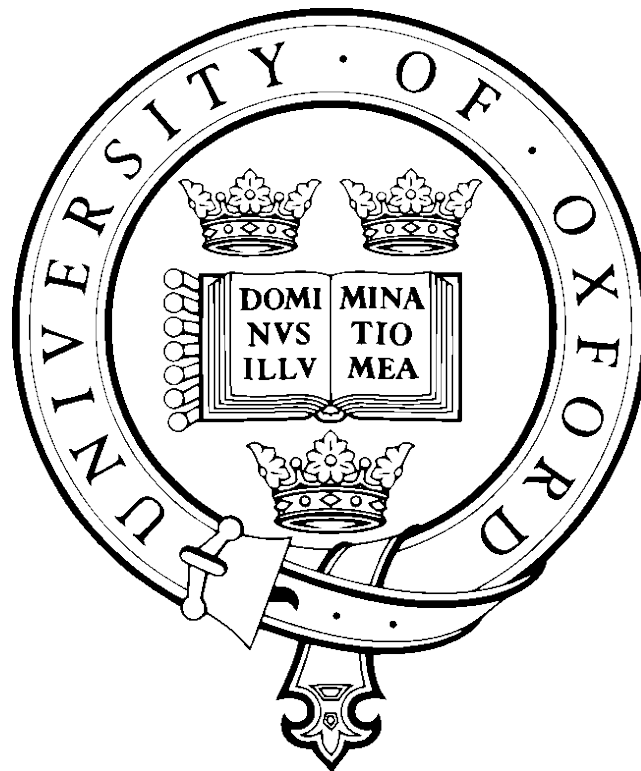


Defect characterisation of multicrystalline silicon

Chalothorn Lotharukpong

St.Cross College



Thesis submitted for the degree of Doctor of Philosophy

Hilary Term 2015

Supervisors: Prof. P.R. Wilshaw

Prof. Chris Grovenor

Defect characterisation in multicrystalline silicon

Chalothorn Lotharukpong

St. Cross College, Department of Materials, University of Oxford

Thesis submitted for the Degree of Doctor of Philosophy, Hilary Term 2015

Electron beam induced current (EBIC) and atom probe tomography (APT) were used in this study to determine electrical activities and impurity compositions at extended defects in multicrystalline silicon (mc-Si) samples. The results provide, for the first time, information regarding the chemical species present at defects whose electrical activity has previously been measured.

A new APT specimen fabrication process was developed with the ability to select a specific defect for APT analysis. Development of the APT specimen fabrication process proceeded by first selecting and optimising the preferential etching for nano-scale defect delineation. Three etchants were evaluated, namely Secco, Sirtl and Dash, from which the Secco etch was selected. Three parameters were optimised to produce etch pits with geometries that meet the requirements imposed by APT specimen fabrication methods. The optimum parameters were 0.05M potassium dichromate concentration, 20°C etch temperature, and 30sec etch time.

In the second stage, marking techniques were developed in order for the defects to be located throughout the APT specimen fabrication process. However, it became apparent that the conventional APT specimen fabrication method could not be used to fabricate APT specimens containing selected defects in a mc-Si sample. This led to the development of a novel APT specimen fabrication approach which allowed APT specimens to be fabricated, reproducibly, containing grain boundaries and isolated dislocations.

In order to evaluate accurately iron contamination in mc-Si, four atom probe parameters were optimised to maximise detection sensitivity: the evaporation rate, the laser beam energy, the pulse repetition rate and the specimen temperature. The optimisation process can be divided into two parts. In the first part, a matrix of pre-sharpened single-crystal silicon specimens was subjected to a variety of experimental parameters. The optimised parameters were determined to be 0.3% evaporation rate, 0.5nJ beam energy, 160kHz repetition rate and 55K specimen temperature. The second part was to determine the iron detection efficiency –the percentage of detected Fe ions that can be correctly identified as Fe– and sensitivity using these parameters to analyse a specially prepared iron calibration specimen. The values were determined to be a detection efficiency of about 35% and sensitivity of 54ppm or 2.70×10^{18} atom/cm³.

The APT specimen fabrication process and the optimised APT analysis parameters were used to analyse four extended defects in mc-Si samples subjected to three different processing conditions, namely gold-contaminated, as-grown and phosphorus diffusion gettering (PDG). The important aspects of the analysis are listed below:

- Gold was not detected at the grain boundary and its associated dislocations in the gold-contaminated specimen. The binding enthalpy of gold to such defects is thus less than 0.63eV.
- Iron was not detected in any specimen.
- Copper was observed at the grain boundary in the as-grown specimen in the form of individual atoms as well as clusters with diameters ranging between 4nm and 9nm. The electrical activity of the grain boundary was about 58%.
- Nickel and carbon were detected at the grain boundary in the post-PDG specimen with the former having platelet structures with diameters and thicknesses ranging between 4nm-7nm and 2nm-4nm, respectively. The recombination strength of the defect was about 22%.
- Two nickel clusters were found at the isolated dislocation in the post-PDG specimen. The clusters were spherical with an average diameter of 10nm. The distance between the two clusters was 35nm. The recombination strength of the defect was about 4%.

Preface

This thesis is an account of the work carried out by the author in the Department of Materials, University of Oxford, under the supervision of Dr P.R. Wilshaw from Michaelmas Term 2009 to Hilary Term 2015.

No part of this thesis has previously been submitted for a degree at this University or elsewhere. The work of other authors has been freely drawn upon and is duly acknowledged in the text. A list of references is given at the end of each chapter.

Some of the work described in the thesis has been presented in one conference (GADEST 2014) and published in the following paper:

Moldovan, G., Lotharukpong, S., & Wilshaw, P. (2014, November). Automated Defect Analysis in Solar Cells Using EBIC. In *ISTFA 2014: Conference Proceedings from the 40th International Symposium for Testing and Failure Analysis* (p. 156).

Acknowledgements

First and foremost, I would like to express my most sincere appreciation to my supervisor, Prof. Peter Wilshaw, for his continuous support, motivation, enthusiasm and many whiteboard discussions. He taught me various skills needed to conduct good research and how to be an independent thinker. He also spent a great deal of time correcting through my thesis, which made writing up a less painful experience. On a more casual note, I appreciate all the free beers I had in various pubs, particularly The Royal Oak. All in all, I could not have asked for a better supervisor.

I would also like to extend my thanks to Prof. Chris Grovenor, whose insightful knowledge was extremely valuable to my research, Dr. Gareth Hughes for Nvision training, and Dr. Emmanuelle Marquis for Nvision and APT training.

It is also a great pleasure to work with Dr. Grigore Moldovan on several occasions. He was extremely tentative during my experimental visits despite his busy schedule.

I am obligated to many of my friends from the semiconductor group who were always willing to help in various ways, most of which involved finding things around the lab and giving valuable suggestions. The lab would have been a rather lonely place without them. I would particularly like to thank Min Wu and Alan Xu for not only they are good friends outside work, but they also provide technical support on various aspects of my research.

I am truly indebted and thankful to my family, namely my mother, father, brother and sister, for the support they provided me not only during my research but also my entire life. Last but not least, I must acknowledge my wife and best friends who love and unwavering support that saw me through many ordeals throughout the course of my research.

Table of Contents

Chapter 1: Introduction and literature review	1
Chapter 2: Experimental techniques	39
Chapter 3: Defect delineation by preferential etching	68
Chapter 4: The development of atom probe specimen fabrication method	97
Chapter 5: Optimisation of LEAP parameters	153
Chapter 6: Defect characterisation in multicrystalline silicon samples	180
Chapter 7: Summary and future work	227
Appendix	234

1 Introduction and literature review

Table of Contents

1.1	Introduction	- 2 -
1.2	Multicrystalline silicon solar cells	- 2 -
1.2.1	Operating principle of solar cells	- 3 -
1.2.2	Mc-Si solar cell fabrication process.....	- 4 -
1.2.3	Recombination in mc-Si solar cells.....	- 4 -
1.3	Solar cell efficiency.....	- 5 -
1.3.1	Transition metal impurities.....	- 6 -
1.3.2	Extended defects.....	- 13 -
1.3.3	Interaction between metal impurities and extended defects	- 15 -
1.4	Phosphorus diffusion gettering.....	- 20 -
1.4.1	Principles.....	- 21 -
1.4.2	Limitations.....	- 21 -
1.5	Atom probe tomography	- 23 -
1.5.1	Principle of operation	- 24 -
1.5.2	The underlying physics.....	- 24 -
1.5.3	Laser-assisted atom probe tomography	- 26 -
1.5.4	Advantages and disadvantages of APT	- 27 -
1.6	Research overview	- 28 -
1.6.1	Summary of the experimental approach	- 29 -
1.6.2	Challenges	- 30 -
1.6.3	Scope of this thesis	- 32 -
1.6.4	References	- 32 -

1.1 Introduction

As the global economy continues to grow, it is expected that an increase in global energy consumption will continue (from $1.45 \times 10^{17} \text{W}$ in 2007 to a projected $2.17 \times 10^{17} \text{W}$ in 2035¹). However, with non-renewable energy resources (oil and natural gases in particular) predicted to run out in the near future, the current energy infrastructure will not be able to support future growth. Furthermore, public awareness of the impact of greenhouse gases on the environment has led to radical changes in policy-making in many countries, such as Japan, Germany and the United Kingdom. Consequentially, a global shift towards renewable energy resources is necessary in order to sustain, not only future demand, but also the global environment. There are many types of renewable energy resources, including solar photovoltaic (PV), solar thermal, wind, tidal, biomass, geothermal and nuclear.

Solar energy is a type of renewable energy source that involves directly converting sunlight into usable forms, i.e., heat or electricity. An even more encouraging fact is that the amount of sunlight reaching the Earth's surface is calculated as being about $1 \times 10^7 \text{ W}$ [2], which is four orders of magnitude larger than the global energy consumption rate in 2012.³ Therefore, it is theoretically possible to meet the global energy demand by capturing $>0.01\%$ of solar energy, making it one of the most economically and technologically viable energy resources in the world.

1.2 Multicrystalline silicon solar cells

There are two possible ways to utilise the solar energy. One is to use the energy directly, also referred to as 'direct applications', the most common example is solar thermal, whereby, for example, water is heated by solar energy. The other is to convert the solar energy into another form; this is known as an 'indirect application'. In modern society, the most common form of energy is electricity; the devices used to convert solar energy into this form of energy are solar cells.

1.2.1 Operating principle of solar cells

A commercial mc-Si solar cell consists of modules that are interconnected in an array. Each module, shown schematically in Figure 1-1, is a p-type mc-Si wafer that has been intentionally contaminated with impurities to create a one micron thick n-type region near the surface, with the interface between the two regions called the p-n junction. This process is commonly known as doping, and the most common impurity used to create the n-type layer is phosphorous.

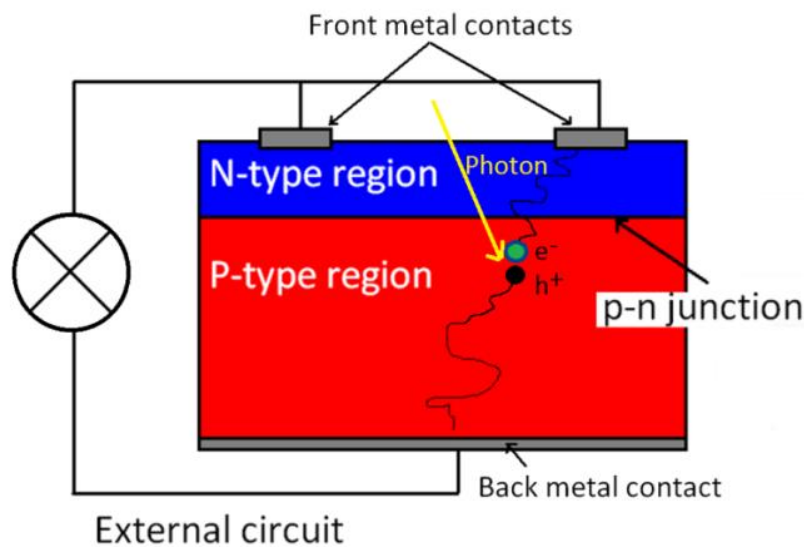


Figure 1-1. Schematic of a mc-Si solar cell module.

The module converts light into electricity by a quantum phenomenon known as ‘the PV effect’. The process is shown schematically in Figure 1-2. Photons, or packages of solar energy, are absorbed by the module. If the energy of the photons equals or exceeds the silicon band gap (1.12eV at 300K [4]), then valence electrons are excited to the conduction band, generating electron-hole pairs. The internal electric field associated with the p-n junction causes these pairs to separate, with the minority carriers, which are electrons in p-type and holes in n-type, drifting towards the junction. Once the carriers reach the junction, they are swept across and collected by metal contacts. A photocurrent is generated in an external circuit, which connects the top and the bottom contacts.

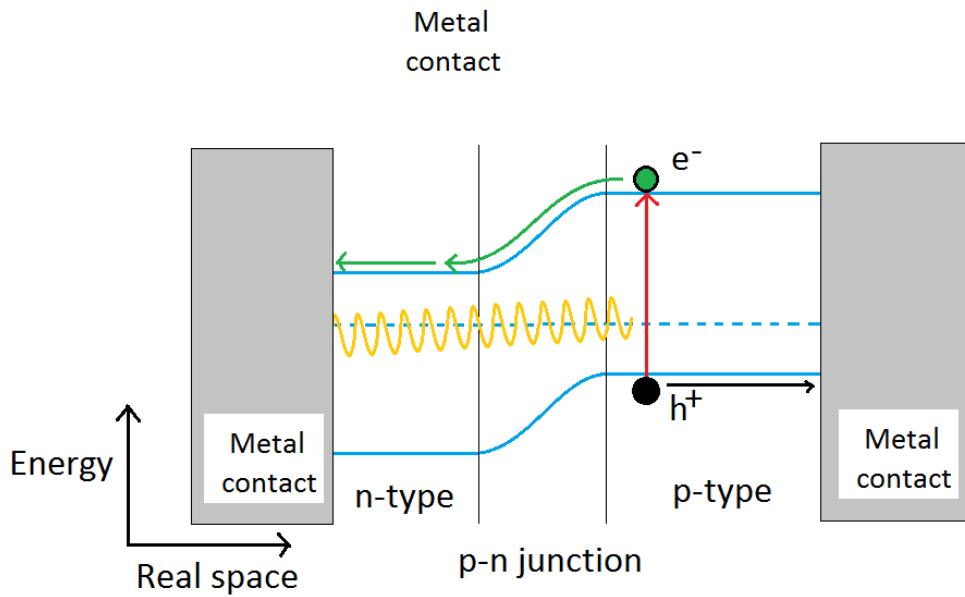


Figure 1-2. A one-dimensional energy diagram illustrating the PV effect.

1.2.2 Mc-Si solar cell fabrication process

Mc-Si wafers begin their life as a large ingot. The ingot is grown using a well-established industrial technique known as directional solidification. The process involves feeding a silicon feedstock into a fused silica crucible, where it slowly solidifies into an ingot. The heat flow and thermal gradient result in most crystals having columnar structures. Once the ingot cools down to room temperature, it is lifted out of the crucible and, subsequently, diced into square wafers using a wire-dicer. The wafers are typically 156 cm (6in) square and about 120 μm thick.

1.2.3 Recombination in mc-Si solar cells

The efficiency of a solar cell is dependent on the concentration of minority carriers reaching the p-n junction. A reduction in the carrier concentration occurs when carriers recombine with opposite charge carriers. This process can occur at the surface or in the bulk of the wafer. Where recombination takes place in the bulk of the wafer it can be separated into three main types: radiative recombination, Auger recombination and Shockley-Read-Hall (SRH) recombination.

Radiative, or band-to-band, recombination is the reverse process to that of photon absorption, i.e., a band-to-band recombination between an electron in the conduction band and a hole in the valence band. This process releases energy in the form of photons. Since Si has an indirect energy band structure, the process has a negligible effect on the efficiency of mc-Si solar cells.

Auger recombination is similar to radiative recombination, but the released energy is absorbed by a third carrier, usually an electron in the conduction band. The electron gradually loses its energy by colliding with atoms in the lattice, and finally drops back to the edge of the conduction band. This process dominates in high charge-injection densities found in heavily-doped regions.

SRH recombination is the recombination of electrons and holes through localised states in the silicon band gap. These states are introduced by impurities, particularly the transition metals. The recombination process is the most important in mc-Si solar cells because these states can trap charges with different momentums, thus allowing them to recombine without phonons.

1.3 Solar cell efficiency

Mc-Si solar cells are widely used in the mainstream solar cell market, but their performance does not yet to match that of sc-Si solar cells. This is due to the presence of extended defects, i.e. grain boundaries and dislocations, which are often decorated with metal impurities. Such impurities are introduced into the material throughout the production process. They introduce deep levels into the Si band gap, providing effective routes for electron and holes recombination. This has a negative impact on the minority carrier lifetime, τ_{minor} , and the minority carrier diffusion length, L_D , both of which are direct measurements of the device performance. Recent wire-dicing techniques employed in wafer production have decreased the wafer thickness to less than 200 μm .

The next section provides information about the metal impurities, particularly 3d-transition metals, and extended defects. The interaction of metal impurities with extended defects is also discussed in detail.

1.3.1 Transition metal impurities

Solar-grade mc-Si used for PV applications contains a high density of impurities, namely the light elements, oxygen and carbon, and highly mobile transition metals. The initial concentration of metal impurities in mc-Si can be as high as 10^{17} cm^{-3} [5], depending on the feedstock quality, the crystal growth techniques and the processing conditions.^{6,7} In neutron activation analysis (NAA) studies of directionally solidified mc-Si ingots,^{8,9} the main metal contaminants were found to be the 3d transition metals, notably iron, nickel, cobalt and copper.

The concentration of metal impurities in mc-Si ingots is known to vary both laterally and along the height of the Si ingot. Metal impurities segregate to three particular regions of the ingot: the bottom, the top and at the edges. The presence of the metal impurities at the bottom and edges can be explained by their in-diffusion from the external environment during crystal growth, i.e., from the crucible walls). Regarding the top, which is the last region to solidify, the segregation of metal impurities in the liquid phase occurs during cooling. The metal-rich liquid at the top of the ingot is the last to solidify, resulting in the accumulation of the metal impurities there.

