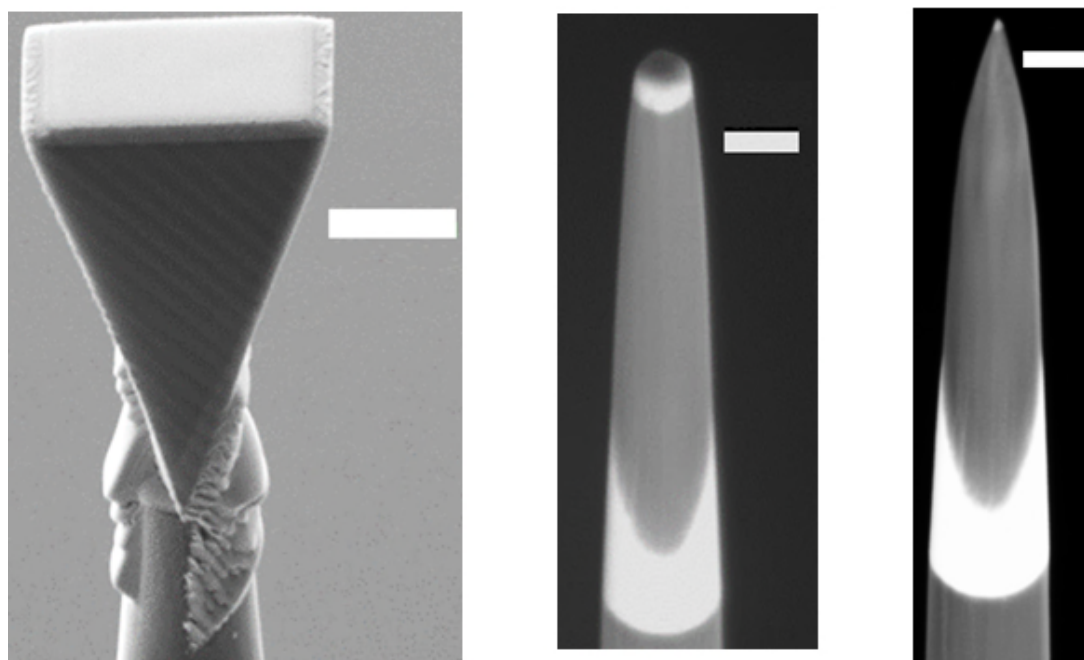
It was found that the maximum thickness of nickel that was possible to evaporate in a single process, using the available equipment, approximately 100 nm, was not sufficient to protect the surface of the silicon through the FIB milling process and so additional GIS deposited tungsten was required in the cases of both the milled micro-posts and the liftout samples. The yield of samples viable to the stresses of the APT experiment was the initial priority. Hence, the native insulating silicon oxide layer was removed using a hydrogen fluoride (HF) acid dip before deposition of the capping layer was carried out. In addition to providing a clean and uniform surface to promote good adhesion, this should have the effect of minimizing the thickness of the insulating oxide layer between the silicon and the capping layer and reduce the chance of sample fracture in the APT experiment when analysing through this interface. The oxide layer can be used as a delineation layer in combination with the capping layer to accurately define the silicon surface.

The main addition to standard FIB liftout procedure was a ten minute e-beam deposition of tungsten on substrate prior to FIB deposition of tungsten in order to further protect the surface from damage during the deposition process [9]. This pre-treatment also has the effect of removing any species that may segregate to this oxide layer, which is possible during thermal processing[23]. In the case of low energy implantation without annealing, a non-trivial amount of phosphorus was also found to implant into this layer and remain there [26, 34, 35].

#### *FIB-based sample preparation*

APT has very specific requirements for specimen geometry. The specimen must take the form of a very sharp needle with a tip radius of less than 100 nm. Furthermore, the feature of interest must be located within tens of nanometres of the apex. For APT analysis of semiconductor materials, for which the use of FIB to fabricate specimens is almost a universal requirement, there are now well established methodologies routinely applied to facilitate sample preparation [36].

There is a large range of control available over the eventual size and shape of an APT sample when utilising a FIB liftout approach. FIB milling was carried out using a Zeiss dual beam FIB/SEM with a GIS able to deposit carbon and tungsten and fitted with a Kleindiek micromanipulator. Standard FIB liftout [36] [37] using typical conditions was carried out from planar regions in between the posts on the ion-implanted micro-post array. These liftout regions were subsequently placed onto a separate unimplanted flat top silicon micro post array. In order to preserve the surface region, annular milling was then carried out till the diameter of the capping layer/substrate interface region was approximately 200-300 nm. At this stage, a small amount of tungsten was still visible and the capping layer was intact, therefore the damage to the silicon layer from the 30 kV beam should be almost entirely confined to the nickel capping layer. A 2 kV 300 pA polishing mill was then used over the entire tip to remove the upper most damaged region of nickel and reduce the tip diameter to less than 100 nm whilst retaining approximately 10-20 nm of nickel. The stages of tip fabrication can be seen in figure 2. SEM secondary electron imaging shows clear contrast between the silicon and nickel layers in the finished sample, as can be seen in SEM secondary electron images in Figure 2.



*Figure 2 – Stages of FIB sharpening. Liftout wedge welded onto a silicon micro-post (left – scale bar 2  $\mu\text{m}$ ), after 30 kV shaping (middle- scale bar 200 nm), after 2 kV polishing (right – scale bar 100 nm).*

For the alternative sample preparation approach, FIB milling of the implanted micro-posts, the flat top post was first subjected to e-beam deposition of tungsten for two minutes FIB deposition of tungsten was carried out for 2 minutes using 30 kV. A single stage annular mill using 30 kV ions was then carried out, followed by a 2 kV 300 pA polishing mill. This process took approximately 15 minutes per tip compared to the 60 minutes per liftout tip.

Milled micro post samples and liftout samples from the same implanted micro post array were analysed then in a Cameca LEAP 3000X HR system using a base temperature of 50 K, a pulse frequency of 200 kHz, laser wavelength of 532 nm, pulse length of 10 ps and pulse energy of 0.4 nJ. An evaporation rate of 0.5 % was used throughout the analysis and a gradual transition between nickel and silicon was observed during the evaporation of the interface.

## Results

### *APT Mass Spectra and Reconstructions*

Silicon peaks in the APT mass-to-charge-state ratio spectra are expected at 28, 29 and 30 Da in the  $1^+$  charge state and 14, 14.5 and 15 Da in the  $2^+$  charge state. Phosphorus mass spectra peaks are expected at 31 Da in the  $1^+$  charge state and 15.5 Da in the  $2^+$  charge state, while there is also the possibility of phosphorus compound ions at 62 Da and further multiples of 31 Da. Nickel mass spectra peaks can be expected at 58, 60, 61, 62 and 64 Da in the  $1^+$  charge state and 29, 30, 30.5, 31 and 62 Da in the  $2^+$  charge state.