1.3.1.1 Diffusion in Si

Diffusion of metal impurity atoms in the Si matrix can be expressed simply as movements of an atom through a solid solution. This requires the atom to jump over an energy barrier by thermal activation. The diffusion coefficient, D , can be written in the form of the Arrhenius equation:

Equation 1-1
$$D = D_0 \exp\left(-\frac{Q}{kT}\right)$$

Where Q is the activation energy, k is the Boltzmann constant, T is the absolute temperature, and D_0 is the pre-exponential factor that defines the attempt frequency of an atom jumping over the barrier. Metal impurities can occupy either the interstitial or the substitutional sites. The interstitial atoms can diffuse through Si by a direct translation from one interstitial site to another. The energy barrier associated with this transition is low. Furthermore, the Si lattice contains a large

concentration of unoccupied interstitial sites.¹⁰ Consequentially, they can rapidly diffuse through the material.

In contrast, the diffusion of substitutional atoms is mediated by the native point defects, namely vacancies and Si self-interstitials.^{11,12,13} These defects facilitate substitutional atom diffusion by the kick-out and the Frank-Turnbull (or dissociative) mechanisms. In the kick-out reaction, a substitutional atom (M_s) is translated to an interstitial site by replacing a Si self-interstitial (I). The Frank-Turnbull reaction involves a direct transition of the metal atom from the silicon lattice site to an interstitial site, leaving behind a vacancy, V. These mechanisms can be expressed as:



Both models assume that the atom can diffuse by the interstitial mechanism once it is at the interstitial site. It should also be noted that the reactions in Equation 1-2 and Equation 1-3 are exothermic and endothermic, respectively, in the forward direction. The diffusion coefficient of substitutional atoms can be written as:

Equation 1-4
$$D_{\text{substitutional}} = D_0 \exp\left(-\frac{(Q+Q_d)}{kT}\right)$$

Where Q_d is an extra energy term accounting for the formation of a point defect. The D values of atoms diffused by substitutional mechanisms are expected to be significantly lower than those diffused by the interstitial mechanism, due to the addition energy required for translation from the substitutional to the interstitial site, and a much lower concentration of native point defects.¹⁴

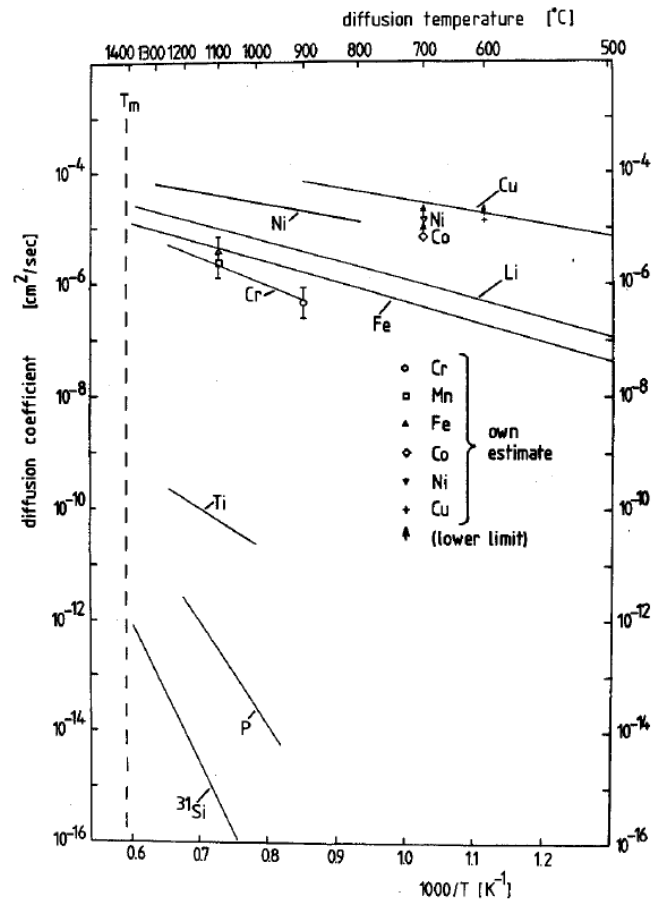


Figure 1-3. Dependence of the diffusion coefficient [cm²/sec] on temperature for different metal impurities, Si and P. The data are obtained from various sources and summarised by Weber et al.¹⁵.

Figure 1-3 shows the diffusivity of the metal impurities, primarily the 3d transition metals, in relation to a dopant (P) and the self-diffusion (³¹Si), as a function of temperature. It can be established that the diffusion coefficient of the 3d transition metals generally increases with atomic mass. This can be explained by the fact that the heavier metal impurities (e.g. Cu and Ni) mainly occupy the interstitial sites. Since the energy associated with the transition between the interstitial sites is small, these impurity atoms can diffuse rapidly through the silicon matrix. However, for the lighter elements (e.g. Ti and Mo), the substitutional component becomes significant. The activation energies of these elements are in the range of 0.5-1.0 eV, with the exception of Ti. It should also be noted that the diffusivity of transition metals is significantly higher than P and Si, which predominantly remain as substitutional atoms.

1.3.1.2 Solubility

Solubility is the metal concentration in the solution, at thermal equilibrium, at a defined temperature. Similar to diffusivity, solubility follows the Arrhenius equation:

Equation 1-5
$$C = C_0 \exp\left(-\frac{\Delta E}{kT}\right)$$

Where C_0 is the pre-exponential factor and ΔE is the energy of formation. However, this equation is only suitable for temperatures below the eutectic temperature (E_T) because no liquid component is involved. Therefore, the equation for temperatures above E_T is modified to:

Equation 1-6
$$\frac{C_s}{C_l} = \exp\left(\frac{\Delta S}{k} - \frac{\Delta H}{kT}\right)$$

Where C_s and C_l are the metal concentration in the solid and the liquid forms, respectively, ΔS and ΔH are the entropy and the enthalpy of formation from liquid to solid, respectively. The solubility data is often determined at high temperatures, so the solubility of metal impurities at lower temperatures is usually obtained by extrapolating the solubility line. It should be noted that the metal solubility is more temperature dependent than the diffusivity: high temperature results in exceptionally large solubility but decreases very rapidly towards room temperature, as illustrated in Figure 1-4.

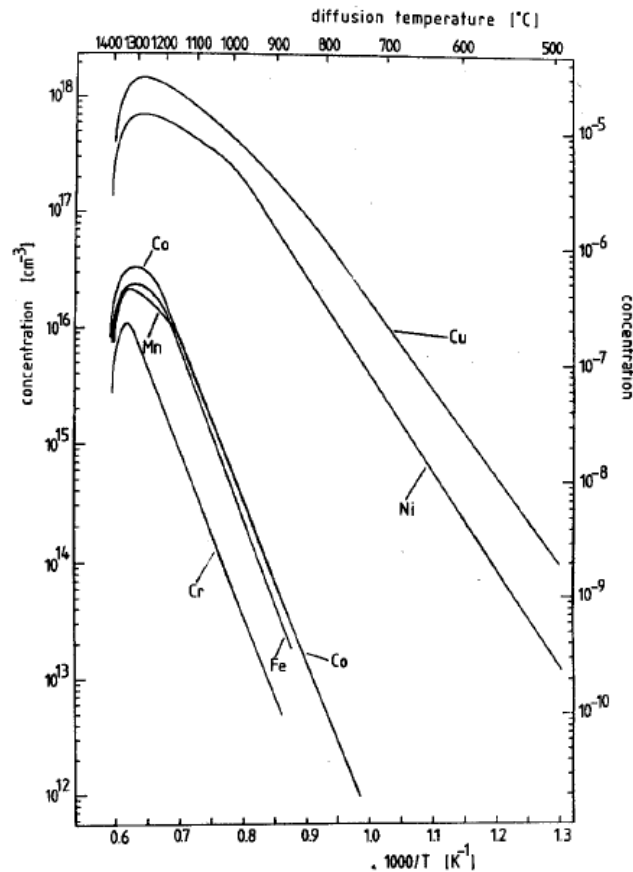


Figure 1-4. The calculated solubility lines of 3d-transition metals¹⁵.

1.3.1.3 Electrical activity of transition metal impurities

Transition metals are regarded as the most detrimental contaminants in the solar cell industry, owing to their electrical activity: they introduce deep states into the silicon band gap, allowing recombination of charge carriers. SRH theory is often used to describe the electrical activities of these impurities. The theory states that recombination of charge carriers is caused by a combination of the four different processes illustrated in Figure 1-5: electron emission/capture and hole emission/capture.

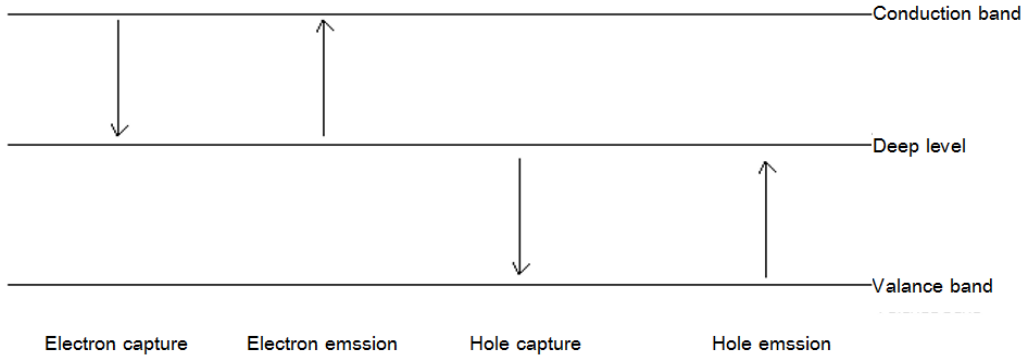


Figure 1-5. The four processes that make up the recombination, through a deep state, of the band gap.

At steady state, where the rate of all the reactions is in dynamic equilibrium, the net rate of recombination for a single level U_{SRH} is given by:

Equation 1-7
$$U_{SRH} = \frac{pn - n_i^2}{\tau_{p0}(n + n_1) + \tau_{n0}(p + p_1)}$$

With

Equation 1-8
$$\tau_{n0} = \frac{1}{\sigma_n v_{th} N_t}, \tau_{p0} = \frac{1}{\sigma_p v_{th} N_t}, n_1 = n_i \exp\left(\frac{E_t - E_i}{kT}\right), p_1 = n_i \exp\left(\frac{E_i - E_t}{kT}\right)$$

Where, τ_{n0} : fundamental lifetime of electrons;

τ_{p0} : fundamental lifetime of holes;

σ_n : capture cross-section of electrons;

σ_p : capture cross-section of holes;

n : concentration of electrons;

p : concentration of electrons and holes;

n_i : intrinsic charge carrier concentration;

v_{th} : thermal velocity of the charge carrier;

N_t : concentration of the metal impurity atom;

E_t : energy level of the impurity atom; and

E_i : intrinsic Fermi level.

The relationship between the SRH lifetime τ_{SRH} and U_{SRH} is given by $\tau_{SRH} = \Delta n_b / U$, where Δn_b is the excess carrier density in the bulk of the wafer. Therefore, Equation 1-7 can be rewritten as:

$$\text{Equation 1-9} \quad \tau_{SRH} = \frac{\tau_{p0}(n+n_1+\Delta n_b) + \tau_{n0}(p+p_1+\Delta n_b)}{p_0+n_0+\Delta n_b}$$

It is evident that the τ_{SRH} is dependent on the concentration of dopant (via n_0 and p_0), and trap-related parameters, namely the trap concentration (N_t), their capture cross-sections (via τ_{n0} and τ_{p0}) and their energy levels (E_t). In particular, the theory also states that the closer the energy level to the middle of the band gap, the more recombination active it will become. Furthermore, the τ_{SRH} can be further simplified in the case of low injection and high injection conditions. In the case of low injection, $\tau_{SRH} = \tau_{n0}$ in p-type Si while $\tau_{SRH} = \tau_{p0}$ for n-type Si. For high injection condition, $\tau_{SRH} = \tau_{n0} + \tau_{p0}$ for both n-type and p-type Si.

Table 1-1 presents the values of E_t , σ_n and σ_p for the transition metals. However, the values for high mobility metals, i.e. copper, cobalt and nickel, are not shown here. This is because isolated metal atoms are unstable at room temperature and, therefore, electrical parameters have yet to be unambiguously determined¹⁶. Another important property of the transition metals is that their capture cross sections are asymmetrical. Therefore, the recombination activity of a given metal impurity can vary depending on whether the Si wafer is n-type or p-type.

Impurity	RT lattice site	Type	Group	Energy (eV)	σ_n (cm ²)	σ_p (cm ²)	$k = \sigma_n / \sigma_p$
Ti	Interstitial	Donor	4	$E_C - 0.27$	3.1×10^{-14}	1.4×10^{15}	22
	Interstitial	D. donor		$E_V + 0.26$	1.3×10^{-14}	2.8×10^{-17}	460
V	Interstitial	D. donor	5	$E_V + 0.36$	5×10^{-14}	3.0×10^{-18}	17000
Cr	Interstitial	Donor	6	$E_C - 0.22$	2.3×10^{-13}	1.1×10^{-13}	2
Mo	Interstitial	Donor	6	$E_V + 0.28$	1.6×10^{-14}	6.0×10^{-16}	30
Fe	Interstitial	Donor	8	$E_V + 0.38$	5×10^{-14}	7×10^{-17}	700
Au	Substitutional	Acceptor	11	$E_C - 0.55$	1.4×10^{-16}	7.6×10^{-15}	0.02
Zn	Substitutional	Acceptor	12	$E_V + 0.33$	1.5×10^{-15}	4.4×10^{-15}	0.34
	Substitutional	D. acceptor		$E_C - 0.47$	1.3×10^{-19}	6.6×10^{-15}	0.00002

Table 1-1. Recombination parameters of various transition metals in silicon at room temperature¹⁷.

1.3.2 Extended defects

In addition to the metal impurities, extended defects, namely dislocations and grain boundaries, are common features in mc-Si.¹⁸ Dislocations are inhomogeneously distributed throughout the Si ingot,^{19,20} resulting in the presence of dislocation-free regions as well as those with dislocation density in the region of 10^4 – 10^6 cm⁻² within the same Si wafer. Still, defect density does tend to increase with the ingot height, due to the seeding effect.²¹ The following section describes the type of extended defects in mc-Si, and particularly their electrical activities.

1.3.2.1 Dislocations

Dislocations in Si crystals lie in the {111} glide plane and have Burgers vector $a/2\langle 110 \rangle$. There are two possible sets of {111} glide systems, namely the shuffle set and the glide set. The difference between these sets relates to the spacing between the {111} planes: the former are relatively wider than the latter. Since they have different core structures, their electrical properties must be different.

Given the standard solar cell processing temperature, the majority of dislocations are from the glide set^{20,22}. The dislocations that are mostly introduced into the mc-Si are screw and 60° dislocations. The screw dislocations can also dissociate into 90° and 30° Shockley partial dislocations, and the 60° dislocations into two 30° Shockley partial dislocations.

The effect of dislocation density on the τ_{minor} was theoretically studied by Donolato,²³ which suggests that the minority carrier recombination is significantly enhanced when the dislocation density is greater than 10^4 cm⁻². Although this seems to imply that the dislocations are electrically active, it is known that the dislocations themselves do not usually act as efficient recombination sites for the excess charge carriers.^{24,25,26} This is because ‘clean’ dislocations only introduce shallow states into the Si bandgap: (a) one-dimensional (1D) bands caused by the elastic strain field; and (b) a filled two-dimensional (2D) band induced by the Shockley stacking fault. The empty bands are located a short distance below the conduction band while the filled band is situated above the valence band. In

addition, the strain energy associated with the partial dislocations leads to the formation of the 2D band deeper into the band gap.²⁷ These shallow bands are responsible for the trapping effect often observed in minority carrier lifetime measurements.

It is well-established that the electrical activity dislocations are in fact caused by the decoration of impurities, particularly by the transition metals.^{28,29,30,31} These impurities introduce deep energy levels in the silicon band gap, thus providing effective recombination paths for minority charge carriers to recombine.

1.3.2.2 Grain boundaries

A grain boundary is an interface between two grains of different crystallographic orientations. The lattice mismatch between these grains causes disruptions in atomic arrangement, resulting in changes in the electrical property of the material. The electrical activity of grain boundaries originates from structural disorders and decorated metal impurities. The former can be separated into two types: (a) lattice strain and (b) dangling bonds. Lattice strain generally induces bending of the conduction and valence bands and, therefore, is electrically inactive. However, a grain boundary can become active if the strain is sufficiently large to force either the valence or the conduction bands deep into the silicon band gap. Dangling bonds introduce shallow bands into the band gap and do not lead to efficient recombination paths for minority carriers.

Similar to dislocations, the electrical activity of grain boundaries is significantly enhanced by the decoration of metal impurities.^{32,33} The degree of this enhancement is dependent on the characteristic of the grain boundary, with those having a larger degree of randomness (i.e. higher Σ value)^{34,35} having higher electrical activity, as illustrated in Figure 1-6. This effect can be explained by the increase in the dislocation's density at the grain boundary with its degree of randomness. Dislocations are known to act as favourable nucleation sites, which, in turn, form active recombination sites for minority carriers. Chen et al.³⁶ have reported that the electrical activity of some small angle grain boundaries can be stronger than that of the special or random grain

boundaries when they are intentionally contaminated with iron, due to the unusually high density of shallow bands and dislocations.

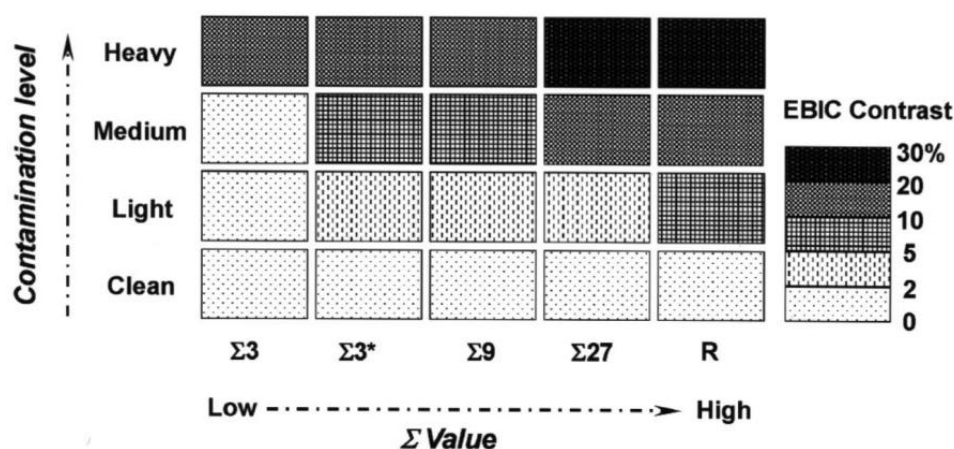


Figure 1-6. A graph showing the dependence of EBIC contrast on the characteristic of the grain boundary and contamination levels³⁷.

1.3.3 Interaction between metal impurities and extended defects

It can now be established that the 3d transition metals generally have high diffusivity, due to the high interstitial component, and this increases with temperature. Their solubilities are known to be strongly temperature dependent and extremely low at room temperature. In addition, extended defects are known to be preferential precipitation sites for metal impurities.^{38,39,40,41} Therefore, the distribution of these impurities in Si wafer and their electrical activity are influenced not only by their concentration in the bulk of the wafer, but also the cooling rate and the presence of dislocations. These two factors will be the focus of this review.

1.3.3.1 Metal impurities in mc-Si

In Si ingots, metal impurities are present in various forms: isolated metal atoms, complexes, metal silicide nanoparticles and metal-rich inclusions.

1.3.3.1.1 Isolated atoms

Isolated atoms can be located either in the interstitial or in the substitutional sites. The relative concentration of atoms between these sites depends on the type of metal impurities. In the 3d

transition metals, light metal atoms (from Ti to Fe) are mostly present as interstitials. As the metal becomes heavier, the isolated atoms tend to take the form of substitutional atoms. Note that the concentration of these atoms is very low since they are very mobile, and thus they tend to form precipitates.

The interaction between isolated metal atoms and dislocations has recently been summarised by Seibt et al.⁴², and can be categorised into five situations: (a) metal atom is chemically bound to a dislocation core; (b) segregation of metal atoms to the dislocation strain field as a result of elastic interaction (the strain field can accommodate both positive and negative misfit metals since the dislocation is associated with both compression and tension zones); (c) accumulation of metal impurities near the dislocation via intrinsic point defects (such migration occurs due to the ability of the dislocation to absorb these defects); (d) metal impurities heterogeneously precipitated at dislocations; and (e) dislocation-assisted precipitates growth by accommodating the volume misfit of the precipitates in the Si matrix.

1.3.3.1.2 Complexes

The electrically active interstitial atoms are unstable in silicon at room temperature. They tend to form complexes with dopants, mainly P and B in n-type and p-type Si, respectively. The most common type of complex is donor and acceptor pairs, which are bound by the electrostatic force between the two states. For example, pairs formed between the positively charged Fe interstitials and negatively charged B substitutional atoms are the most common in p-type Si. The pair have a donor and an acceptor state at $E_v+0.1$ eV and $E_c-0.29$ eV, respectively⁴³. Therefore, they act as recombination centres, reducing the minority carrier lifetime.

1.3.3.1.3 Metal silicides

Metal silicide nanoparticles up to tenths of a nanometre in diameter are the most frequently observed metal-rich particles in mc-Si. They are formed via a combination of processes⁴⁴: (a) metal impurities that are in solution during the high temperature processing become supersaturated upon

cooling, forming metal silicide precipitates at extended defects; (b) fast-diffusing metals can accumulate and form silicide precipitates at room temperature since they remain mobile even at lower temperature; and (c) if the local metal concentration in the melt is sufficiently high then a direct precipitation at the dislocations can occur. Such a situation can occur at the liquid–solid interface during the cooling of a specimen.

The chemical composition of metal silicide of the late 3d-transition metals (i.e. Co, Ni, Fe) takes the form MSi_2 [20], where M denotes the metal impurity—with the exception of copper, which has the equilibrium state Cu_3Si . The lattice misfit of Cu silicide is very large (150%) whereas other metal silicides have minor lattice misfits. Consequentially, precipitation of copper silicides is accompanied by dislocation formation in dislocation-free silicon. In contrast, metals such as Ni and Co generally do not form secondary defects unless they are sufficiently large precipitates. For such precipitates, the difference in thermal expansion between the silicide and silicon is sufficiently large that dislocations are punched out during cooling.

Several groups have studied co-precipitation of transition metal impurities.^{45,46} Multiple transition metals were diffused into the wafer and then subjected to low (655°C) and high (1200–1414°C) anneal/cooling regimes. It was found that the precipitates formed by the low-temperature regime were single-metal silicides. In contrast, the high-temperature regime exhibited a very different microstructure: large mixed-metal silicides with nano-scale phase separation. Unlike the precipitates observed in the low-temperature regime, the formation of these precipitates could not be explained using existing precipitation models and thermodynamic understanding.

A study of the precipitation behaviour of copper by Kusanagi et al.²⁶ has shown that this behaviour can be altered by the cooling rate. In their study, copper was introduced into Cz-Si wafers containing Frank partial dislocations. The specimens were then cooled at either high or low rates. The partial dislocations in the slowly cooled wafer were found to be free of impurities. In the wafer that was subjected to sharp cooling rate, however, copper silicides were observed to be decorating the

dislocations. The authors suggested that this was due to the competition between the oxygen precipitates often found in Cz-Si and the partial dislocations. In contrast, Fe impurities segregate to all types of defects, irrespective of the cooling rate⁴⁷. Furthermore, in the study by Wilshaw et al.²⁴ of the precipitation behaviour of Fe and Cu at stacking faults, transmission electron microscopy (TEM) did not observe any Fe precipitates, whereas reasonably large Cu precipitates are detected. It is likely that Fe atoms are uniformly distributed at the stacking faults.

The distribution behaviour of the transition metals is influenced by the cooling rate, and the extent to which this rate is important varies from metal to metal. The parameter that determines this property is the atomic flux of the metals, which is the product of solubility [cm^2/s] and diffusivity [atom/cm^3]. This controls the distance the metal impurity atoms are likely to travel before precipitation, when they become supersaturated.

Figure 1-7 shows that fast-diffusing metals, i.e. copper and nickel, mostly aggregate along the grain boundaries, whereas the low atomic flux species, such as Ti, are distributed in the bulk of the wafer. Iron, on the other hand, has an intermediate atomic flux. Thus, its distribution behaviour involves precipitates at both grain boundaries and in the bulk. However, one cannot conclude that Ti does not interact with grain boundaries. This is because X-ray fluorescence (XRF) can only detect precipitates and not isolated atoms. Another important feature is that metals with low atomic flux tend to form smaller and more closely-spaced precipitates, since their diffusivities are small. Therefore, low atomic flux metals are potentially more harmful to solar cell performance than those with high atomic flux. The results of a study by Rohatgi et al.⁴⁸ of the degradation effect of titanium, copper and iron, clearly reflect this understanding. They have showed that a concentration of Ti as low as 10^{11} cm^{-3} can cause a noticeable deterioration in the device performance, while for copper $2 \times 10^{15} \text{ cm}^{-3}$ is required to produce the same effect.

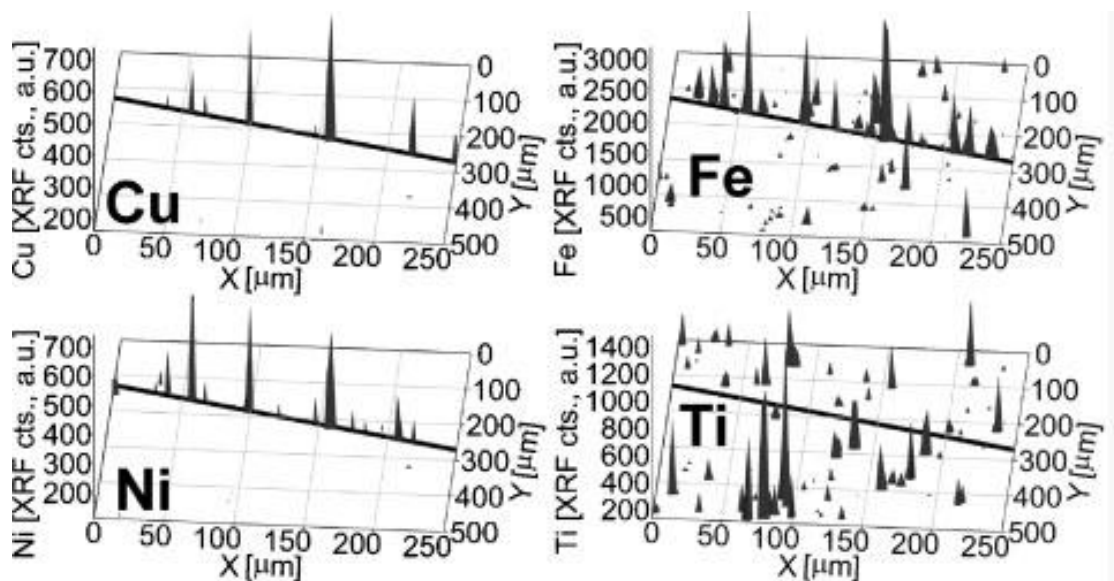


Figure 1-7. μ -XRF maps of four different types of metal impurities, namely Cu, Fe, Ni and Ti, in a mc-Si ingot⁴⁴.

1.3.3.1.4 Inclusions

Metal inclusions are thought to be of extrinsic origin. In other words, they are dissolved into the Si melt during the crystal growth step, rather than formed by the precipitation process. Buonassisi et al.⁴⁴ have suggested three reasons for this. First, the metal inclusions, such as Fe precipitates reported by Hugo et al.⁴⁹, are often found in oxidised chemical states. These states are known to be thermodynamically unstable in silicon⁵⁰ Second, the particles are frequently observed at the edges of the ingot and within the grain. Therefore, it can be suggested that these particles are introduced from the environment, e.g. from the crucible walls. Third, some inclusions are too large to be explained by the precipitation process as a result of metal impurities super-saturation during cooling. The presence of metal inclusions may influence the distribution behaviour of metal impurities in the bulk. Given the size of these particles, dissolution of these particles is very difficult. Thus, redistribution of the metal impurities cannot occur as effectively as redistribution of nanoparticles. This results in localised distributions of metal impurities in proximity to the inclusions.

1.4 Phosphorus diffusion gettering (PDG)

In the previous section, the presence of metal impurities and extended defects in the bulk of mc-Si wafers, and their impact on solar cell performance, was described. One of the methods used in the solar cell industry to reduce this effect is gettering. The technique removes metal impurities from the active region of the device. This is achieved by introducing preferential sites, also known as sinks, for metal impurities, in the regions where the impact of their electrical activity is minimised. Gettering is generally described as a three-step process. The impurities are: a) released from their stable states; b) migrated towards the gettering sites; and c) deposited at the sites.

Gettering of metal impurities can be achieved by exploiting the naturally occurring or intentionally introduced sinks within the bulk (internal gettering) or at the wafer surface (external gettering). Since solar cells are whole-wafer devices, external gettering is preferred. External gettering can be further classified according to the capturing mechanisms: relaxation and segregation. The former operates by introducing heterogeneous precipitation sites away from the active region of the device. Metal impurities are removed when they become supersaturated within the material, which can occur during cooling from a high temperature. The latter mechanism forms a gettering layer that has a higher solubility of metal impurities than the bulk, resulting in the migration of the impurities to the layer. For solar cell processing, segregation gettering is preferred because, unlike relaxation gettering, it does not require super-saturation of the metals.

There are two main gettering techniques that are routinely used in the industry: PDG and aluminium gettering (AG). In addition to their gettering properties, these techniques are integral parts of solar cell production: the phosphorus atoms act as negative emitters, while the aluminium layer serves as a back-surface contact. In the standard mc-Si solar cell manufacturing process, the duration of the phosphorus diffusion process is generally much longer than that of the aluminium metallisation,⁵¹ thus potentially allowing more impurities to be gettered. This section describes the principle, industrial-standard processing steps, and the limitations, of PDG.

1.4.1 Principles

The gettering mechanisms of PDG can be classified into either non-equilibrium or equilibrium processes. The equilibrium processes are segregation processes resulting from Fermi level effects: a) pairing of P with negatively charged metal species; and b) an increase in the solubility of the metal impurities due to the Fermi level shift in the high P concentration region.

Non-equilibrium gettering is facilitated by super-saturation of Si self-interstitials, Si_i , below the P-Si interface. The non-equilibrium Si_i concentration is due to the dissociation of inwardly diffusing phosphorus-interstitial pairs. The interstitials mediate transition metal impurity diffusion by the kick-out reaction.

The SiP precipitates formed in the P-rich region have been observed to act as efficient gettering sites, by providing preferential nucleation sites for the metal impurities. Furthermore, it has been suggested that these precipitates contribute to the production of excess silicon self-interstitials⁵².

The contribution of Si self-interstitials to the gettering efficiency of PDG remains a controversial topic. Kang et al.⁵³ suggested that the model could not explain the degradation in gettering efficiency at temperatures higher than a critical temperature. They have proposed an alternative model to explain this phenomenon. This model states that two rate-determining steps are involved: (a) the dissolution of metallic impurities from their stable states (e.g. precipitates) at low temperature; and (b) the P diffusion at high temperature, which can be described by the segregation model.

1.4.2 Limitations

The mobility of metal impurities plays a vital role in external gettering processes since the impurities have to be mobile in order to diffuse to the gettering layers. Therefore, PDG is effective at gettering metal atoms at interstitial sites.^{54,55} In contrast, the diffusion of substitutional atoms, and particularly the dissolution rate of metal precipitates (i.e. metal silicides and inclusions), are much slower than the interstitial diffusion. Hence, they limit the gettering ability of PDG.

As discussed earlier, the diffusion of the substitutional atoms can only occur if the intrinsic point defects are present. PDG is efficient at gettering substitutional atoms, owing to the unusually high concentration of Si self-interstitials injected into the bulk during the P in-diffusion process. This makes PDG very effective at gettering metal impurities, such as Au^{56,57} and Pt,^{58,59} that mainly reside in the substitutional sites.

Metal silicides are often found decorating the dislocations, producing highly active recombination centres. In order to remove these precipitates, they must first be dissolved back into the bulk. The dissolution rate has been shown by Seibt et al.⁶⁰ to be dependent on the concentration of the metal interstitials, the equilibrium interstitial metal impurity concentration, the precipitate radius and their volume density. This makes the dissolution of large precipitates, such as inclusions, very difficult to achieve unless longer gettering durations are used.

The inhomogeneous nature of dislocations leads to the formation of 'bad' grains, where the dislocation density is excessively high, and, therefore, has a direct impact on gettering. McHugo et al.⁶¹ have conducted a study of different regions of ribbon mc-Si. The specimens were gettered at different temperatures and their minority carrier diffusion lengths (L_D) were measured. The results showed that the degradation of L_D in high dislocation density regions ($10^7 - 10^9 \text{ cm}^{-2}$) increased with temperature while regions with low dislocation densities (less than 10^4 cm^{-2}) remained unaffected. Bentzen et al.⁶² have also conducted a similar study of the upper regions of a mc-Si block, to determine the correlation between the efficiency of PDG and dislocation density. They reported a variation in the minority carrier lifetime within the wafer. A significant enhancement in the minority carrier lifetime after PDG was observed in the good grains. Conversely, the minority carrier lifetime of the bad grains remained the same as the pre-gettered wafer, despite a significant removal of metal impurities by PDG. Bentzen et al. have suggested that this could either be due to (a) the recombination activity of the dislocations, or (b) the metal impurities form non-getterable precipitates at the dislocations.

In addition, there is a maximum gettering temperature for a constant gettering time. This limitation arises from the fact that, at low temperature, the gettering efficiency is limited by: (a) the diffusion of metal impurities towards the gettering layer; (b) the dissolution rate of metal precipitates; and (c) the solubility of the metal impurities in the bulk. At high temperature, the amount of metal gettered is limited by the segregation coefficient, which decreases with higher temperatures. The dissolution of metal silicide and the formation of defects also leads to a higher concentration of smaller particles in the bulk, which contributes to the degradation of the material.⁶³

It is well-established that metal impurities can either segregate to the dislocation strain field or chemically bind to the dislocation core, with the latter being the upper limit for gettering efficiency due to the high binding energy⁶⁴.

Unfortunately, values for binding energies are currently very limited in the literature, and are generally derived mathematically. A theoretical study by Fujita et al.⁶⁵ has suggested that the substitutional copper atoms form a negative U-like ordering between the associated donor and acceptor states at a partial dislocation. Furthermore, the binding energy was found by these authors to be between 1.5eV and 2 eV.

The only experimentally determined binding energy, or more accurately the binding enthalpy, is that of oxygen to a dislocation which was determined by Senkader et al. ⁶⁶. The binding enthalpy of approximately 0.2eV was reported for the temperature range of 540°C to 650°C. At temperatures higher than 650°C, the binding enthalpy was found to be 0.74eV. The authors suggested that different species other than single oxygen atoms were responsible for the diffusion and binding of oxygen in silicon at temperatures below 650°C.

1.5 Atom probe tomography

Field ion microscope (FIM), which is the predecessor of APT, was first introduced by Müller,⁶⁷ in the 1950s. Since then, continuous development of the instruments has led to many groundbreaking capabilities, such as the ability to not only chemically identify individual atoms, but also to observe

their distribution in a very small volume at high spatial resolution. The range of analysable materials has also been expanded from metals to semiconductors,^{68,69,70} and even insulators.^{71,72,73} A review of this technique is provided in the following section.

1.5.1 Principle of operation

A needle-shaped specimen with an apex radius of 50nm to 100 nm is attached to a stage which is cryogenically cooled to a temperature between 20K and 120K.⁷⁴ The analysis chamber is maintained at ultra-high vacuum ($\sim 10^{-10}$ torr). A positive dc potential of tenths of mV is applied to the specimen. The surface atoms are then field evaporated by application of either high voltage (HV) or laser pulses at high frequency. They are then collected by a position-sensitive time of flight (ToF) detector. The chemical nature of the incoming ions is identified by determining their mass-to-charge state ratio. This is given by:

$$\text{Equation 1-10} \quad \frac{m}{n} = \frac{2e}{d^2} (V_{dc} + \alpha V_{pulse}) t^2$$

Where e is the charge of an electron, n is the charge-state of the field evaporated ion, V_{dc} and V_{pulse} are the standing and pulse potentials, respectively, α is a constant and t is the ToF. Thus, the instrument provides the chemistry of individual atoms as well as their positions, which, in conjunction with specimen erosion by field evaporation, allows three-dimensional, atom by atom, reconstructions of the specimen to be produced.

1.5.2 The underlying physics

The fundamental process in APT is the field evaporation (FEV) of surface atoms. This occurs in two stages: a) a thermally activated atom escapes the surface and is progressively ionised as it overcomes an energy barrier; and b) the ion can be further ionised to a higher charge state by 'post-ionisation'.