No measureable peaks at 62 Da due to the evaporation of  $2^{31}\text{P}^+$  molecular ions were detected after the silicon/capping layer interface region in any sample and so only single phosphorus ions at  $^{31}\text{P}^+$

and  $^{31}\text{P}^{2+}$  at 31 Da and 15.5 Da respectively were assigned to phosphorus. A 'background to background' approach was used to ranging of the peaks in these datasets [31, 38].

Distinct peaks at 31 Da and 15.5 Da can be seen in the mass spectra from the milled micro post in Figures 3 and 4 respectively. As expected from the literature[38], the majority of silicon ions were evaporated in the  $2^+$  charge state but approximately equal numbers of phosphorus ions were found in both  $1^+$  and  $2^+$  charge states.

In the mass spectrum resulting from analysis of the FIB liftout prepared sample, presented in Figure 3, there is a clear peak for phosphorus in the  $1^+$  charge state at 31 Da. However, the signal in the  $2^+$  charge state at 15.5 Da is almost completely obscured by thermal tails from delayed evaporation of silicon in the  $1^+$  charge state, as seen in Figure 4. The detrimental effect of this on the analysis, whereby Si atoms distributed randomly throughout the dataset erroneously contribute to the phosphorus signal, can be visually confirmed through the comparison of atom maps of the contribution to phosphorus from the clear  $1^+$  charge state at 31 Da and blurred  $2^+$  charge state at 15.5 Da in Figure 5.

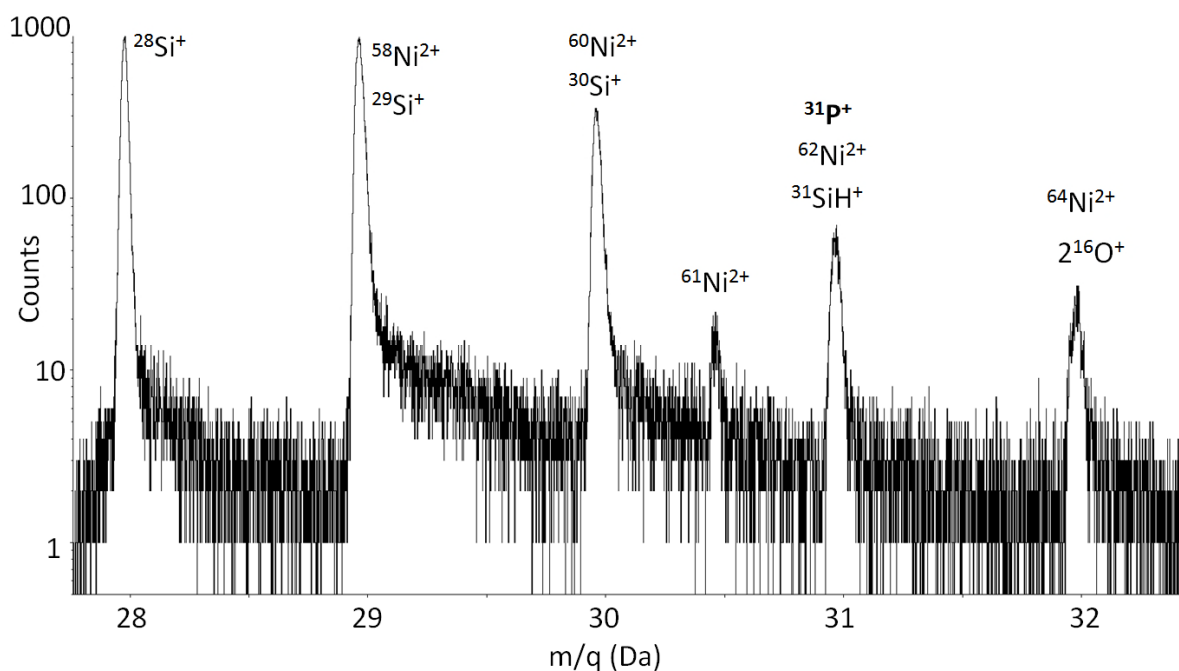
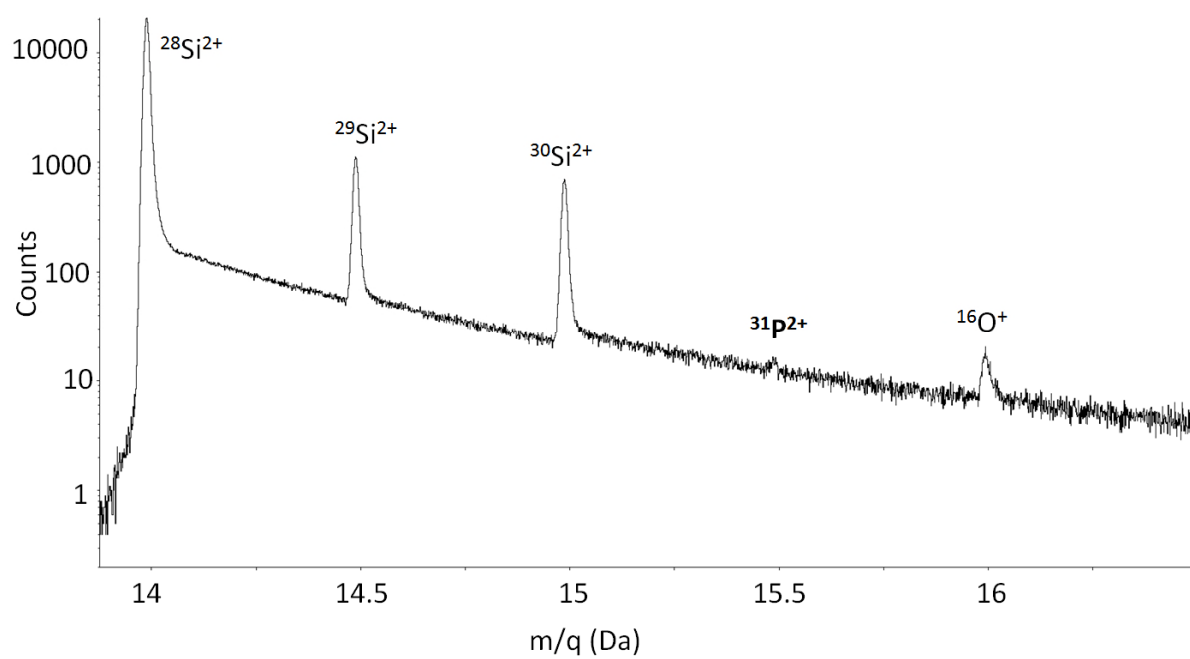
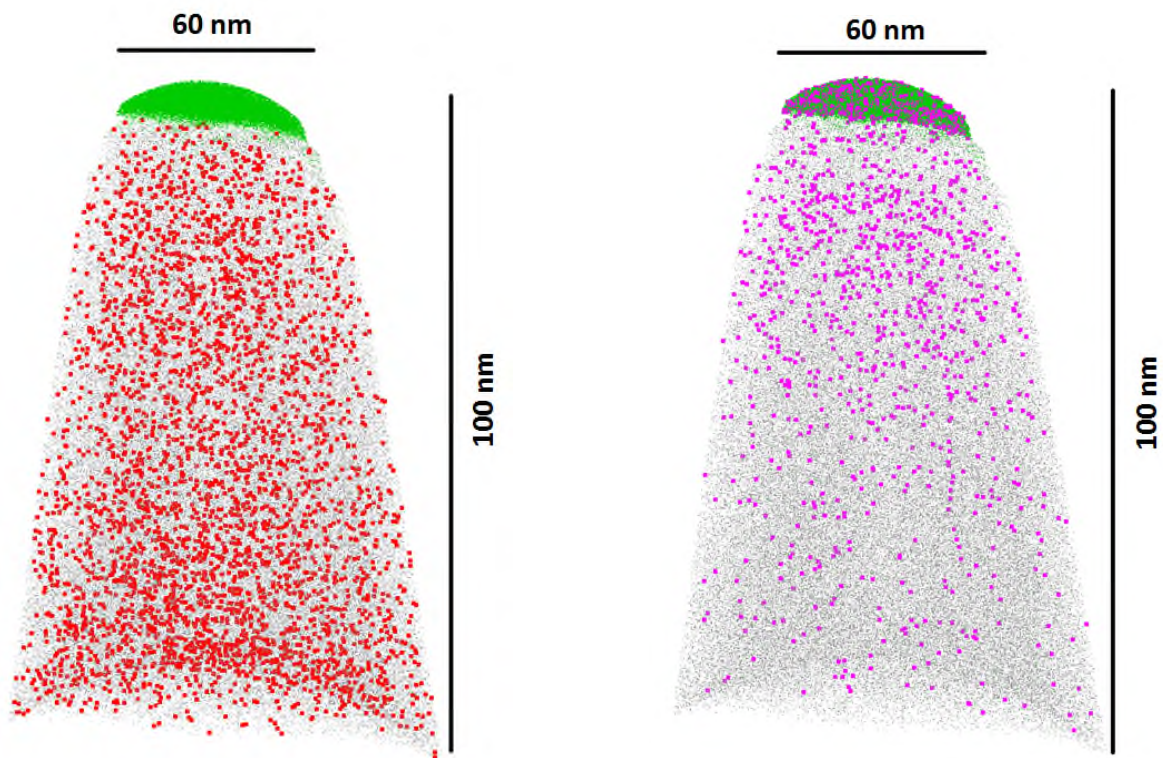