In the first stage, the FEV effect can best be described by a one-dimensional potential energy diagram. Several models have been proposed and they differ in terms of the position of the barrier,

and hence the path in which the surface atoms are ionised and evaporated. After much debate,^{75,76} it is generally agreed that the 'charge-draining' model is in fact the most realistic representation of the FEV effect. The model, shown schematically in Figure 1-8, was first introduced by Gomer⁷⁷ and further refined by Forbes.⁷⁸ In the absence of an electric field, E , the surface atom is considered to be partially ionised and the sublimation energy, which is the energy required to escape into a field-free space, is essentially Λ . However, when E is present, the ionic state of the atom becomes increasingly stable with respect to the distance from the specimen tip. At a critical distance, the ionic and the neutral potential curves combine to produce two distinct curves, which are referred to as the lower and the upper curves—the former being the escape path of the atom. The energy barrier is now reduced to $Q_n(E)$, due to the electric field and, to a smaller extent, the polarisation and partial ionisation of the atom. As the atom progresses along the escape path towards the barrier the electron charge is gradually drained away, resulting in the formation of ion with a departed charge of n . $Q_n(E)$ is sensitive to the function of E in such a way that it decreases with a higher electric field.

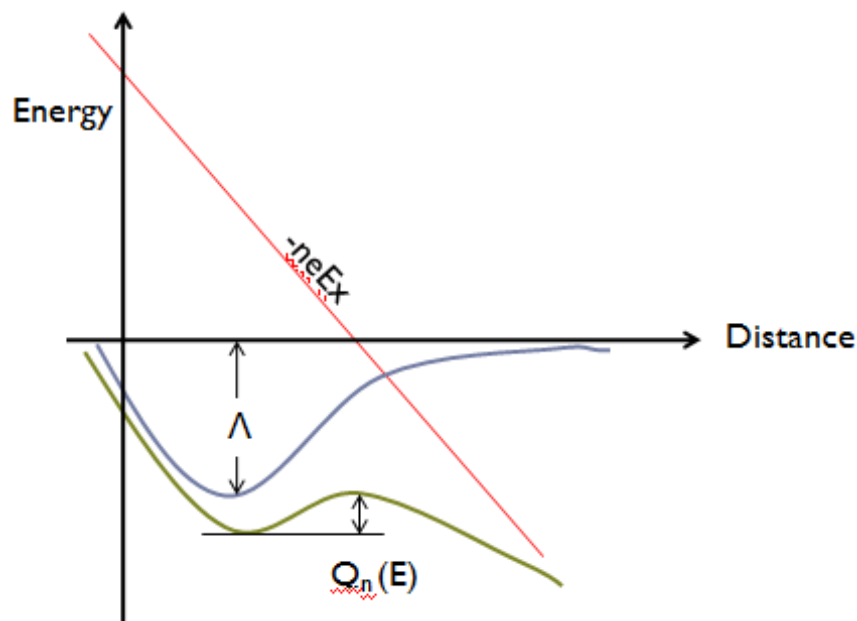


Figure 1-8. The charge-draining model. In the absence of an electric field, the depth of the potential well or the energy required for evaporation is given by Λ . Upon application of the field, the barrier is lowered to $Q(E)$, known as the Schottky hump. The charge of a surface atom is gradually drained away as it moves towards the hump.

Post-ionisation is believed to be responsible for the formation of ions with high charge states, which has been reported in numerous atom probe experiments.^{79,80,81} The process involves further ionisation of an ion to a higher charge state by the tunnelling of electron(s) to the specimen. Such a quantum effect can only occur at a critical distance from the specimen, where the electrons can occupy the empty states above the Fermi level. The relative abundance of different charge states is dependent on the applied field. The extent of this dependence has been thoroughly discussed in work by Kingham.⁸²

1.5.3 Laser-assisted atom probe tomography

In the early stages of APT development, nanosecond HV pulses were used to achieve ion evaporation. There are three problems associated with this. The first is a constraint imposed on the electrical conductivity of the specimen of no less than 10^2 S/m, which can only be obtained in heavily-doped semiconductors or metals. This limitation is caused by the inability to transmit the nanosecond pulse properly through the specimen. Second, low conductivity specimens have also been found to interact with the instrument (e.g. the chamber and the electrode) to form a low-pass resistive-capacitor filter, limiting the frequency of the HV pulses. Finally, there is an 'energy deficit' associated with HV pulses. Due to the wave-like nature of the pulse, a significant proportion of surface atoms evaporate prior to the maximum amplitude of the pulse. This results in an energy spread of the evaporated ions of typically a few hundred eV.⁸³ A study by Tsong et al.⁸⁴ of β -SiC whiskers has illustrated the effect of the energy deficit: the spectrum produced by HV pulsing contains many unidentifiable peaks, hence it has a negative impact on the mass resolution of the instrument.

In the early 1980s, work on FEV by photodissociation^{85,86,87} led to the advent of the first pulse-laser atom probe (PLAP) by Kellogg and Tsong.⁸⁸ In contrast to conventional HV-APT, FEV was induced by laser pulses. This has two advantages: (a) low conductivity materials, such as semiconductors and oxides, could be analysed;⁸⁹ and (b) the energy deficit caused by the HV pulses is eliminated—thus

higher mass resolution can be achieved without the aid of energy compensating devices¹⁰⁰. Despite these advantages, lasers were not widely implemented in the 1990s. This had to do with the additional cost of the laser, the difficulties in aligning the laser to the specimen tip, and uncertainties regarding various operation parameters.^{90,91} These technical problems could be overcome by using shorter laser pulses and better electronics.⁹² At the beginning of the 21st century, as the size of electronic devices became increasingly smaller, the topic regained momentum. With advances in laser technology and electronics, laser capability was significantly improved, and the technical limitations in relation to the early PLAP were successfully resolved.⁹³ In particular, a laser with the capability of producing pico or femtosecond pulses has been produced.⁹⁴

The FEV mechanism of laser pulses is not well understood, despite intensive research efforts. In the early studies by Kellogg et al. and Tsong et al.,^{95,96} nanosecond laser pulses were applied to semiconductors and metals using nanosecond pulses. Based on the findings of these studies, two mechanisms have been proposed: namely, thermal activation and photo-excitation. The former involves introducing a sharp temperature elevation of typically a few hundred Kelvin to the tip.⁹⁷ This sudden change in temperature causes the surface atoms to be field evaporated by thermal activation. This is known to be the dominant mechanism when using high-intensity laser pulses on silicon specimens and in a metallic sample where temperature fluctuation can be quantitatively measured. However, several studies of the application of ultra-short laser pulses in PLAP have raised questions regarding the validity of this theory. This is because the laser-specimen interaction time is reduced so much that an increase in temperature of that magnitude is improbable. For such case, the evaporation is assumed to be caused by the electrical component of the pulse, whereby the localised field is formed at the apex of the specimen and leads to subsequent evaporation.⁹⁸

1.5.4 Advantages and disadvantages of APT

The advantages and disadvantages of APT have been well summarised by Kelly and Miller.⁹⁹ The outstanding features of APT are the ability to obtain three-dimensional images so that compositional

variations can be observed with high analytical sensitivity. Three-dimensional reconstruction provides unmatched flexibility in term of data analysis and extremely high-resolution images, with a depth and lateral resolution of $<0.1\text{nm}$ and 0.3nm , respectively.

However, APT also has limitations. The first, and possibly the most critical issue, is the geometry of the specimen. To obtain data from a feature on a specimen surface, the specimen must first be lifted out of the surface and attached to a post. This is followed by sharpening the specimen until the tip has a suitable apex radius. This process can be very difficult to perform, especially when it is intended that small features, such as a dislocation, lie at the very tip of the needle. The mechanical stress imparted to the tip of the specimen is close to the adhesive strength of the specimen. When the stress becomes too large, the specimen fractures. Fortunately, the use of laser pulses reduces the fracture probability since the standing field is lowered by 10%–20%, and given that the stress in a specimen is proportional to the square of the applied field the mechanical stress is decreased by 20%–40%. The amount of data obtainable from the instrument is also limited by its field of view and the detection efficiency. The detection efficiency of the micro-channel detector used in today's APT is around 50%, and even less in the instrument used in this work (LEAP 3000HR), which has a detection efficiency of about 37%. This might be an important issue in experiments where 100% detection rate is needed. Nonetheless, from studies of semiconductor nanowires,^{100,101} small traces of metal impurities, such as Ge and Au, are observed. Therefore, this is not a major concern in most cases. The analysis volume of 80nm by 80nm by 200nm limits the use of the instrument for imaging larger features. Nonetheless, this should not prevent the usefulness of the instrument for characterising extended defects because they are much smaller than the analysis volume.

1.6 Research overview

Metal decorated defects in mc-Si wafers are known to reduce the performance of solar cells by acting as active recombination sites for electrons and holes^{102,103}. In the industry, the effect is usually minimised by the introduction of performance enhancement steps in to the fabrication process:

phosphorus in-diffusion (PDG) and aluminium back surface deposition gettering (ALG)). Bulk hydrogenation, which is an indirect result of silicon nitride surface deposition, is also used. Although these processes are known to increase the cell performance, some defects remain electrically active. This is thought to be due to the incomplete removal of metal impurities from the defects. However, the chemical nature of these impurities has yet to be experimentally determined.

The aim of this project is therefore to identify the impurities responsible for the electrical activity of defects, through the use of EBIC and APT. The former measures the recombination strength of defects by collecting excess charge carriers, which are created as a result of excitation by the incident electron beam. Since metal- decorated dislocations act as efficient recombination sites, the concentration of collected charge near to such a defect will be less than in the regions with clean dislocations or no dislocation, hence strongly recombination active defects can be selected. APT can create a three-dimensional reconstruction of the chemical composition of defects in the silicon matrix, thus allowing the observation, at the atomic scale, of impurities at the defects.

1.6.1 Summary of the experimental approach

This work represents the first time that individual dislocations have been subjected to atom by atom analysis of the impurities present in them. Thus, in the first instance, mc-Si samples were taken from the top of a commercial mc-Si ingot grown by directional solidification. This section of the ingot is located in the red-zone, which is usually discarded by the industry due to high concentrations of both metal impurities and defects. However, it provides a large number of defects that can be characterised and, hence, was chosen for this work. It is envisaged that future work would involve analysis from dislocations located at different positions throughout an ingot. The samples in this work are subjected to industrial-standard PDG in order to mimic the processing, and hence electrical activity, of defects in a commercial mc-Si solar cell. The phosphorus-rich layer is then removed to reveal the underlying 'gettered' region.

EBIC is the first characterisation step to be performed on the sample because, unlike APT, it is a non-destructive technique. The EBIC technique reveals the recombination activity of different defects and allows particular defects with, for example, strong activity to be identified. Preferential wet chemical etching is then used to physically mark the position at which the defects intersect the surface. Etching is chosen due to its simplicity and short preparation time. An APT specimen is then fabricated from a selected defect using a FIB-SEM dual beam system (Zeiss, Nvision40, hereafter referred to as the Nvision). This instrument possesses both an SEM and an FIB column that can operate simultaneously to perform high-precision machining in real-time. A micromanipulator and a gas-injector inside the specimen chamber also allow the instrument to carry out in-situ lift-out, whereby a small sample is removed from the bulk material and then attached to a specialised holder. Various APT fabrication methods have been postulated in the literature.^{104,105,106} However, they lack the accuracy to select specific defects and, hence, it was necessary for this work to develop a new method.

The APT specimen is then imaged in the TEM to check that the specimen contained the selected defect, and to perform some characterisation of the defect. The image can also be used to aid the specimen reconstruction from APT images. The specimen is then analysed using APT, and the data is then used to determine the chemical nature of the impurities and their compositions in the defect.

1.6.2 Challenges

The previous section gave an overview of the experimental approach followed in the course of this work. However, there are a number of particular challenges that need to be overcome if the electrical activity of dislocations is to be correlated with the impurity atoms decorating them. These challenges include the following:

- No previous work has been done to establish such correlations due to the difficulty in isolating individual defects within APT specimens. This is because APT requires a needle-shape specimen with an apex diameter of no more than 100nm.

- It was discovered during the course of the project that dislocations do not run normal to the mc-Si wafer surface, i.e., the orientation of the defects is a more complicated problem since not only is the position of the intersection of the dislocation surface important but so is its angle of inclination to that surface, as illustrated in Figure 1-9.

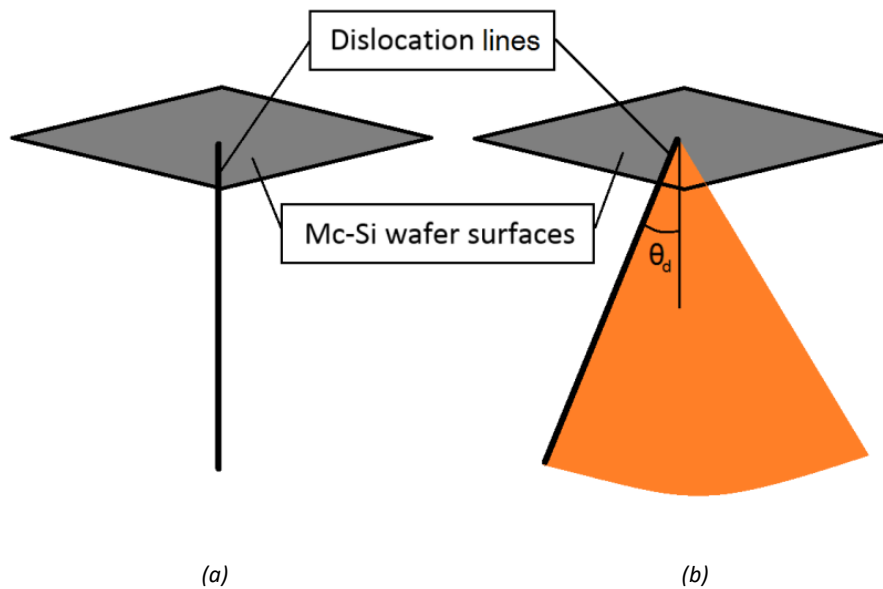


Figure 1-9. Schematic illustrations of a dislocation propagating through the mc-Si wafer, where (a) is propagation orientation expected at the start of the project, which is normal to the surface, and (b) is an observed propagation orientation, where the orange cone represent typical possible propagation directions. The angle between the dislocation line and the surface normal is labelled as ϑ_d .

- The long, thin atom probe specimens had to be fabricated such that a section of a selected dislocation lay within the $\sim 50\text{nm}$ radius of the specimen.
- Iron is expected to be a major impurity in defects.^{107,108} Hence, the APT analysis parameters must be optimised in order to maximise the iron detection sensitivity.
- Since a number of instruments are employed in this work, it is necessary to move specimens between the instruments. It is, therefore, important to minimise the chances of the specimens breaking during the transition.

1.6.3 Scope of this thesis

This thesis describes the development of preferential etching for the location of dislocations previously imaged in EBIC; and the optimisation of APT parameters, particularly the development of fabrication methods to produce atom probe specimens for the two defect types, i.e., grain boundaries and dislocations. The thesis includes a discussion of the sensitivity, as regards analysis by APT, of iron impurity atoms; and, finally, it presents data on the impurity decoration of phosphorus diffusion gettered dislocations in multi-crystalline material. Because of time constraints the specimen preparation techniques, once developed, could only be applied to a limited number of specimens, and thus impurity analyses were performed on relatively few grain boundaries and dislocations. These analysis results are presented in Chapter 6.

1.6.4 References

- ¹ JJ, C. (2010). International Energy Outlook 2010. Washington DC: U.S. Energy Information Administration.
- ² Grätzel, M. (2006). Photovoltaic performance and long-term stability of dye-sensitized meosocopic solar cells. *Comptes Rendus Chimie*, 9(5), 578-583.
- ³ Reddy, P. J. (2012). Solar Power Generation: Technology, New Concepts & Policy. CRC Press., 1-2.
- ⁴ Precker, J. W., & da Silva, M. A. (2002). Experimental estimation of the band gap in silicon and germanium from the temperature–voltage curve of diode thermometers. *American Journal of Physics*, 70(11), 1150-1153.
- ⁵ Davis Jr, J. R., Rohatgi, A., Hopkins, R. H., Blais, P. D., Rai-Choudhury, P., McCormick, J. R., & Mollenkopf, H. C. (1980). Impurities in silicon solar cells. *Electron Devices, IEEE Transactions on*, 27(4), 677-687.
- ⁶ Buonassisi, T., Istratov, A. A., Pickett, M. D., Rakotoniaina, J. P., Breitenstein, O., Marcus, M. A., ... & Weber, E. R. (2006). Transition metals in photovoltaic-grade ingot-cast multicrystalline silicon: Assessing the role of impurities in silicon nitride crucible lining material. *Journal of Crystal Growth*, 287(2), 402-407.
- ⁷ Kvande, R., Geerligs, L. J., Coletti, G., Arnberg, L., Di Sabatino, M., Øvrelid, E. J., & Swanson, C. C. (2008). Distribution of iron in multicrystalline silicon ingots. *Journal of applied physics*, 104(6), 064905.
- ⁸ Istratov, A. A., Buonassisi, T., McDonald, R. J., Smith, A. R., Schindler, R., Rand, J. A., ... & Weber, E. R. (2003). Metal content of multicrystalline silicon for solar cells and its impact on minority carrier diffusion length. *Journal of applied physics*, 94(10), 6552-6559.
- ⁹ Macdonald, D., Cuevas, A., Kinomura, A., Nakano, Y., & Geerligs, L. J. (2005). Transition-metal profiles in a multicrystalline silicon ingot. *Journal of Applied Physics*, 97(3), 033523.
- ¹⁰ Pritchard, R. E., Ashwin, M. J., Tucker, J. H., & Newman, R. C. (1998). Isolated interstitial hydrogen molecules in hydrogenated crystalline silicon. *Physical Review B*, 57(24), R15048.
- ¹¹ Aleksandrov, O. V., & Krivoruchko, A. A. (2007). Out-diffusion of impurity via the kick-out mechanism during gettering. *Semiconductors*, 41(9), 1048-1055.