Figure 3 - Mass spectra range selected for silicon and phosphorus in  $1^+$  charge state (28 to 32 Da).  
Taken from full dataset of all atoms in liftout sample.



*Figure 4 - Mass spectra range selected for silicon and phosphorus in  $2^{+}$  charge state (14 to 16 Da).  
Taken from full dataset of all atoms in liftout sample.*



*Figure 5 - Atom map for the liftout samples. Nickel atoms are shown in green, silicon atoms are shown in gray. Phosphorus mass spectra atoms in the 1<sup>+</sup> charge state shown in purple on the right, phosphorus mass spectra ions in the 2<sup>+</sup> charge state are shown in red on the left.*

Distinct peaks at 31 Da and 15.5 Da can be seen in the mass spectra from the milled micro post in Figures 6 and 7 respectively. The contributions to phosphorus from both charge states were combined and can be seen in the atom map in Figure 8.

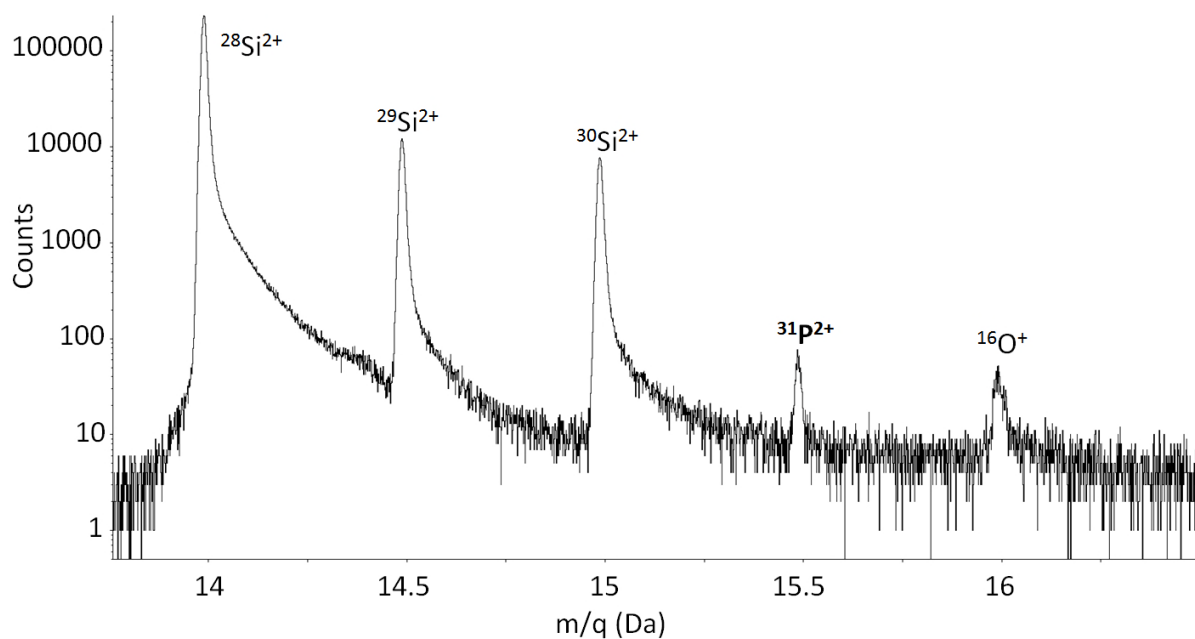


Figure 6 - Mass spectra range selected for silicon and phosphorus in  $2^+$  charge state (14 to 16 Da).  
Taken from full dataset of all atoms in milled micropost sample.