- ¹² Car, R., Kelly, P. J., Oshiyama, A., & Pantelides, S. T. (1985). Microscopic theory of impurity-defect reactions and impurity diffusion in silicon. *Physical review letters*, 54(4), 360.
- ¹³ Car, R., Kelly, P. J., Oshiyama, A., & Pantelides, S. T. (1985). Microscopic theory of impurity-defect reactions and impurity diffusion in silicon. *Physical review letters*, 54(4), 360.
- ¹⁴ Bracht, H., Stolwijk, N. A., & Mehrer, H. (1995). Properties of intrinsic point defects in silicon determined by zinc diffusion experiments under nonequilibrium conditions. *Physical Review B*, 52(23), 16542.
- ¹⁵ Weber, E. R. (1983). Transition metals in silicon. *Applied Physics A*, 30(1), 1-22.
- ¹⁶ Istratov, A. A., & Weber, E. R. (1998). Electrical properties and recombination activity of copper, nickel and cobalt in silicon. *Applied physics A*, 66(2), 123-136.
- ¹⁷ Macdonald, D., & Geerligs, L. J. (2004). Recombination activity of interstitial iron and other transition metal point defects in p-and n-type crystalline silicon. *Applied Physics Letters*, 85(18), 4061-4063.
- ¹⁸ Hartman, K., Bertoni, M., Serdy, J., & Buonassisi, T. (2008). Dislocation density reduction in multicrystalline silicon solar cell material by high temperature annealing. *Applied Physics Letters*, 93(12), 122108-122108.
- ¹⁹ Seibt, M., Khalil, R., Kveder, V., & Schröter, W. (2009). Electronic states at dislocations and metal silicide precipitates in crystalline silicon and their role in solar cell materials. *Applied Physics A*, 96(1), 235-253.
- ²⁰ Baetzner, D, Tan, J, Hanton, K et al 2005, 'Dependence of phosphorous gettering of multicrystalline silicon on diffusion sheet resistance and ingot position', *European Photovoltaic Solar Energy Conference 2005*, ed. W Palz, H Ossenbrink, P Helm, WIP-Renewable Energies, Munich, Germany, 655-658.
- ²¹ Rynningen, B., Stokkan, G., Kivambe, M., Ervik, T., & Lohne, O. (2011). Growth of dislocation clusters during directional solidification of multicrystalline silicon ingots. *Acta Materialia*, 59(20), 7703-7710.
- ²² Bertoni, M. I., Colin, C., & Buonassisi, T. (2010). Dislocation engineering in multicrystalline silicon. *Solid State Phenomena*, 156, 11-18.
- ²³ Donolato, C. (1998). Modeling the effect of dislocations on the minority carrier diffusion length of a semiconductor. *Journal of Applied Physics*, 84(5), 2656-2664.
- ²⁴ Wilshaw, P. R., Fell, T. S., & Coteau, M. D. (1991). EBIC contrast of defects in semiconductors. *Le Journal de Physique IV*, 1(C6), C6-3.
- ²⁵ Kittler, M., Kveder, V. V., & Schröter, W. (1999). Temperature Dependence of the Recombination Activity at Contaminated Dislocations in Si: A Model Describing the Different EBIC Contrast Behaviour. *Solid State Phenomena*, 69, 417-422.
- ²⁶ Kusanagi, S., Sekiguchi, T., Shen, B., & Sumino, K. (1995). Electrical activity of extended defects and gettering of metallic impurities in silicon. *Materials science and technology*, 11(7), 685-690.
- ²⁷ Lehto, N., Marklund, S., & Yong-Liang, W. (1994). Electron states of a stacking fault ribbon in silicon. *Solid state communications*, 92(12), 987-989.
- ²⁸ Kittler, M., Seifert, W., Arguirov, T., Tarasov, I., & Ostapenko, S. (2002). Room-temperature luminescence and electron-beam-induced current (EBIC) recombination behaviour of crystal defects in multicrystalline silicon. *Solar energy materials and solar cells*, 72(1), 465-472.
- ²⁹ Radzimski, Z. J., Zhou, T. Q., Buczkowski, A., Rozgonyi, G. A., Finn, D., Hellwig, L. G., & Ross, J. A. (1992). Recombination at clean and decorated misfit dislocations. *Applied physics letters*, 60(9), 1096-1098.

- ³⁰ Kveder, V., Kittler, M., & Schröter, W. (2001). Recombination activity of contaminated dislocations in silicon: A model describing electron-beam-induced current contrast behavior. *Physical Review B*, 63(11), 115208.
- ³¹ Knobloch, K., Kittler, M., & Seifert, W. (2003). Influence of contamination on the dislocation-related deep level C1 line observed in deep-level-transient spectroscopy of n-type silicon: A comparison with the technique of electron-beam-induced current. *Journal of applied physics*, 93(2), 1069-1074.
- ³² Feklisova, O. V., Yu, X., Yang, D., & Yakimov, E. V. (2013). Influence of metal impurities on recombination activity of dislocations in multicrystalline silicon. *Semiconductors*, 47(2), 232-234.
- ³³ Maurice, J. L., & Colliex, C. (1989). Fast diffusers Cu and Ni as the origin of electrical activity in a silicon grain boundary. *Applied physics letters*, 55(3), 241-243.
- ³⁴ Ihlal, A., Rizk, R., & Duparc, O. H. (1996). Correlation between the gettering efficiencies and the energies of interfaces in silicon bicrystals. *Journal of applied physics*, 80(5), 2665-2670.
- ³⁵ Buonassisi, T., Istratov, A. A., Pickett, M. D., Marcus, M. A., Cizek, T. F., & Weber, E. R. (2006). Metal precipitation at grain boundaries in silicon: Dependence on grain boundary character and dislocation decoration. *Applied Physics Letters*, 89(4), 042102.
- ³⁶ Chen, J., Sekiguchi, T., Xie, R., Ahmet, P., Chikyo, T., Yang, D., ... & Yin, F. (2005). Electron-beam-induced current study of small-angle grain boundaries in multicrystalline silicon. *Scripta materialia*, 52(12), 1211-1215.
- ³⁷ Chen, J., Sekiguchi, T., Yang, D., Yin, F., Kido, K., & Tsunekawa, S. (2004). Electron-beam-induced current study of grain boundaries in multicrystalline silicon. *Journal of Applied Physics*, 96(10), 5490-5495.
- ³⁸ Kveder, V., Kittler, M., & Schröter, W. (2001). Recombination activity of contaminated dislocations in silicon: A model describing electron-beam-induced current contrast behavior. *Physical Review B*, 63(11), 115208.
- ³⁹ Bailey, J., Mc Hugo, S. A., Hieslmair, H., & Weber, E. R. (1996). Efficiency-limiting defects in silicon solar cell material. *Journal of electronic materials*, 25(9), 1417-1421.
- ⁴⁰ Kittler, M., Ulhaq-Bouillet, C., & Higgs, V. (1995). Influence of copper contamination on recombination activity of misfit dislocations in SiGe/Si epilayers: Temperature dependence of activity as a marker characterizing the contamination level. *Journal of applied physics*, 78(7), 4573-4583.
- ⁴¹ Périchaud, I. (2002). Gettering of impurities in solar silicon. *Solar Energy Materials and Solar Cells*, 72(1), 315-326.
- ⁴² Seibt, M., Kveder, V., Schröter, W., & Voß, O. (2005). Structural and electrical properties of metal impurities at dislocations in silicon. *physica status solidi (a)*, 202(5), 911-920.
- ⁴³ Brotherton, S. D., Bradley, P., & Gill, A. (1985). Iron and the iron-boron complex in silicon. *Journal of applied physics*, 57(6), 1941-1943.
- ⁴⁴ Buonassisi, T., Istratov, A. A., Pickett, M. D., Heuer, M., Kalejs, J. P., Hahn, G., ... & Weber, E. R. (2006). Chemical natures and distributions of metal impurities in multicrystalline silicon materials. *Progress in Photovoltaics: Research and Applications*, 14(6), 513-531.
- ⁴⁵ Buonassisi, T., Heuer, M., Istratov, A. A., Pickett, M. D., Marcus, M. A., Lai, B., ... & Weber, E. R. (2007). Transition metal co-precipitation mechanisms in silicon. *Acta Materialia*, 55(18), 6119-6126.
- ⁴⁶ Istratov, A. A., Buonassisi, T., Pickett, M. D., Heuer, M., & Weber, E. R. (2006). Control of metal impurities in "dirty" multicrystalline silicon for solar cells. *Materials Science and Engineering: B*, 134(2), 282-286.

- ⁴⁷ Shen, B., Sekiguchi, T., Zhang, R., Shi, Y., Shi, H., Yang, K., ... & Sumino, K. (1996). Precipitation of Cu and Fe in dislocated floating-zone-grown silicon. *Japanese journal of applied physics*, 35(6R), 3301.
- ⁴⁸ Rohatgi, A., Davis, J. R., Hopkins, R. H., Rai-Choudhury, P., McMullin, P. G., & McCormick, J. R. (1980). Effect of titanium, copper and iron on silicon solar cells. *Solid-State Electronics*, 23(5), 415-422.
- ⁴⁹ McHugo, S. A., Thompson, A. C., Mohammed, A., Lambie, G., Perichaud, I., Martinuzzi, S., ... & Häßler, C. (2001). Nanometer-scale metal precipitates in multicrystalline silicon solar cells. *Journal of Applied Physics*, 89(8), 4282-4288.
- ⁵⁰ Buonassisi, T., Marcus, M. A., Istratov, A. A., Heuer, M., Cizek, T. F., Lai, B., ... & Weber, E. R. (2005). Analysis of copper-rich precipitates in silicon: chemical state, gettering, and impact on multicrystalline silicon solar cell material. *Journal of applied physics*, 97(6), 063503.
- ⁵¹ Fenning, D. P. (2013). High-temperature defect engineering for silicon solar cells: predictive process simulation and synchrotron-based microcharacterization (Doctoral dissertation, Massachusetts Institute of Technology).
- ⁵² Seibt, M., Döller, A., Kveder, V., Sattler, A., & Zozime, A. (2000). Phosphorus Diffusion Gettering of Platinum in Silicon: Formation of Near-Surface Precipitates. *physica status solidi (b)*, 222(1), 327-336.
- ⁵³ Kang, J. S., & Schroder, D. K. (1989). Gettering in silicon. *Journal of Applied Physics*, 65(8), 2974-2985.
- ⁵⁴ Morehead, F. F., & Lever, R. F. (1986). Enhanced "tail" diffusion of phosphorus and boron in silicon: Self-interstitial phenomena. *Applied physics letters*, 48(2), 151-153.
- ⁵⁵ Phang, S. P., & Macdonald, D. (2011). Direct comparison of boron, phosphorus, and aluminum gettering of iron in crystalline silicon. *Journal of Applied Physics*, 109(7), 073521.
- ⁵⁶ Sveinbjörnsson, E. Ö., Engström, O., & Södervall, U. (1993). Phosphorus diffusion gettering of gold in silicon: The reversibility of the gettering process. *Journal of applied physics*, 73(11), 7311-7321.
- ⁵⁷ Kveder, V., Schröter, W., Sattler, A., & Seibt, M. (2000). Simulation of Al and phosphorus diffusion gettering in Si. *Materials Science and Engineering: B*, 71(1), 175-181.
- ⁵⁸ Falster, R. (1985). Platinum gettering in silicon by phosphorus. *Applied Physics Letters*, 46(8), 737-739.
- ⁵⁹ Spiecker, E., Seibt, M., & Schröter, W. (1997). Phosphorous-diffusion gettering in the presence of a nonequilibrium concentration of silicon interstitials: A quantitative model. *Physical Review B*, 55(15), 9577.
- ⁶⁰ Seibt, M., Sattler, A., Rudolf, C., Voß, O., Kveder, V., & Schröter, W. (2006). Gettering in silicon photovoltaics: current state and future perspectives. *physica status solidi (a)*, 203(4), 696-713.
- ⁶¹ McHugo, S. A., Hieslmair, H., & Weber, E. R. (1997). Gettering of metallic impurities in photovoltaic silicon. *Applied Physics A*, 64(2), 127-137.
- ⁶² Bentzen, A., Holt, A., Kopecek, R., Stokkan, G., Christensen, J. S., & Svensson, B. G. (2006). Gettering of transition metal impurities during phosphorus emitter diffusion in multicrystalline silicon solar cell processing. *Journal of Applied Physics*, 99(9), 093509.
- ⁶³ Rinio, M., Yodyunyong, A., Keipert-Colberg, S., Mouafi, Y. P. B., Borchert, D., & Montesdeoca-Santana, A. (2011). Improvement of multicrystalline silicon solar cells by a low temperature anneal after emitter diffusion. *Progress in Photovoltaics: Research and Applications*, 19(2), 165-169.

- ⁶⁴ Kittler, M., & Seifert, W. (2003). Estimation of the upper limit of the minority-carrier diffusion length in multicrystalline silicon: Limitation of the action of gettering and passivation on dislocations. *Solid State Phenomena*, 95, 197-204.
- ⁶⁵ Fujita, N., Jones, R., Öberg, S., Briddon, P. R., & Blumenau, A. T. (2008). A Theoretical Study of Copper Contaminated Dislocations in Silicon. *Solid State Phenomena*, 131, 259-264.
- ⁶⁶ Senkader, S., Giannattasio, A., Falster, R. J., & Wilshaw, P. R. (2002). On the dislocation–oxygen interactions in Czochralski-grown Si: oxygen diffusion and binding at low temperatures. *Journal of Physics: Condensed Matter*, 14(48), 13141.
- ⁶⁷ E.W. Müller, (1951) *Z. Physik* 136, 131.
- ⁶⁸ van Benthem, K., Lupini, A. R., Kim, M., Baik, H. S., Doh, S., Lee, J. H., ... & Pennycook, S. J. (2005). Three-dimensional imaging of individual hafnium atoms inside a semiconductor device. *Applied Physics Letters*, 87(3), 034104-034104.
- ⁶⁹ Cadel, E., Vurpillot, F., Lardé, R., Duguay, S., & Deconihout, B. (2009). Depth resolution function of the laser assisted tomographic atom probe in the investigation of semiconductors. *Journal of Applied Physics*, 106(4), 044908.
- ⁷⁰ Riley, J. R., Bernal, R. A., Li, Q., Espinosa, H. D., Wang, G. T., & Lauhon, L. J. (2012). Atom probe tomography of a-axis GaN nanowires: analysis of nonstoichiometric evaporation behavior. *ACS nano*, 6(5), 3898-3906.
- ⁷¹ Marquis, E. A., Yahya, N. A., Larson, D. J., Miller, M. K., & Todd, R. I. (2010). Probing the improbable: imaging C atoms in alumina. *Materials Today*, 13(10), 34-36.
- ⁷² Mazumder, B., Vella, A., & Deconihout, B. (2011). Evaporation mechanisms of MgO in laser assisted atom probe tomography. *Ultramicroscopy*, 111(6), 571-575.
- ⁷³ Blanc, W., Saint-Cyr, H. F., Martin, I., Le Coustumer, P., Hombourger, C., Neuville, D. R., ... & Guillermier, C. (2014, July). Erbium environment in glass-ceramics investigated by atom probe tomography. In *International Conference on Luminescence*.
- ⁷⁴ Miller, M. K., & Forbes, R. G. (2009). Atom probe tomography. *Materials Characterization*, 60(6), 461-469.
- ⁷⁵ Forbes, R. G. (1995). Field evaporation theory: a review of basic ideas. *Applied surface science*, 87, 1-11.
- ⁷⁶ Miller, M. K., & Smith, G. D. W. (1987). Atom probe microanalysis: Principles and applications to materials problems. Oak Ridge National Lab., TN (USA).
- ⁷⁷ Müller, E. W. (1956). Field desorption. *Physical Review*, 102(3), 618.
- ⁷⁸ Forbes, R. G. (1981). Charge hopping and charge draining: two mechanisms of field desorption. *Surface Science*, 102(1), 255-263.
- ⁷⁹ Müller, E. W., & Krishnaswamy, S. V. (1976). High Ionic Charges in Field-Evaporating 5 d Transition Metals. *Physical Review Letters*, 37(15), 1011.
- ⁸⁰ Krautz, E., & Leisch, M. (1980). Single-atom analysis of metals and alloys with the field-ion microscope atom-probe. *Microchimica Acta*, 74(5-6), 435-444.
- ⁸¹ Kellogg, G. L. (1981). Experimental evidence for multiple post-ionization of field-evaporated ions. *Physical Review B*, 24(4), 1848.
- ⁸² Kingham, D. R. (1982). The post-ionization of field evaporated ions: A theoretical explanation of multiple charge states. *Surface Science*, 116(2), 273-301.

- ⁸³ Tsong, T. T. (1984). Pulsed-laser-stimulated field ion emission from metal and semiconductor surfaces: A time-of-flight study of the formation of atomic, molecular, and cluster ions. *Physical Review B*, 30(9), 4946.
- ⁸⁴ Tsong, T. T., McLane, S. B., & Kinkus, T. J. (1982). Pulsed-laser time-of-flight atom-probe field ion microscope. *Review of Scientific Instruments*, 53(9), 1442-1448.
- ⁸⁵ Tsong, T. T., Block, J. H., Nagasaka, M., & Viswanathan, B. (1976). Photon stimulated field ionization. *The Journal of Chemical Physics*, 65(6), 2469-2470.
- ⁸⁶ Hagmann, M. J. (1999). Simulations of photon-assisted field emission: their significance in basic science and device applications. *Ultramicroscopy*, 79(1), 115-124.
- ⁸⁷ Niu, B. H., Beacham, J. R., & Bryant, P. J. (1977). Photon assisted field ionization. *The Journal of Chemical Physics*, 67(5), 2039-2042.
- ⁸⁸ Kellogg, G. L., & Tsong, T. T. (1980). Pulsed-laser atom-probe field-ion microscopy. *Journal of Applied Physics*, 51(2), 1184-1193.
- ⁸⁹ Kelly, T. F., Larson, D. J., Thompson, K., Alvis, R. L., Bunton, J. H., Olson, J. D., & Gorman, B. P. (2007). Atom probe tomography of electronic materials. *Annu. Rev. Mater. Res.*, 37, 681-727.
- ⁹⁰ Gault, B., Vurpillot, F., Vella, A., Gilbert, M., Menand, A., Blavette, D., & Deconihout, B. (2006). Design of a femtosecond laser assisted tomographic atom probe. *Review of Scientific Instruments*, 77(4), 043705.
- ⁹¹ Hashizume, T., Hasegawa, Y., Kobayashi, A., & Sakurai, T. (1986). Atom-probe investigation of III-V semiconductors: Comparison of voltage-pulse and laser-pulse modes. *Review of scientific instruments*, 57(7), 1378-1380.
- ⁹² Tsong, T. T., Liou, Y., & McLane, S. B. (1984). Methods for a precision measurement of ionic masses and appearance energies using the pulsed-laser time-of-flight atom probe. *Review of scientific instruments*, 55(8), 1246-1254.
- ⁹³ Bunton, J. H., Olson, J. D., Lenz, D. R., & Kelly, T. F. (2007). Advances in pulsed-laser atom probe: Instrument and specimen design for optimum performance. *Microscopy and Microanalysis*, 13(06), 418-427.
- ⁹⁴ Gault, B., Vurpillot, F., Vella, A., Gilbert, M., Menand, A., Blavette, D., & Deconihout, B. (2006). Design of a femtosecond laser assisted tomographic atom probe. *Review of Scientific Instruments*, 77(4), 043705.
- ⁹⁵ Kelly, T. F., & Miller, M. K. (2007). INVITED REVIEW ARTICLE: Atom probe tomography.
- ⁹⁶ Kellogg, G. L., & Tsong, T. T. (1980). Pulsed-laser atom-probe field-ion microscopy. *Journal of Applied Physics*, 51(2), 1184-1193.
- ⁹⁷ Kellogg, G. L. (1981). Determining the field emitter temperature during laser irradiation in the pulsed laser atom probe. *Journal of Applied Physics*, 52(8), 5320-5328.
- ⁹⁸ Vella, A., Vurpillot, F., Gault, B., Menand, A., & Deconihout, B. (2006). Evidence of field evaporation assisted by nonlinear optical rectification induced by ultrafast laser. *Physical Review B*, 73(16), 165416.
- ⁹⁹ Kelly, T. F., & Miller, M. K. (2007). INVITED REVIEW ARTICLE: Atom probe tomography.
- ¹⁰⁰ Perea, D. E., Allen, J. E., May, S. J., Wessels, B. W., Seidman, D. N., & Lauhon, L. J. (2006). Three-dimensional nanoscale composition mapping of semiconductor nanowires. *Nano letters*, 6(2), 181-185.