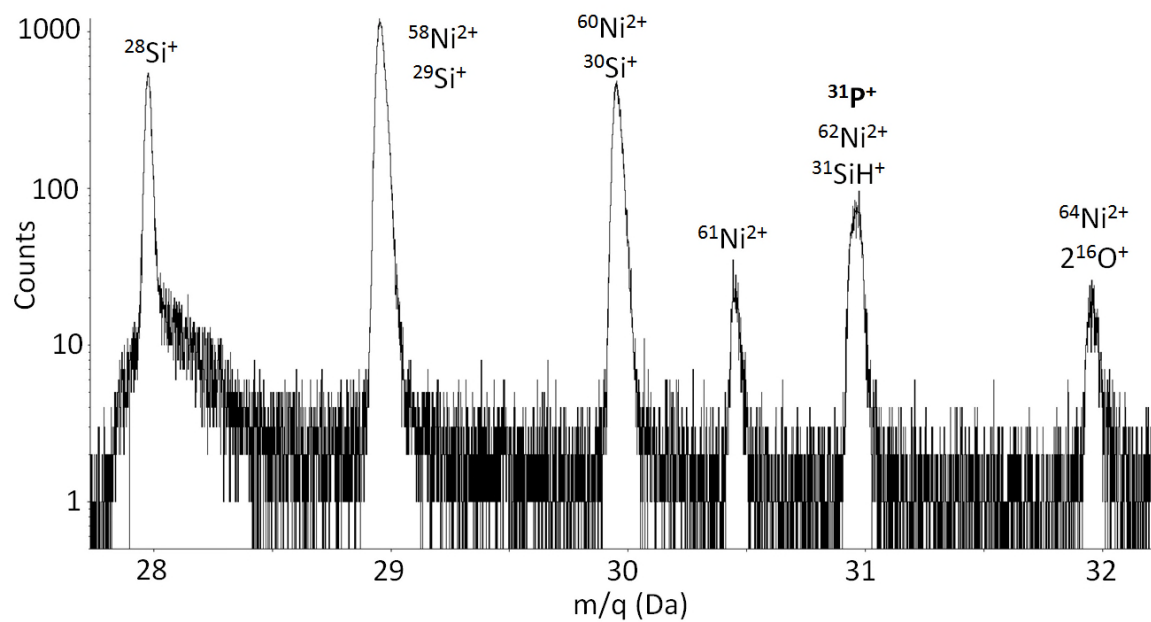
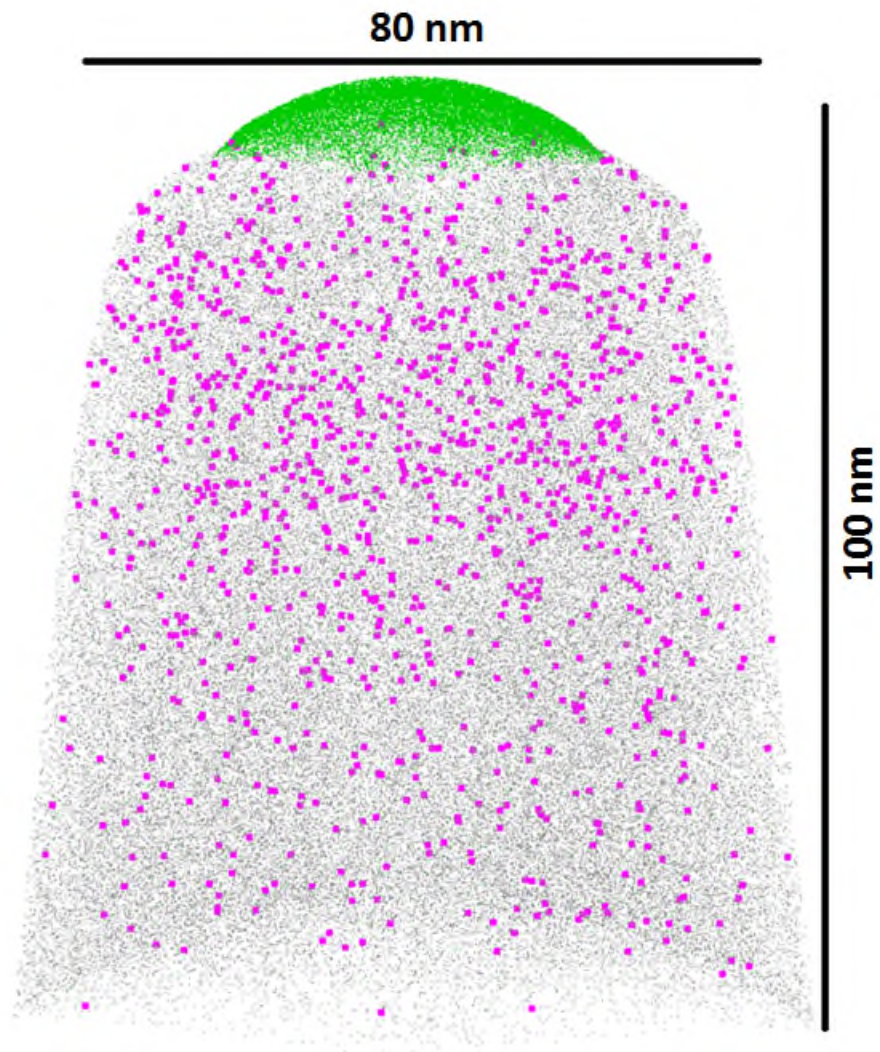


Figure 7 - Mass spectra range selected for silicon and phosphorus in  $1^+$  charge state (28 to 32 Da).  
Taken from full dataset of all atoms in milled micro post sample.



*Figure 8 - Atom map for the milled micro post sample. Nickel atoms are shown in green, silicon in gray and phosphorus in pink. The majority of silicon atoms are removed and phosphorus atoms are enlarged for clarity.*

### Phosphorus Implantation Profile

The phosphorus implantation profile from the APT analysis the milled micro post sample is presented in Figure 9. The characterisation from the implantation directly into the micro-post, as opposed to the FIB liftout sample, was selected for this analysis due to superior clarity in its mass spectrum, especially in the vicinity of the phosphorus peaks. An iso-concentration surface of 3% nickel ions in the 1+ charge state was used to define the interface between the capping layer and silicon substrate. This is to prevent blurring of the interface through overlaps between nickel  $^{58}\text{Ni}^+$  and  $^{60}\text{Ni}^{2+}$  and silicon  $^{29}\text{Si}^+$  and  $^{30}\text{Si}^+$  respectively. This concentration was chosen as the lowest value at which a smooth and uniform layer of nickel was present. A proximity histogram was then projected from this interface and hence the amount of phosphorus as a function of distance from this is then plotted to give a concentration profile as a function of depth.