- ¹⁰¹ Perea, D. E., Hemesath, E. R., Schwalbach, E. J., Lensch-Falk, J. L., Voorhees, P. W., & Lauhon, L. J. (2009). Direct measurement of dopant distribution in an individual vapour–liquid–solid nanowire. *Nature Nanotechnology*, 4(5), 315-319.
- ¹⁰² Seifert, W., Morgenstern, G., & Kittler, M. (1993). Influence of dislocation density on recombination at grain boundaries in multicrystalline silicon. *Semiconductor science and technology*, 8(9), 1687.
- ¹⁰³ McHugo, S. A., Thompson, A. C., Perichaud, I., & Martinuzzi, S. (1998). Direct correlation of transition metal impurities and minority carrier recombination in multicrystalline silicon. *Applied physics letters*, 72(26), 3482-3484.
- ¹⁰⁴ Miller, M. K., Russell, K. F., Thompson, K., Alvis, R., & Larson, D. J. (2007). Review of atom probe FIB-based specimen preparation methods. *Microscopy and Microanalysis*, 13(06), 428-436.
- ¹⁰⁵ Cairney, J. M., Saxey, D. W., McGrouther, D., & Ringer, S. P. (2007). Site-specific specimen preparation for atom probe tomography of grain boundaries. *Physica B: Condensed Matter*, 394(2), 267-269.
- ¹⁰⁶ Choi, P. P., Al-Kassab, T. A., Kwon, Y. S., Kim, J. S., & Kirchheim, R. (2007). Application of focused ion beam to atom probe tomography specimen preparation from mechanically alloyed powders. *Microscopy and Microanalysis*, 13(05), 347-353.
- ¹⁰⁷ Coletti, G., Kvande, R., Mihailetchi, V. D., Geerligs, L. J., Arnberg, L., & Øvrelid, E. J. (2008). Effect of iron in silicon feedstock on p-and n-type multicrystalline silicon solar cells. *Journal of applied physics*, 104(10), 104913.
- ¹⁰⁸ Nærland, T. U., Arnberg, L., & Holt, A. (2009). Origin of the low carrier lifetime edge zone in multicrystalline PV silicon. *Progress in Photovoltaics: Research and Applications*, 17(5), 289-296.

2 Experimental techniques

Table of Contents

2.1	Introduction	- 41 -
2.2	Defect characterisation procedure	- 41 -
2.3	Materials	- 42 -
2.4	Sample preparation	- 42 -
2.4.1	Gold-contaminated mc-Si	- 42 -
2.4.2	Phosphorus diffusion into mc-Si	- 43 -
2.4.3	Iron-implanted s-Si.....	- 44 -
2.5	Electron Beam Induced Current (EBIC)	- 45 -
2.5.1	Operating principle	- 45 -
2.5.2	EBIC sample preparation.....	- 46 -
2.5.3	Recombination strength calculation	- 46 -
2.6	Preferential etching	- 47 -
2.6.1	Introduction	- 47 -
2.6.2	Experimental set-up.....	- 49 -
2.7	The Nvision.....	- 49 -
2.7.1	Instrumentation	- 49 -
2.7.2	SEM	- 51 -
2.7.3	FIB.....	- 52 -
2.7.4	APT/TEM specimen fabrication method.....	- 53 -
2.8	Transmission electron microscopy (TEM).....	- 57 -
2.9	APT	- 58 -
2.9.1	Instrumentation	- 58 -
2.9.2	Specimen alignment.....	- 58 -
2.9.3	Mass spectrum analysis	- 59 -
2.9.4	Three-dimensional reconstruction	- 59 -
2.9.5	Optimisation of LEAP parameters.....	- 60 -
2.9.6	Atom probe data interpretation	- 61 -
2.9.7	Compositional analysis.....	- 61 -
2.9.8	Calculation method for concentrations in atom/cm ³	- 62 -
2.9.9	Solute detection sensitivity.....	- 62 -
2.9.10	Manual noise correction	- 63 -
2.10	Miscellaneous techniques.....	- 64 -
2.10.1	Polishing.....	- 64 -

Chapter 2 – Experimental techniques

2.10.2	RCA cleaning procedure.....	- 65 -
2.10.3	Dimensional measurement methods.....	- 65 -
2.10.4	Sample holders.....	- 66 -
2.11	References	- 66 -

2.1 Introduction

This chapter describes the various instruments and techniques employed to characterise defects in mc-Si samples. The samples were subject to different processing conditions, as described in Section 2.4. The electrical activity of the defects was determined by EBIC. Mc-Si samples were preferentially etched to reveal surface defects. The Nvision was used to fabricate specimens for TEM and APT. TEM was used to verify the presence of the defect(s) in the APT specimens, and to observe their geometry. APT was used to identify impurities and their distribution behaviour at the defects. Other techniques relevant to this work are described in Section 2.10.

2.2 Defect characterisation procedure

A variety of instruments and techniques were used to characterise defects in mc-Si samples. The samples were subjected to different processing conditions, as described in Section 2.4. The instruments and techniques were applied to the 5mm square as-grown samples in the following order.

1. Sample polishing
2. RCA cleaning procedure
3. Silicon processing to simulate different stages in cell fabrication (see Section 2.4)
4. RCA cleaning procedure
5. EBIC specimen preparation
6. EBIC imaging
7. Preferential etching
8. Selection of a defect of interest
9. APT specimen fabrication
10. TEM imaging of the APT specimen
11. Low-energy cleaning of APT specimen
12. APT analysis of the APT specimen

Note that EBIC analysis was not performed on the gold-contaminated sample prior to the fabrication of the APT specimen (Section 6.4.1) because its only purpose was to determine whether the APT fabrication methods developed in Chapter 4 could be used to successfully fabricate APT specimens containing a defect.

2.3 Materials

Two types of materials were used in this work. The first type was a p-type mc-Si wafer with an electrical resistivity of $1\Omega\text{cm}$. This was taken from the top region of a commercial ingot produced by directional solidification. The wafer was diced into 5mm-square pieces using a wafer dicer at Begbroke Science Park, Oxford. The samples were used either as received or subjected to further processing. The processing is described in Section 2.4.

The second types of material used were two sc-Si wafers taken from two different ingots, both of which were grown using the Czochralski method. The electricity resistivities of these wafers were $11.43\Omega\text{cm}$ and $15.15\Omega\text{cm}$. Both wafers were diced into 10mm-square pieces using a wafer dicer at Begbroke Science Park, Oxford. They were then RCA cleaned to remove surface contaminants. A sample taken from the lower resistivity sample was used as received. A sample taken from the higher resistivity wafer was iron-implanted using the method described in Section 2.4.3.

All the wafers were kindly provided by Dr. Semih Senkader, REC Solar ASA, Skøyen, Oslo, Norway.

2.4 Sample preparation

2.4.1 Gold-contaminated mc-Si

The gold-contaminated sample was used to determine whether the APT fabrication method developed in Chapter 4 could successfully fabricate an APT specimen containing a defect. The intention was to decorate extended defects in the sample with Au atoms. The mass-to-charge state ratio of gold (195amu) is much higher than that of other chemical species normally found in mc-Si.

Hence, one would expect Au to be easily identified in the mass spectrum and the reconstruction of the specimen.

The sample was fabricated by mechanically and chemo-mechanically polishing one side of an as-grown mc-Si sample. The mechanical polishing stage was used to remove saw damage regions and comprised three steps. The grit size of the polishing pad was decreased after each step, from 8microns to 1micron to 1/4micron, with a polishing time of about 30min, 60min and 120min, respectively. A Chem-H polishing pad was used for the chemo-mechanical polishing stage, to remove sub-surface damage induced by the previous polishing stage. The polishing time was about 240min. All the polishing pads and the polishing machines were manufactured by Kemet International Ltd, Maidstone, Kent, UK. Surface contaminants were then removed using the RCA cleaning procedure. Prior to gold deposition, the sample was given an hydrofluoric acid (HF) dip to remove surface oxides. A ~50nm thick layer of gold was deposited onto the unpolished surface using a thermal evaporator at Begbroke Science Park, Oxford. The sample was then placed in an inert atmosphere, by encapsulating it inside a quartz tube filled with argon gas. The sample was annealed at 1000°C for one hour, and subsequently quenched in oil. According to the study of Au diffusion in Si by Jorden,¹ these conditions are sufficient to approximately homogenise the gold concentration throughout the wafer at its solid solubility value, which is about 10^{16} atom/cm³.

2.4.2 Phosphorus diffusion into mc-Si

Phosphorus diffusion was performed on a mc-Si sample, in an industrial-size furnace (suitable for 8" diameter wafers) manufactured by Thermco Systems©, to mimic the industrial standard emitter formation process that also results in PDG during solar cell processing. The specimen was annealed at 875°C for 22min while POCl₃, O₂ and N₂ gases were introduced into the system at flow rates of 650 SCCM, 500 SCCM, and 13.5 SLPM, respectively. The temperature was then ramped down at 10°C/min to 800°C, during which the POCl₃ and O₂ flows were turned off, while N₂ was allowed to flow. The sample was then taken out and allowed to cool to room temperature. Prior to EBIC

specimen preparation (step 6 in Section 2.2), the phosphorus silicate glass (PSG) layer and the P-rich layer, which were formed after PDG, were removed, in order to study the effect of PDG in the active region of the sample. This was achieved by submerging the sample in hot hydrochloric acid (HCl) for ten minutes, followed by chemo-mechanical polishing for another two hours.

I would like to thank Mr. Abu Bakr, who carried out PDG on the sample using the instrument and the procedure described above.

2.4.3 Iron-implanted s-Si

Iron is often considered to be the most important metal impurity in mc-Si solar cells because it is readily available in silicon feedstock, ingot crucibles and in the solar cell processing environment. The impurity can segregate to extended defects, which then act as effective recombination paths for minority carriers, reducing the solar cell performance. Various issues arise when detecting iron in silicon using the local electrode atom probe (LEAP): see Section 5.2 for an explanation in this regard. Therefore, the optimisation of the LEAP parameters was carried out, as described in Chapter 5, in order to maximise the detection sensitivity of iron. The iron-implanted sample was used to determine the iron detection efficiency of the optimised LEAP's parameters, as described in Chapter 5. Iron-implantation was performed on one wafer at the University of Surrey, Guildford, UK. Iron atoms were projected at the sample at a 7° angle relative to the surface normal. The iron-implantation dosage was 3.33×10^{15} ions/cm². The implantation energy was 100keV, and the current was 100.0 μ A/cm². Figure 2-1 shows the calculated depth iron concentration profile of the sample, calculated using the TRIM software. APT specimens were fabricated from the sample using the lift-out procedure, followed by annular milling techniques. This is described in Sections 2.7.4.1 and 2.7.4.2, respectively.

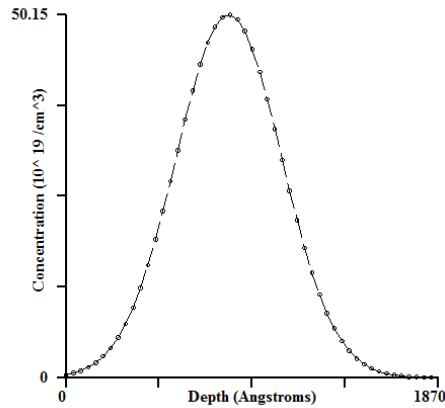


Figure 2-1. The iron concentration profile as a function of depth calculated using TRIMsoftware.

2.5 Electron Beam Induced Current (EBIC)

2.5.1 Operating principle

EBIC is a common technique for determining the electrical activity of the defects in semiconductor materials.^{2,3,4} A schematic of the instrument is shown in Figure 2-2. Similar to an SEM, an EBIC image is created by raster scanning a focused electron beam over the sample. Inelastic interactions between the incident electrons and the sample generate electron-hole pairs, which are separated and collected by the electrical contacts on either surface of the sample. The charges then create a small current in an external circuit, which is amplified and measured. This process is performed at each point of the raster scan position. The amount of current measured is then converted to the brightness value of the corresponding pixel on the display screen. The EBIC contrast of a defect C_d is defined as $C_d = (I_b - I_d) / I_b$, where I_b and I_d are the background and defect EBIC current, respectively.

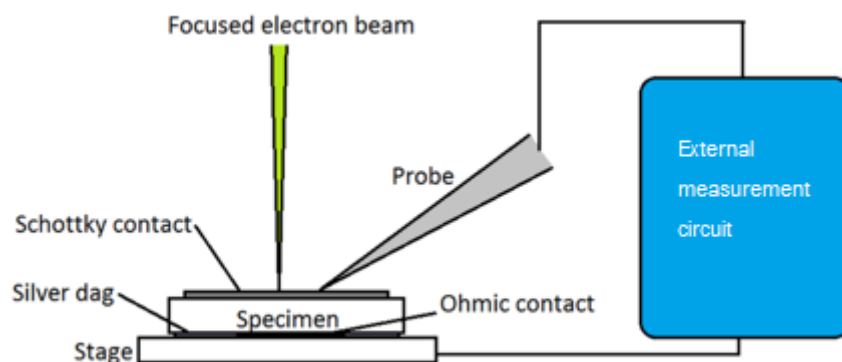


Figure 2-2. A schematic to illustrate the operating principle of the EBIC technique.

2.5.2 EBIC sample preparation

All EBIC specimens comprised Schottky and Ohmic contacts situated at the top (polished) and bottom (unpolished) surfaces of the samples, respectively.

The Schottky contact collects excess minority charge carriers by restricting the flow of charges in one direction. Schottky contacts were formed by depositing (through a shadow mask) a 3mm diameter, 30nm thick, aluminium layer using a thermal evaporator in the clean room at Begbroke Science Park, Oxford.

The Ohmic contact allows flow of charges in both directions. It was created by scratching the back sample surface using a pair of metal tweezers, on which InGa eutectic was applied. Scratching of the back-surface was carried out to allow the InGa to evenly wet the surface.

After EBIC analysis, the contacts were removed by immersing the specimen in hydrochloric acid at 50°C for 10min.

2.5.3 Recombination strength calculation

The measured EBIC contrast of a defect not only depends on its inherent properties as a centre for recombination (its recombination strength) but also geometric and instrument parameters. The larger the recombination strength of a defect the worse its impact on the efficiency of a solar cell. Donolato⁵ has shown that the relationship between defect contrast, C_d , and recombination strength, γ , can be written as:

Equation 2-1
$$C_d = \gamma F(R, d, L)$$

Where F is a function dependent on the range of the incident electrons (R), the defect depth (d) and the minority carrier diffusion length (L). In this work the accelerating voltage was kept constant at 20kV and the defects always ran approximately perpendicular to the specimen surface. The thickness of the Al contact was kept the same and variations in background diffusion length were assumed to have only a small effect on contrast. Thus, it is reasonable to assume that greater defect

contrast implies a larger recombination strength, and that contrast measurements between different specimens are broadly comparable.

Prior to taking contrast value measurements, the image contrast must be normalised: the brightness histogram of the image is stretched such that the histogram occupies the entire greyscale (from a contrast value of 0 to 255). A line was then drawn across the defect, from which a contrast profile along the line was determined. I_d was selected as the minimum defect brightness value. I_b was obtained by taking an average over a small distance range away from the defect. The normalisation and contrast measurements were carried out using **ImageJ** software.

I would like to take this opportunity to acknowledge Dr. Grigore Moldovan from Oxford Instruments NanoAnalysis, UK, for providing all of the EBIC images. EBIC imaging was performed using a commercial SEM (MIRA FEG-SEM) manufactured by Tescan®, Kohoutovice, Czech Republic. The instrument was equipped with an Omniprobe® 200 nanomanipulator, which was connected to the specimen stage via a signal amplifier. EBIC images were taken at 20kV accelerating voltage, 11.4mm working distance and a 19.8nm depth of focus. The images were taken at two different magnifications: 100x and 1000x. The beam intensities used at 100x and 1000x magnifications were set at 4 and 5, respectively.

2.6 Preferential etching

2.6.1 Introduction

Preferential etching was used to reveal defects intersecting the sample surface. The etch pits (dislocations) or grooves (grain boundaries), so formed, were then used as markers of the defect position for further processing in the FIB. In order for the pits or grooves to accurately locate the defects their width had to be small ($< \sim 100\text{nm}$) and reproducible.

The etching process relies on the oxidation of the silicon, followed by the dissolution of the oxides. By slowing down the oxidation reaction, etching at the perfect lattice occurs at a slower rate than at the defects, where the atomic bonds are weaker.

Most preferential etchants for silicon utilise hydrofluoric acid as a dissolving agent. At the same time, the oxidising agents and the chemical composition can vary significantly from one etchant to another, resulting in different etching behaviours. Table 2-1 contains a list of common preferential etchants, taken from S. J. Moss (1987).

Name	Composition	Etch rate at 20°C (µm/min)	Use
Dash etch	1 HF (49%): 3 HNO ₃ (70%): 10 CH ₃ COOH (100%)	0.13 (100) 0.005 (111)	Works on (100) and (111) planes
Sirtl etch	1 HF (49%): 1 CrO ₃ (5M)	3.0	Works on (111)
Secco etch	2 HF (49%): 1 K ₂ Cr ₂ O ₇ (0.15M)	1.5	Works on all crystallographic planes. Best with agitation
Yang etch	1 HF (49%): 1 CrO ₃ (1.5M)	1.5	Works on (100), (110) and (111) planes
Sopori etch	36 HF (49%): 20 CH ₃ COOH (glacial): 1-2 HNO ₃	5-20	Good for poly-silicon
Schimmel etch	2 HF (49%): 1 CrO ₃ (5M)	1.7-3.2	Sensitive to doping and agitation. Works for (100)

Table 2-1. Common preferential etchants for silicon, including their composition and etch rate at the temperature of 20°C, and crystallographic planes at which they etch well.