As the phosphorus concentration is based upon the contributions to the peaks at 15.5 and 31 Da, this also incorporates a contribution at 31 Da from nickel  $^{62}\text{Ni}^{2+}$  ions. This results in an apparent increase in phosphorus in first few nm of depth directly under the nickel capping layer. This contribution from nickel cannot easily be extracted and so these regions are still difficult to precisely quantify when using a nickel capping layer. This experimentally measured implantation profile was then directly compared to those calculated using SRIM and Crystal- Transmission of Ions in Matter (C-TRIM) degrees and plotted together in Figure 9. It can be seen that when using with a tilt of  $\theta=4^\circ$  and twist of  $\phi=0^\circ$ , the C-TRIM matches much more closely to the APT measured value. The SRIM significantly underestimates the degree of depth straggle and shows that crystallographic information must be included in such implantation simulations.

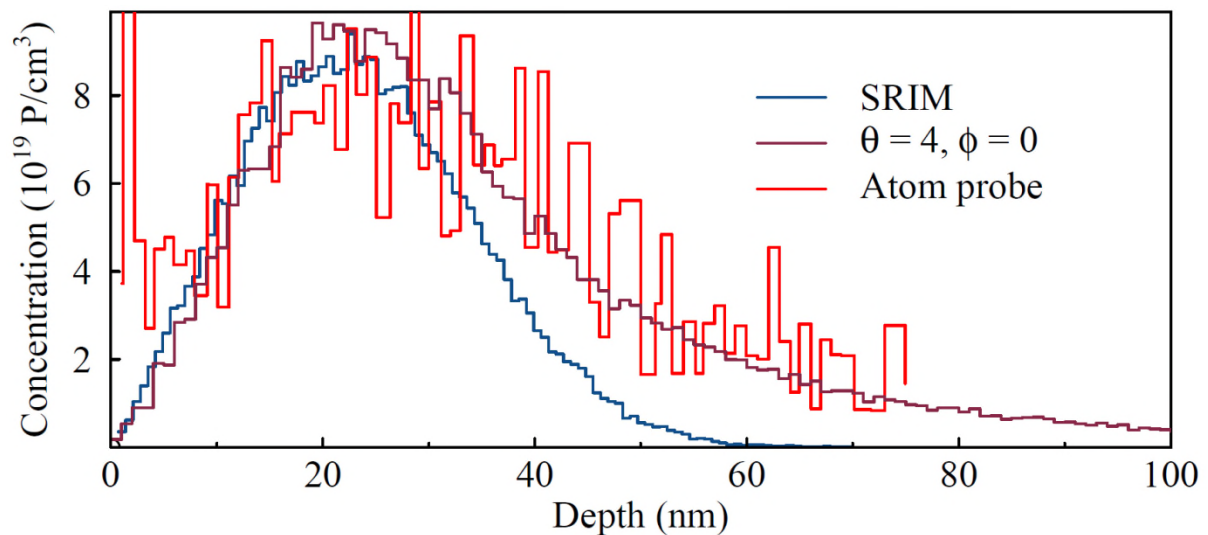


Figure 9- Comparison between phosphorus concentration measured by APT (red), simulated using SRIM (blue) and simulated using C-TRIM (purple)

## Discussion

Numerous methods of optimising both APT sample preparation and analysis for semiconductor materials and devices have been extensively covered in the literature [11]. This optimisation is typically concerned with the physical process of sample preparation, e.g. FIB milling conditions, sample shape and size, and atom probe analysis parameters, such as sample temperature or voltage/laser pulse conditions. There are a number of specific challenges for analysing the small volumes required for near surface analysis of low concentrations that can be affected by parameter selection and which are not normally considered when analysing bulk APT samples. All of these artefacts can lead to significant limitations in reconstruction accuracy, lack of chemical resolution and a general degradation in data quality.

### *APT 3D Reconstruction artefacts*

It is common practice to remove the initial stages of analysis from the dataset before reconstruction as most datasets do not require these surface regions. This may not be an option for near surface analysis and so their effects must be known and minimised in order to maximise data quality in these initial states of analysis.

In order to be able to measure the phosphorus implantation profile accurately, there must be a clear interface between the capping layer and the silicon substrate that covers the entire tip surface. If the capping layer is not present, either due to accidental removal during sample preparation or due to a microfracture event during analysis through the capping layer, or if there is reason to believe that the capping layer is damaged then the data cannot be used. A microfracture is the sudden removal of a relatively large amount of material from the sample surface, damaging the steady-state evaporation form of the tip and can lead to a temporary or permanent reduction in data quality. It can be difficult to determine if a microfracture has indeed taken place and if so, how much of the material has been removed and so will add error to depth profiling measurements. This is an even greater problem when the interface is between two materials of greatly differing evaporation field requirements as the rise in voltage from the increase in diameter from a larger, fractured tip can be hidden within the rise in voltage from the change in layer.

The lack of a coherent capping layer or samples fracturing during the capping layer/substrate interface was identified as the major cause of yield loss when attempting to analyse the implanted samples. A uniform capping layer is required to delineate the surface of the silicon substrate and also a proximity histogram to be used to measure the implantation profile. It was found that using 1D concentration profiles projected through the interface without using a proximity histogram approach had the effect of reducing the sharpness of the profile, this is due to the capping layer not being completely flat and so a 1D line projection through a curved surface leads to apparent shifting in the location of atoms.

Higher sample base temperatures during the analysis are known to reduce sample fracture rate but also have the effect of decreasing spatial resolution due to the increase in surface migration of mobile species. This can lead to a loss of crystallographic information within the data which is often used to calibrate the final 3D reconstruction[38]. This in turn has the potential to limit the accuracy of length measurements, i.e. the dopant distribution profiles, within the reconstruction.

The rate of increase in tip diameter is likely also higher in the initial stages of analysis, which leads to a rapid and non-linear increase in standing voltage required to maintain a constant evaporation rate. Ideally, reconstructions should be carried out over a region of uniform standing voltage in order to remove voltage based reconstruction artefacts. This also allows easier integration of total implanted dose due to the effectively cylindrical symmetry of the sample [18].

### *Comparison with SIMS*

As with all time-of-flight mass spectrometry techniques including SIMS and APT, mass spectra overlaps between different species can lead to difficulty in determining their concentration and location. Deconvolution of signal contributions to overlapping mass spectra peaks can allow a statistical determination of the contributions of each species to a specific peak. However, this deconvolution is a statistical approach, and does not resolve the identities of individual ions contributing to the overlapping peaks. This can limit the characterisation of local chemistry in regions of the analysis.

Phosphorus 'pile up' at the silicon/silicon oxide interface [39], known interfacial mixing artefacts [4], reduced sensitivity to changes in composition at sharp interfaces compared to APT [27] and mass spectra overlaps between silicon hydride  $^{31}\text{SiH}^+$  and phosphorus  $^{31}\text{P}^+$  ions [23, 26] [40] can all lead to difficulty in quantifying precise phosphorus profiles using SIMS. A major advantage of APT over SIMS is the ability to select a nano-scale region for analysis, this could be used to analyse a section of implanted material perpendicular to the plane of implantation in order to minimise the effect of hydrides when analysing through the capping layer. This approach has been used successfully when analysing multilayer systems [31] and would also allow a large implanted region to be analysed. This approach is much more time and cost intensive and would likely only be performed in order to give a comparisons to the more conventional top down analysis.

### *Capping layers*

In order to successfully preserve the implanted surface of material for optimal APT analysis, the most practical approach is to first bury this surface underneath an appropriate capping material. This capping layer must have sufficient thickness so as to protect the substrate during FIB preparation. Furthermore, it should enable a smooth transition through the interface into the implanted material during APT analysis in a similar manner to SIMS analysis of surfaces.

Nickel has good adhesion to the silicon substrate and a similar evaporation field to silicon, meaning minimal changes in required sample voltage when passing through the interface region. This will reduce the stress on the sample in the interface region and reduce fracture risk. However, there are mass spectra overlaps between  $^{62}\text{Ni}^{2+}$  and  $^{31}\text{P}^+$  ions, as well as  $^{62}\text{Ni}^+$  and  $2^{31}\text{P}^+$  compound ions. Whilst nickel and silicon have similar evaporation field requirements [38], there can still be artefacts at planar interfaces due to large discrepancies in required evaporation fields between layers of significantly different chemical compositions. This results in non-uniform field evaporation and ultimately leads to reconstruction artefacts which can distort the shape and apparent composition of volumes. This has been shown to significant problem when dealing with highly insulating gate oxides such as hafnium dioxide used in high-k dielectrics [41] inside nanoelectronic devices.

Chromium is another possible candidate for the capping material as it is highly adhesive [32, 42] but it also quickly oxidises into insulating chromium oxide, increasingly the likelihood sample fracture. Deposited polysilicon can also be used [18] but the high temperatures required for the formation of polysilicon are likely to cause diffusion of phosphorus ions away from their original implant location and so would not be viable for this material system. Changing to the use of cobalt will remove the overlap problem between the nickel and silicon and instead reduce it with the potential introduction of compound ions at 59 Da in the form of Co or SiP. This is a compound ion and is likely to only be present when using relatively high laser energies and low voltages.

A reduction in sample fracture risk through surface oxide removal before deposition of capping has not been observed in this study, but can be considered to be generally good practise in those situations where adhesion of capping layers may be difficult. However, there will be cases where a significant amount of phosphorus may be present in the silicon oxide layer and would thus be removed by such a treatment, it would be appropriate to attempt to analyse samples with a fully intact oxide layer. Exact causes for sample fracture during atom probe analysis are difficult to determine and can vary within and between material systems, however it is known that the application of higher fields in the experiment will cause higher stress on the samples[43].

It is often beneficial to first analyse control samples with identical capping layers and FIB preparation in order to determine the expected background levels of majority and minority species and species charge ratios. In the case of low concentration phosphorus in silicon, a control sample would also give an indication of the level of  $^{31}\text{SiH}^+$  that can be expected at the silicon/capping layer interface, as this can give a false positive addition to apparent levels of phosphorus at  $^{31}\text{P}^+$ . Although APT analysis is carried out in high vacuum, there is still a non-negligible amount of adsorbed gases present on the tip surface, and these will be evaporated alongside the constituent sample material. This not only has the effect of observing oxygen, hydrocarbons and hydrogen peaks in the mass spectra, but also the increased chance of evaporating substrate material as a complex ions, which in turn increases the chance of significant overlaps in the mass spectra, e.g.  $^{31}\text{SiH}^+$  overlapping with  $^{31}\text{P}^+$ . This increase in hydrides can also be observed when evaporating through a deposited capping layer, as water and other contaminants can be trapped during deposition.

#### *Direct implantation into pre-fabricated silicon micro-posts*

A reduction in thermal tails was seen in the milled micro posts compared to a standard liftout when analysed under identical condition. This is believed to be due to the lack of a GIS deposited tungsten 'glue' section used in the liftout procedure which introduces a section of material of different thermal and electrical conductivity between the liftout material and the silicon post to which it is mounted. The overall background noise level was also found to be lower despite the similar number of ions present in both datasets.

Statistical extraction of the contribution of phosphorus to the region under the thermal tail can be carried out. However, like the peak deconvolution approach, it cannot be determined which of those individual ions contributing to the peak are phosphorus, just the relative fraction of them. As demonstrated by Figure 5, if these contribution cannot be discriminated on an ion-by-ion basis then

this peak will limit the accuracy of the measured phosphorus implantation profile, especially when low concentrations are being investigated.

Direct implantation of phosphorus ions into arrays of pre-fabricated micro posts was found to be a viable method of reducing sample preparation time by removing the requirement for FIB liftout of planar substrates. However, delamination of capping layers from these structures during APT analysis was found to occur and had destructive effect on neighbouring samples and local electrodes.

#### *Mass spectra overlaps*

Mass spectra overlaps due to thermal tails was shown to be more of an issue for the 2+ charge state than the 1+ due to the increased proximity of the mass peaks of silicon and phosphorus in the 2+ state and the majority of silicon ions preferentially evaporating in the 2+ state.

Unlike silicon, phosphorus is shown to be present in significant quantities both in the 1+ and 2+ charge states and full contributions from each are required in order to gather an accurate implantation profile. By either reducing the thermal tail contributions in the 2+ charge state or by ensuring the majority of phosphorus evaporates in the 1+ state, the quantification of the phosphorus concentration and its spatial distribution becomes substantially easier.