2.6.2 Experimental set-up

All the etching experiments were performed using the set-up shown in Figure 2-3. A polypropylene beaker containing the etchant sat in a Grant GD120 temperature-controlled bath. 20 ml of etchant was used for each sample. The beaker was covered with a polypropylene lid, with a small aperture at the centre through which a plastic-encapsulated thermocouple was inserted to measure the temperature of the solution directly. The beaker was left for about 30min prior to etching, to allow the solution to reach and stabilise at a desired temperature. Etching was performed by removing the thermocouple and carefully immersing the sample into the etchant through the aperture in the lid. After the specimen was removed from the etchant, it was immediately rinsed with plenty of deionised water to stop further reaction.

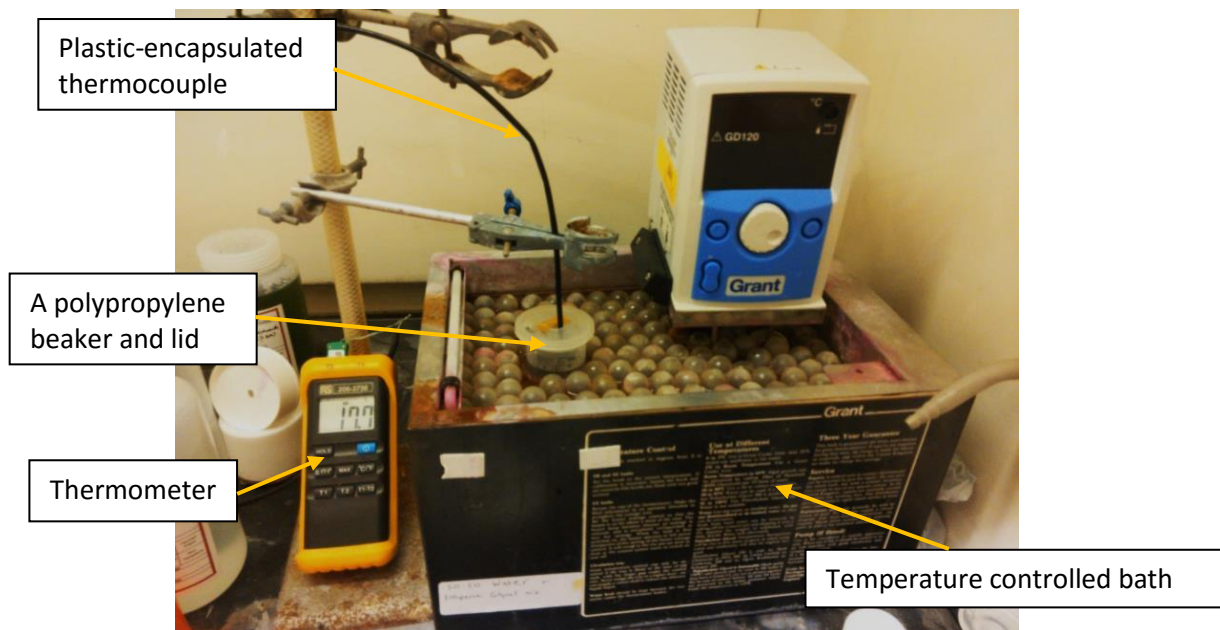


Figure 2-3. Equipment set-up for etching experiments.

2.7 The Nvision

2.7.1 Instrumentation

A commercial SEM-FIB dual-beam system (Nvision[®] cross-beam workstation), shown schematically in Figure 2-4, was used in this work. It was manufactured by Carl Zeiss Microscopy GmbH, Jena,

Germany. It was used to develop atom probe specimen fabrication methods, as well as to fabricate atom probe specimens.

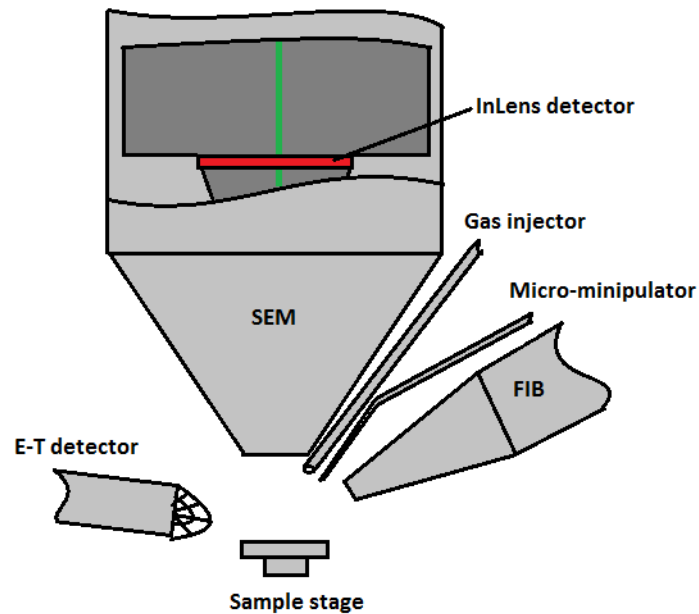


Figure 2-4. A schematic of the sample chamber inside the Nvision.

The instrument contained a vertical SEM column and a FIB column at 54° inclination, with the two beams coinciding at about a 5mm working distance. The SEM and the FIB columns utilised a Schottky field emission gun and a liquid-metal ion source (LMIS), respectively. The operating principles of SEM^{6,7} and FIB^{8,9,10} are well-documented and will not be described here. The parameters used to perform various operations associated with these columns are described, respectively, in Sections 2.7.2 and 2.7.3. The specimen stage had six-degrees of freedom, with range restrictions in most directions, as illustrated in Figure 2-5. A multi-channel gas-injector system (GIS) with a single extendable nozzle was used in conjunction with either the FIB or the SEM to perform a site-specific deposition. A tungsten micro-manipulator with adjustable translation steps was used to perform sample lift-out.

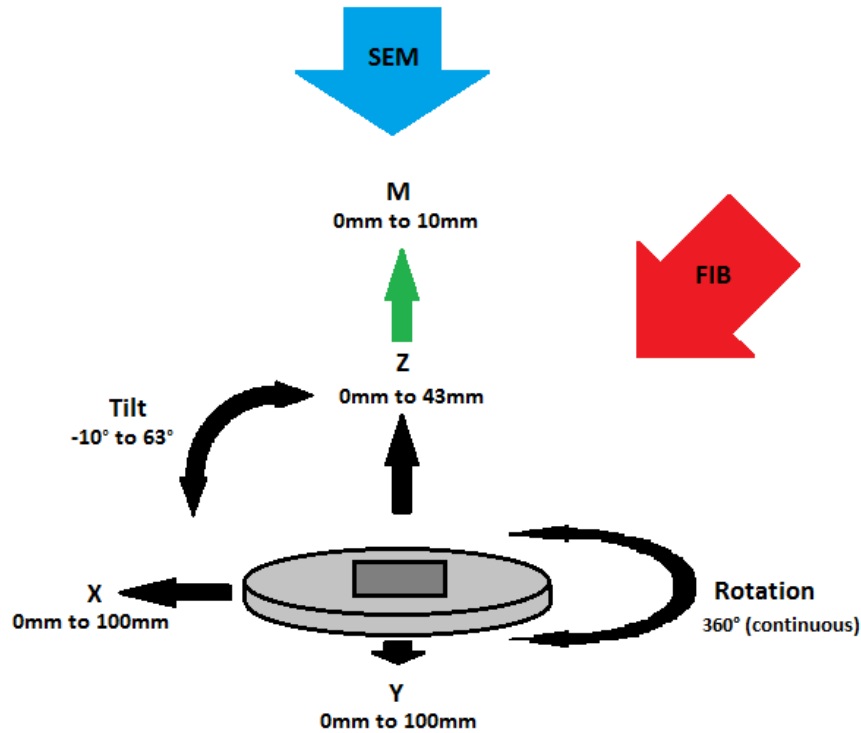


Figure 2-5. A schematic illustrating the six-degrees of freedom of the sample stage, with their mobility ranges.

2.7.2 SEM

The SEM functionality of the Nvision FIB was used in this work for imaging and depositing of the tungsten dots/pillars, with the latter being a part of the defect-marking techniques developed in this work. SEM imaging was usually performed at 5kV accelerating voltage and 120 μ m aperture size. Different imaging parameters were used when performing tungsten deposition in the spot mode due to the fact that the parameters must be the same for both imaging and the deposition in order to avoid misalignments between the intended and the deposited positions. The parameters were optimised, as described in Section 4.4.2.2. Both imaging and deposition were performed at a 5mm working distance.

2.7.3 FIB

FIB was used in this work to perform four operations: imaging, milling, material deposition and low-energy ion cleaning. The procedure and the instrument parameters for each operation are described here.

Imaging

FIB imaging is a necessary step prior to carrying out a milling or material deposition, because the milling/depositing shape can only be produced in the imaging mode. Imaging was performed at 30kV accelerating voltage and 40pA gallium ion beam current, which provide sufficient image resolution while minimising surface damage caused by the incident gallium ions.

Milling

FIB milling was also performed at 30kV but over a wide range of milling currents, from 3nA to 40pA, depending on the application. The operation also has two additional parameters: one is the pixel fill factor (PFF) – the percentage of a pixel of the screen that is covered by the ion beam; and the other is the dwell time – the time the ion beam spent at each point of the pattern. The PFF and the dwell time for milling were kept constant at 150% and 0.8 μ Sec, respectively.

Deposition

FIB deposition was performed with the gas injector in the extended position. The precursor gas was released into the system for at least 10sec before performing the deposition, to allow the gas to reach the sample surface. Similar to milling, the deposition also required FIB imaging of the sample surface, in order to place the depositing pattern. The accelerating voltage for deposition was 30kV while the beam current was varied depending on the depositing material. Tungsten and carbon deposition was normally performed at a beam current of 80pA and 40pA, respectively. The PFF was always kept below 50%. As with the variations in the beam current, different dwell times were used for tungsten and carbon, with the former being 0.8 μ Sec and the latter being 0.4 μ Sec. Surface

irregularities were discovered when depositing a 15µm by 4µm tungsten strip using the settings mentioned above. This problem was resolved, as described in Section 4.4.2.1.1.

Low-energy ion cleaning

After the APT fabrication process, the specimen suffered from surface damage caused by the implantation of high energy gallium ions. The damaged regions are approximately 30nm thick in silicon specimens¹¹ and can cause the specimen to fracture prematurely during the APT analysis.

The surface damage regions were removed by raster scanning, i.e., in the imaging mode) the specimen with a low-energy ion beam.¹² In this work, the cleaning procedure was performed by FIB imaging at 2kV accelerating voltage and 40pA beam current. The image was switched to SEM mode at regular intervals, to monitor the progress. The removal height varied between 100nm to 300nm, depending on the specimen. The specimen was inserted into the APT soon after the cleaning procedure, to prevent excessive surface oxidation.

2.7.4 APT/TEM specimen fabrication method

As mentioned above, an Nvision dual-beam FIB was used in this work to fabricate APT and TEM specimens. This section describes the fabrication methods.

The APT fabrication method used in the early stages of the work was an adaption of the method described by Thompson.¹³ New fabrication methods were later developed for characterising grain boundaries and dislocations. These are described separately in Chapter 4. Nevertheless, all the aforementioned methods start off with the same step, known as the lift-out technique. Hence, this technique is described separately in the next section.

2.7.4.1 *The lift-out technique*

The lift-out technique was used throughout this work as a precursor step to the APT or TEM specimen fabrication from a feature of interest. The process involves fabricating a cantilever from the feature

of interest. The wedge component containing the feature of interest is then lifted out using a micromanipulator.

For the cantilver fabrication process, a $15\mu\text{m}$ long and $4\mu\text{m}$ wide strip is deposited over the area of interest. In the case of the marking technique developed in Section 4.4 and the TEM fabrication method described in Section 2.7.4.3, the depositon of the strip was carried out as part of the process. The strip is used to mark the width of the wedge component of the cantilever. Two undercut trenches are then milled on either side of the strip at 9° inclination. The milling time for each trench is 5min. After having performed the cuts, a v-groove is formed underneath the overhanging wedge containing the region of interest, as illustrated in Figure 2-6.

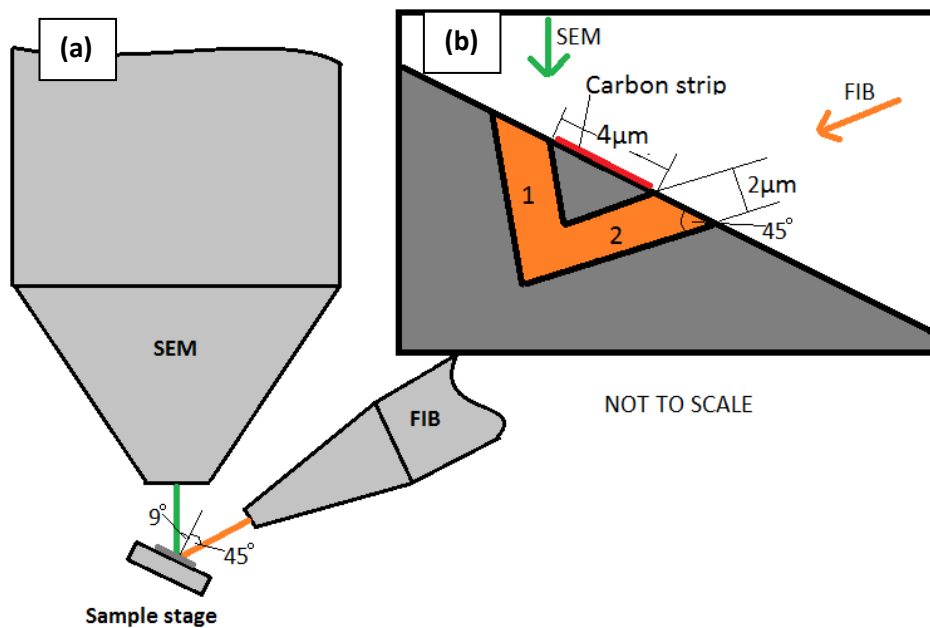


Figure 2-6. (a) A schematic showing the tilt angles between the sample surface normal and the two columns, i.e., SEM and FIB. (b) A schematic illustrating the positions of the two undercut trenches, labelled 1 and 2, relative to the carbon strip.

The specimen is then tilted by 54°, following which a vertical trench is milled at one end of the wedge in preparation for the lift-out. An SEM image of a typical cantilever is shown in Figure 2-7.

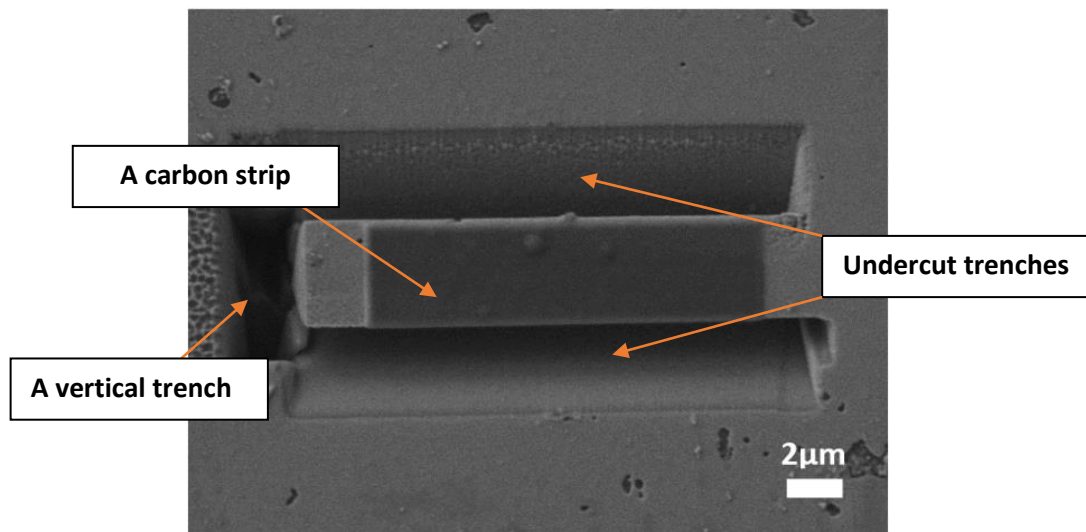


Figure 2-7. An SEM image of a typical cantilever.

A micro-manipulator is carefully lowered and attached to the detached end of the wedge by carbon deposition. Note that the gas injector is inserted before the manipulator is lowered, to avoid physical contact between them, and the precursor gas is introduced just before the manipulator touches the wedge because the emission of the gas causes the stage to vibrate, which can damage both the specimen and the manipulator. Once attached, the wedge is detached from the bulk specimen by cutting off the other end of the wedge. After the detachment, the stage is lowered before the wedge is lifted out of the bulk, to prevent physical contact between the wedge and the bulk.

2.7.4.2 The annular milling technique

The annular milling technique is described in the early part of Chapter 4 and was used to fabricate APT specimens from defects delineated by the marking techniques developed in Section 4.4. In addition, this technique was also used to fabricate APT specimens from the iron-implanted s-Si sample. This section describes the fabrication procedure using this technique.

After the lift-out technique described in Section 2.7.4.1 was carried out, the wedge was transferred to a holder. A section of the wedge was attached to the holder by applying tungsten deposition to both sides of the wedge. The wedge was tilted by 54° to face the FIB column and then sharpened into a needle by performing a series of annular milling steps. The annular pattern initially had a large inner diameter of 2–3 microns, and was gradually decreased to a size slightly larger than the apex diameter of the APT specimen (100–150nm). In the meantime, the milling current was systematically decreased from 3nA to 40pA. A high beam current was used at the beginning of the milling process to allow a faster material removal rate. However, higher beam current leads to a larger beam energy spread, which reduces the accuracy of the milling pattern. Hence, the beam current was lowered as the milling process progressed towards the final stages.