Since there is a greater separation between silicon and phosphorus peaks when both are in the 1+ charge state, maximising the number of ions evaporated in the 1+ charge state would be ideal. This can be carried out through increasing the laser energy per pulse which has the effect of reducing the voltage required for field evaporation for a given evaporation rate. It can also have the effect of increasing the amount of delayed evaporation in the form of 'thermal tails', therefore it would be preferable to balance the electric field conditions in the APT experiment so as to minimise the thermal tails as much as possible, while favouring evaporation in the 1+ charge state. For the LEAP 3000X HR, laser pulse energies of up to 1 nJ, can be used to increase evaporation in the 1+ charge state but this has the effect of high preferential evaporation from the laser incident side, causing preferential evaporation and a non-hemispherical tip shape which can cause reconstruction artefacts [44]. High laser pulse energies also can lead to surface migration of mobile species such as phosphorus[45]. This laser induced surface migration would also reduce the effectiveness of cluster based analysis due to the artificial segregation of mobile species to the laser incident side. It was been found that 0.4 nJ per pulse at 200 kHz gives approximately equal contributions from phosphorus in the 2+ and 1+ charge states with minimal silicon thermal tails in milled micro-post specimens. Analysis of liftout samples using identical conditions gave reduced phosphorus contributions in the 2+ charge state and increased thermal tails such that any spatial information from that contribution would be reduced.

APT analysis using a UV laser in newer generation commercial instruments has been shown to reduce the thermal tails in silicon samples [46, 47] due to the decreased skin penetration depth and smaller spot size. This could be an approach that would increase the visibility of low concentration phosphorus. Changing the capping layer from nickel to a similarly behaving element such as cobalt (which has a single isotope and does not have any mass spectra overlaps with phosphorus apart from the compound silicon phosphide  $^{59}\text{SiP}^+$  ion) may improve the quantification of phosphorus ions closer to the surface or embedded in the oxide layer. When using laser pulsing in APT, the greater

the contribution of the laser to the evaporation process, the lower the standing voltage is required and therefore a reduction in sample stress. Laser energies of approximately 0.4 nJ to 0.6 nJ are at the upper range of those used for silicon whilst still retaining some spatial resolution [44, 45].

## Conclusions

The challenges of analysing low concentration species with nanometres of surfaces using APT been presented in detail. Known artefacts for such analyses and general approaches to minimise them have been discussed and applied to the example of the APT analysis of low concentration, sub surface phosphorus implantation profiles in single crystal silicon

- APT has been demonstrated to be a viable method of analysing near-surface implantation profiles of low concentration phosphorus in single crystal silicon.
- Direct implantation into pre-fabricated silicon micro-posts in order to reduce sample preparation time was successful and showed superior mass spectra than those of the liftout sample. Sample preparation for the milled micro posts took approximately one quarter of the time that the same number of liftout samples required.
- Nickel shown to be a reasonable initial choice for the implanted silicon substrates in terms of adhesion and evaporation field requirements but has the disadvantage of the mass spectra overlaps between the  $^{62}\text{Ni}^{2+}$  ion with  $^{31}\text{P}^+$  and the  $^{62}\text{Ni}^+$  ion with the  $2^{31}\text{P}^+$  compound ion peak.
- It was found that mass spectra overlaps from silicon, due to 'thermal tails' caused by delayed evaporation and the presence of the  $^{31}\text{SiH}^+$  ion at the capping layer/substrate interface, are the largest obstacle in accurately quantifying the phosphorus implantation profile due to the extremely low concentrations involved.
- In order to accurately characterise the implantation profile, contributions from phosphorus from each charge state that is detected in the experiment are required and analysis conditions must be optimised in order to maximise signal-to-noise ratio of each charge state.
- Dopant implantation profiles measured by APT demonstrated very good agreement with predicted by SRIM and C-TRIM. Comparison indicates that SRIM does not predict the long tail length of the profile which is likely due to channelling effects but C-TRIM performs better using reasonable tilt/twist parameters.

## References

1. Saxey, D.W., et al., *Atom probe specimen fabrication methods using a dual FIB/SEM*. Ultramicroscopy, 2007. 107(9): p. 756-760.
2. Kambham, A.K., et al., *3D site specific sample preparation and analysis of 3D devices (FinFETs) by atom probe tomography*. Ultramicroscopy, 2013. 132: p. 65-69.
3. Koenraad, P.M. and M.E. Flatte, *Single dopants in semiconductors*. Nat Mater, 2011. 10(2): p. 91-100.
4. Baryshev, S.V., et al. *High resolution SIMS depth profiling of nanolayers*. ArXiv e-prints, 2012. 1204.
5. Syre, M., et al., *Evaluation of possible mechanisms behind P gettering of iron*. Journal of Applied Physics, 2011. 110(2): p. 024912.
6. Simons, D., et al., *Round-robin study of arsenic implant dose measurement in silicon by SIMS*. Applied Surface Science, 2006. 252(19): p. 7232-7235.
7. Rai, R.S. and S. Subramanian, *Role of transmission electron microscopy in the semiconductor industry for process development and failure analysis*. Progress in Crystal Growth and Characterization of Materials, 2009. 55(3-4): p. 63-97.
8. Pettersson, H., et al., *A Method for Producing Site-Specific TEM Specimens from Low Contrast Materials with Nanometer Precision*. Microscopy and Microanalysis, 2013. 19(01): p. 73-78.
9. Kempshall, B.W., et al., *Comparative evaluation of protective coatings and focused ion beam chemical vapor deposition processes*. Journal of Vacuum Science & Technology B, 2002. 20(1): p. 286-290.
10. Ronsheim, P., et al., *Impurity measurements in silicon with D-SIMS and atom probe tomography*. Applied Surface Science, 2008. 255(4): p. 1547-1550.
11. Thompson, K., et al., *Characterization of ultralow-energy implants and towards the analysis of three-dimensional dopant distributions using three-dimensional atom-probe tomography*. Journal of Vacuum Science & Technology B, 2006. 24(1): p. 421-427.
12. Inoue, K., et al., *Dopant distributions in n-MOSFET structure observed by atom probe tomography*. Ultramicroscopy, 2009. 109(12): p. 1479-1484.
13. Kuo-Fu, L., L. Yiming, and H. Chih-Hong, *Asymmetric gate capacitance and dynamic characteristic fluctuations in 16 nm bulk MOSFETs due to random distribution of discrete dopants*. Semiconductor Science and Technology, 2010. 25(4): p. 045006.
14. Yiming, L., et al., *Discrete Dopant Fluctuations in 20-nm/15-nm-Gate Planar CMOS*. Electron Devices, IEEE Transactions on, 2008. 55(6): p. 1449-1455.
15. Koelling, S., et al., *Direct Imaging of 3D Atomic-Scale Dopant-Defect Clustering Processes in Ion-Implanted Silicon*. Nano Letters, 2013. 13(6): p. 2458-2462.
16. Gorman, B. and T. Kelly, *Discussion of Standard Specimens for Performance Evaluation in Atom Probe Tomography*. Microscopy and Microanalysis, 2011. 17(SupplementS2): p. 850-851.
17. Polley, C.M., et al., *Exploring the Limits of N-Type Ultra-Shallow Junction Formation*. ACS Nano, 2013. 7(6): p. 5499-5505.
18. Prosa, T.J., et al., *Analysis of implanted silicon dopant profiles*. Ultramicroscopy, 2013. 132: p. 179-185.

19. Saeedi, K., et al., *Room-Temperature Quantum Bit Storage Exceeding 39 Minutes Using Ionized Donors in Silicon*. Science, 2013. 342(6160): p. 830-833.
20. Kane, B.E., *A silicon-based nuclear spin quantum computer*. Nature, 1998. 393(6681): p. 133-137.
21. Ruffell, S., P.J. Simpson, and I.V. Mitchell, *Electrical characterization of 5 keV phosphorous implants in silicon*. Journal of Applied Physics, 2005. 98(1): p. 013713.
22. Alves, A.D.C., et al., *Controlled deterministic implantation by nanostencil lithography at the limit of ion-aperture straggling*. Nanotechnology, 2013. 24(14): p. 145304.
23. Schenkel, T., et al., *Critical issues in the formation of quantum computer test structures by ion implantation*. Nuclear Instruments and Methods in Physics Research B, 2009. 267: p. 2563-2566.
24. Shyh-Horng, Y., et al., *Monte Carlo simulation of arsenic ion implantation in (100) single-crystal silicon*. IEEE Transactions on Semiconductor Manufacturing, 1996. 9(1): p. 49-58.
25. Rubanov, S., et al., *TEM Study of the Damage Profiles induced by 14 keV P+ Implantation in Silicon and Germanium*. Microscopy and Microanalysis, 2007. 13(SupplementS02): p. 654-655.
26. Bolorizadeh, M.A., et al., *Quantitative depth profiling of ultra-shallow phosphorus implants in silicon using time-of-flight secondary ion mass spectrometry and the nuclear reaction  $31P(\alpha, p0)34S$* . Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2004. 225(3): p. 345-352.
27. Jamieson, D.N., et al., *Controlled shallow single-ion implantation in silicon using an active substrate for sub-20-keV ions*. Applied Physics Letters, 2005. 86(20): p. 202101.
28. Q.Yang, et al., *A combined approach for deposition and characterization of atomically engineered catalyst nanoparticles*. Catalysis, Structure & Reactivity, 2015. 1(3): p. 125-131.
29. Thompson, K., D.J. Larson, and R.M. Ulf, *Pre-sharpened and Flat-top Microtip Coupons: a Quantitative Comparison for Atom-Probe Analysis Studies*. Microscopy and Microanalysis, 2005. 11(SupplementS02): p. 882-883.
30. Mutas, S. and C. Klein, *Importance of the Protective Layers and the Specimen Preparation for Reproducible APT Results*. Microscopy and Microanalysis, 2011. 17(SupplementS2): p. 730-731.
31. Larson, D.J.T.J.P.R.M.U.B.P.G.T.F.K., *Local electrode atom probe tomography : a user's guide* 2013: Springer-Verlag New York. xvii, 318 pages.
32. Kölling, S. and W. Vandervorst, *Failure mechanisms of silicon-based atom-probe tips*. Ultramicroscopy, 2009. 109(5): p. 486-491.
33. Hoummada, K., et al., *Arsenic clustering during formation of the transient Ni silicide*. Scripta Materialia, 2012. 67(2): p. 169-172.
34. Griffin, P.B., S.W. Crowder, and J.M. Knight, *Dose loss in phosphorus implants due to transient diffusion and interface segregation*. Applied Physics Letters, 1995. 67(4): p. 482-484.
35. Stinger, G., *Determination of phosphorus distribution in the silicon dioxide/silicon layer system by secondary ion mass spectrometry*. Analytical Chemistry, 1988. 60(15): p. 1524-1529.
36. Thompson, K., et al., *In situ site-specific specimen preparation for atom probe tomography*. Ultramicroscopy, 2007. 107(2-3): p. 131-139.
37. Thompson, K., et al., *Minimization of Ga Induced FIB Damage Using Low Energy Clean-up*. Microscopy and Microanalysis, 2006. 12(SupplementS02): p. 1736-1737.
38. Gault, B., et al., *Atom probe microscopy*. Springer series in materials science 2012, New York: Springer. xxiii, 396 p.
39. Hofmann, S., *Approaching the limits of high resolution depth profiling*. Applied Surface Science, 1993. 70-71, Part 1: p. 9-19.

40. Moraru, D., et al., *Atom devices based on single dopants in silicon nanostructures*. Nanoscale Research Letters, 2011. 6(1): p. 1-9.
41. Gilbert, M., et al., *Atom probe analysis of a 3D finFET with high-k metal gate*. Ultramicroscopy, 2011. 111(6): p. 530-534.
42. Cojocaru-Mirédin, O., et al., *Atomic-scale redistribution of Pt during reactive diffusion in Ni (5% Pt)–Si contacts*. Ultramicroscopy, 2009. 109(7): p. 797-801.
43. Moy, C.K.S., et al., *Macroscopic electrical field distribution and field-induced surface stresses of needle-shaped field emitters*. Ultramicroscopy, 2011. 111(6): p. 397-404.
44. Gault, B., et al., *Impact of laser pulsing on the reconstruction in an atom probe tomography*. Ultramicroscopy, 2010. 110(9): p. 1215-1222.
45. Gault, B., et al. *Impact of directional walk on atom probe microanalysis*. ArXiv e-prints, 2015. 1510.
46. Bunton, J.H., et al., *Advances in Pulsed-Laser Atom Probe: Instrument and Specimen Design for Optimum Performance*. Microscopy and Microanalysis, 2007. 13(06): p. 418-427.
47. Kelly, T.F., et al., *Laser-Specimen Interactions in Atom Probe Tomography*. Microscopy and Microanalysis, 2012. 18(SupplementS2): p. 584-585.