2.7.4.3 *TEM specimen preparation*

A 10 μ m long tungsten line was deposited directly over the grain boundary, previously revealed using preferential etching. The tungsten line was deposited using FIB at 1pA ion beam current, to mark its location and maintain its visibility during further milling steps. A strip of carbon of equal length and 4 μ m in width was then applied over the tungsten line such that the carbon ran along its length, with about 2 μ m excess on both sides. The lift-out technique described in Section 2.7.4.1 was performed on the marker, with the length of the lift-out wedge being 15 μ m. The wedge was then attached to a post by depositing tungsten at both ends. The specimen was tilted by 54° , following which an electron-transparent (about 100nm thick) lamella sheet was fabricated at the marker by applying a series of mill cuts at both sides of the line. The milling current was systematically reduced from 3nA to 40pA as the cut progressed towards the marker, to produce sharp surfaces. Figure 2-8 (b) shows the final TEM specimen.

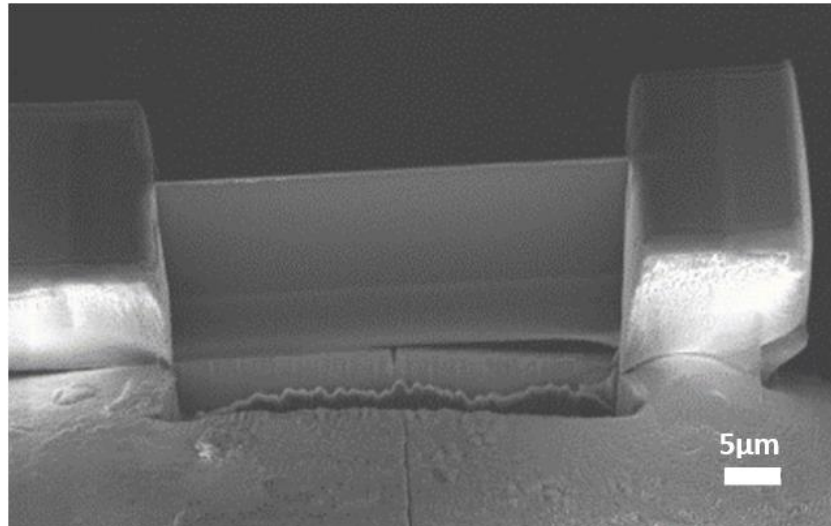


Figure 2-8. SEM image of a TEM specimen.

2.8 Transmission electron microscopy (TEM)

TEM was used to verify the presence of defects in the specimens. The instrument operates by focusing an electron beam at an electron-transparent specimen. The incident electrons can either be scattered by the specimen's lattice or pass through the specimen. The interference between the scattered electrons creates a diffraction pattern on a phosphor screen situated below the specimen. Images can be created from either the transmitted electrons or one of the scattered electron beams. These are known as, respectively, bright field and dark field images.

The instrument used to observe defects in APT and TEM specimens was a Philips JEOL 2000FX microscope. The instrument, operating at the accelerating voltage of 200kV, was equipped with a double tilt holder, with one of the tilt axes being eccentric. All TEM images were taken initially by film and later by a charge-coupled device (CCD) camera, after this was installed. All images of APT specimens were taken in bright field mode because this was easier to set-up than dark field mode, and the main purpose of using the instrument was to verify the presence of defects in the specimens. TEM imaging was performed by Miss Min Wu, of the University of Oxford, Oxford, UK.

2.9 APT

2.9.1 Instrumentation

The instrument used in this work was a laser-assisted, local electrode atom probe (LEAP 3000X HR) manufactured by Imago, which is now a part of Cameca, Gennevilliers, France. The atom probe was equipped with a local electrode that can generate a highly-localised electric field, allowing multiple specimens to be successively analysed without having to transfer the specimens between chambers. The electrode was tested prior to every set of experiments, to reduce the background noise and artefacts from the electrode. An energy compensated reflectron yields a mass resolution of 1/1000 amu while sacrificing field of view and detection efficiency, with the latter being about 37% (as opposed to about 50% in a straight flight path APT). A diode-pumped Nd:YVO₄ solid-state laser emitted a focused laser beam with a spot size of <10µm. This operated at a wavelength of 532nm, with a repetition time of approximately 10 to 15ps. The laser impinged on the specimen apex region normal to the specimen axis. All APT data obtained from the instrument was analysed using IVAS[®] software.

2.9.2 Specimen alignment

The specimen alignment procedure was performed for each analysis, to ensure steady field-evaporation and high quality data. The first step was to bring the specimen into the proximity of the electrode by applying large-stage translation steps to the specimen stage with the assistance of a pair of optical microscopes. The second step was to line up the specimen apex with the electrode by performing smaller translation steps with the aid of the laser beam and a pair of high-resolution microscopes. The third step was to align the specimen apex with the centre of the detector by adjusting the specimen stage according to the incoming ions on the detector map such that the area covered the entire area of the map.

The laser beam alignment procedure was carried out after turning on the laser or changing the local electrode. The laser beam was roughly focused on the specimen tip prior to the initiation of the

analysis, by moving either the specimen, the beam, or both. An automatic laser scanning procedure was performed at the initial stage of the analysis to obtain the optimal evaporation flux, by changing the x and y coordinates, and the focus point of the laser spot relative to the specimen.

Once the optimum coordinates had been established, the instrument was set to automatic acquisition, whereby the laser periodically scanned over the specimen apex to ensure that the specimen and the laser remained at optimum positions. Also, the DC voltage was systematically elevated to maintain the evaporation rate at a user-specified value.

2.9.3 Mass spectrum analysis

The ions collected from the atom probe analysis are often represented in the form of a mass spectrum. The spectrum is simply a histogram that plots the frequency of the detected ions with their mass-to-charge state ratios (m/n).

The position of the peaks obtained directly from the raw data can deviate from the theoretical positions, particularly at low DC potentials. Such deviation was compensated for by applying a scaling factor and shifting the peaks to the correct positions. The mass peaks were then assigned to different elements and possible molecular ions using atomic weights and relative abundance of isotopes. In addition, the m/n range was defined around the centre of the peaks to determine the number of ions being considered for compositional analysis and APT specimen reconstruction. There is currently no standard protocol for determining the bin size of each mass peak. Therefore, this factor must be taken in to consideration when performing chemical compositional measurements.

2.9.4 Three-dimensional reconstruction

One of the important features of the LEAP is its ability to reconstruct the atom probe specimen. The reconstruction is carried out based on the ions within the previously defined range of the identified peaks in the mass spectrum and their positions on the detector, with the latter providing the hit coordinates, x_d and y_d . The original position of an ion on the sample surface can be calculated in terms of x and y by:

Equation 2-2
$$x = \frac{x_d \beta r_0}{a}$$

Equation 2-3
$$y = \frac{y_d \beta r_0}{a}$$

Where β is the image compression factor, r_0 is the instantaneous radius of curvature of the specimen apex, and a is the distance between the surface of the specimen apex and the detector. The depth (the z-coordinate) is determined by¹⁴:

Equation 2-4
$$z_i = \sum \partial z + \frac{x_d^2 + y_d^2}{2r_0 G^2}$$

Where ∂z is the elemental depth increase, r_0 is the initial radius of the specimen apex and G is the magnifying factor. The equation determines the z value of the ion based on the ion hit sequence, assuming that the ion that arrives later in the course of the analysis lies deeper in the specimen surface. Once the x, y and z coordinates have been determined, they are combined with the chemical information of the ions to generate the reconstruction. Note the reconstruction algorithm assumes that the specimen tip is hemispherical.

Three-dimensional reconstructions of the specimens were generated using the voltage profile. This option is effective if the specimen is mostly made from one material. The default reconstruction parameters were used, unless stated otherwise.

2.9.5 Optimisation of LEAP experimental parameters

The LEAP parameters were optimised, as described in Chapter 5, to maximise the iron detection sensitivity, since iron is considered to be one of the most important impurities responsible for reduction in the performance of mc-Si solar cells.^{15,16,17} Three parameters were employed to optimise the LEAP parameters: (a) $\text{Si}^+/\text{Si}^{2+}$ ratio; (b) $\text{Si}_2^+/\text{Si}_{\text{total}}$ and (b) the signal-to-noise ratio. The importance of these parameters will be discussed in Chapter 5.

2.9.6 Atom probe data interpretation

Hydrogen and gallium were excluded when determining the chemical composition of a feature of interest. The reason for excluding hydrogen is that the solute atoms are expected to have an extremely low concentration in the mc-Si samples. Also, hydrogen originates from the hydrogen gas that remains in the analysis chamber and, hence, is not part of the specimen. The mass peaks associated with hydrogen, i.e., 1amu, 2amu and 3amu, were excluded as well as the hydrogen in their complexes, e.g. SiOH_x complexes were assigned as SiO. Gallium was introduced during the APT specimen fabrication process via the FIB and, hence, was not originally present in the mc-Si samples in significant amounts. The mass peaks associated with gallium being excluded were 69amu and 71amu.

2.9.7 Compositional analysis

Chemical compositions derived directly from the APT dataset are generally given in the form of at%. This is because the specimen is analysed on an atom-by-atom basis. The atomic fraction C_{solute} of a given solute atom is given by¹⁸:

Equation 2-5
$$C_{solute} = \frac{N_{solute}}{N_{total}}$$

where N_{solute} and N_{total} are the number of the chemical species and the total number of atoms, respectively. C_{solute} can then be converted into at% simply by multiplying the value by 100%. The compositional error, σ_{error} , is based on the counting statistics, i.e. the error is assumed to be represented by a binomial distribution, and is given by:

Equation 2-6
$$\sigma_{error} = \sqrt{\frac{C_{solute}(1-C_{solute})}{N_{total}}}$$

There were occasions where it was more appropriate to represent the concentration of a solute atom in terms of atom/cm³.

The methods used to determine chemical compositions at grain boundaries and dislocations, as well as at clusters decorating the defects, are described in Chapter 6.

2.9.8 Calculation method for concentrations in atom/cm³

The solute concentrations in Chapter 5 and 6 are often reported in terms of atom/cm³, rather than at%, in order to directly compare the results with those in the literature. The equation used to calculate the solute concentrations in atom/cm³ is given by:

$$\text{Equation 2-7} \quad C \text{ (atom/cm}^3\text{)} = \frac{N_{\text{solute}}}{N_{\text{Si}} + N_{\text{solute}}} * C_{\text{Si perfect lattice}}$$

where N_{solute} and N_{Si} , are the concentrations of the impurity and the silicon, respectively. $C_{\text{Si perfect lattice}}$ is the concentration of silicon in a perfect lattice in atom/cm³ (5×10^{22} atom/cm³).

2.9.9 Solute detection sensitivity

The detection sensitivity of a solute ion was used, as described in Chapter 5 and 6, to determine the minimum concentration of solute counts required to distinguish the mass peak of the solute from the background noise in the mass spectra of the specimens. The detection sensitivity, $D_{\text{sensitivity}}$, is given by:

$$\text{Equation 2-8} \quad D_{\text{sensitivity}} = \frac{2N_{\text{noise}}}{N_{\Sigma\text{Si}}} \times C$$

where N_{noise} and $N_{\Sigma\text{Si}}$ are the 'noise' range and the sum of silicon ions, including those in complexes, e.g. Si in SiO complexes, and C is a constant that defines the unit of D_{Fe} , with the constant being equal to 10^6 and 5×10^{22} for ppm and atom/cm³, respectively. The equation assumes that the signal at the peak position has to be twice that of the background noise in order for the peak to be distinguishable.

2.9.10 Manual noise correction

Despite the mass spectra derived from APT analyses generally having excellent signal-to-noise ratios, the background noise, particularly the thermal tails behind each mass peak, can contribute to an overestimation of the concentration of the selected solute atom. Consequently, a manual noise correction method was performed, as described in Chapter 5 and Chapter 6, in order to improve the accuracy of the measured composition.

The method introduced by Muller involves taking the average of two noise ranges on either side of each mass peak, with the exception of asymmetrical mass peaks with pronounced thermal tails, in which case only the noise ranges on the lower mass-to-charge side the peaks, i.e., the range to the left of the peak, were used to represent the background noise. The reason for this is because the tail region of the peak does not only contain noise, but also ions arriving late. This background noise is then used to reduce the number of counts associated with the mass peak, taking into account the local noise contribution.

The accuracy of this method depends on how a user defines which mass peak is symmetrical. In addition, the noise ranges on either side of the most 'symmetrical' mass peaks were found to contain very similar numbers of 'noise' ions, with the differences being within statistical errors (σ_{error}) defined in Section 2.9.7. Hence, taking an average of the two noise ranges did not lead to a statistically significant change in the number of noise ions. Consequently, the method was simplified by taking the noise range positioned immediately to the left of the peak as its background noise, as demonstrated on Si^{2+} peaks in Figure 2-9.

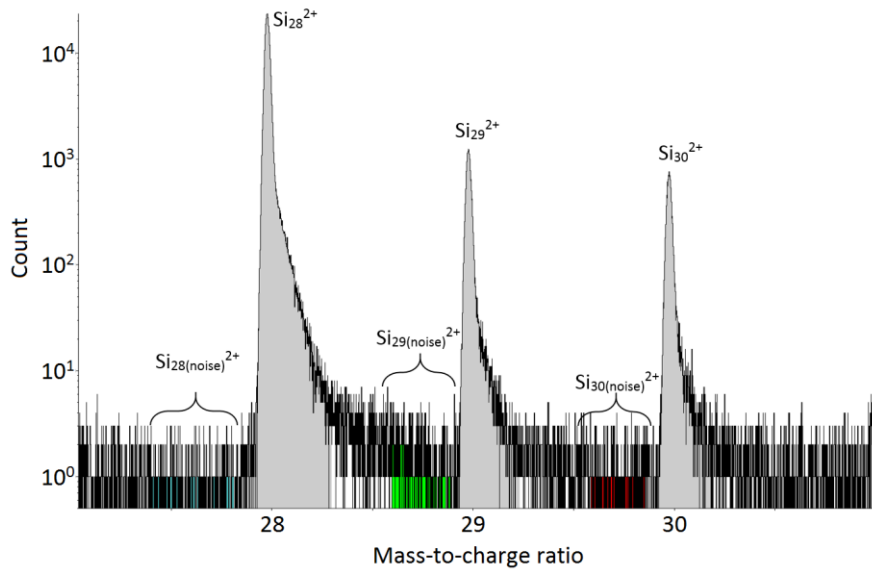


Figure 2-9. A mass spectrum illustrating the manual noise correction method performed on three Si^{2+} peaks (grey) with pronounced thermal tails. The mass ranges highlighted in blue, green and red correspond to the background noise at Si_{28}^{2+} , Si_{29}^{2+} and Si_{30}^{2+} peaks, respectively.

2.10 Miscellaneous techniques

2.10.1 Polishing

All the polishing equipment and products used in this project were manufactured by Kemet International. The polishing process was performed in three stages:

1. Mechanical polishing for one hour using NLH pad, 6 μm diamond polishing paste and lubricant.
2. Mechanical polishing for one hour using NLH pad, 1 μm diamond polishing paste and lubricant.
3. Chemo-mechanical polishing for four hours using CHEM-H pad soaked with colloidal silica, also known as “Syton”.

In the first and second stages, the lubricant was replenished every 30min. In the last stage, syton was replenished every 15min. In addition, large silica particles were removed from the solution by filtration, to minimise surface scratches.

2.10.2 RCA cleaning procedure

The RCA cleaning procedure is a standard cleaning process for removing both organic and metallic contaminants on the sample surface. The procedure used was as follows:

1. Acetone at room temperature in ultrasonic bath for 10min.
2. Methanol at 60°C for 10min.
3. Trichloroethylene at 60°C for 10min.
4. Rinse in deionised water.
5. A mixture of water, hydrogen peroxide and ammonium hydroxide ($\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{NH}_4\text{OH}$) at a 5:1:1 ratio for 15min. The mixture was held at the temperature of 75°C.
6. Rinse in deionised water.
7. Dilute hydrofluoric acid ($\text{H}_2\text{O}:\text{HF}$ at 50:1 ratio) at room temperature for 2min.
8. Rinse in deionised water.
9. A mixture of water, hydrogen peroxide and hydrochloric acid ($\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}$) at a 6:1:1 ratio for 15min. The mixture was held at the temperature of 75°C.
10. Rinse in deionised water.
11. Immersed in dilute hydrofluoric acid ($\text{H}_2\text{O}:\text{HF}$ at a 50:1 ratio) at room temperature for 2min.
12. Rinse with plenty of deionised water.

Steps 1–3 remove heavy contaminants, such as fingerprints and diamond paste residuals. Step 4 dissolves organic contaminants; it also creates native oxide on the wafer surface, which is removed in Step 5. Step 6 gets rid of metallic contaminants. This step also produces native oxides, which are removed in Step 7.

2.10.3 Dimensional measurement methods

Various measurement methods were employed, as described in Chapter 3 and Chapter 4, to measure, respectively, the dimensions of the pits associated with etched defects and the components of the marker techniques developed, as described in Section 4.4. These methods are

described in the relevant chapters. All the measurements were carried out using the ImageJ software, unless stated otherwise.

2.10.4 Sample holders

A number of holders were used at various stages of the defect characterisation process. This section provides a brief description of these holders.

2.10.4.1 5mm pin aluminium stub

Al stubs were used to mount silicon samples for the Nvision and EBIC characterisation. Prior to mounting the sample, the stub was cleaned in acetone with ultrasonic agitation for a minimum time of 20min. It was rinsed in de-ionised water and then dried using an air gun. The sample was attached to the stub using silver conductive paint. In the case of an EBIC sample, the conductive paint was applied directly over the Ohmic contact (liquid InGa eutectoid).

The samples were removed from the stubs by simply immersing them in acetone with ultrasonic agitation until the sample was completely detached from the stub. Note that the sample must undergo the RCA cleaning procedure before further operations are performed on the sample (e.g. preferential etching), due to the deposition of silver paint on the surfaces. For EBIC samples, removal of the Schottky and Ohmic contacts was done prior to the RCA cleaning procedure.

2.10.4.2 Atom probe specimen holders

APT specimen holders were an essential part of the APT specimen fabrication process. They were used to mount lift-out wedges, which were then sharpened into needle shape specimens. APT specimen holders were developed in conjunction with the APT fabrication method (Chapter 4). The development processes are described in Section 4.5.2.

2.11 References

¹ Jordan D.M., (2011). Semi-insulating silicon (published doctoral thesis). University of Oxford, Oxford, United Kingdom.

Chapter 2 – Experimental techniques

- ² De Coteau, M. D., Wilshaw, P. R., & Falster, R. J. (1992, January). Gettering of Copper and Iron to Extended Surface Defects in Silicon. In *Materials Science Forum* (Vol. 83, pp. 185-190).
- ³ Wilshaw, P. R., Fell, T. S., & Coteau, M. D. (1991). EBIC contrast of defects in semiconductors. *Le Journal de Physique IV*, 1(C6), C6-3.
- ⁴ Sameshima, T., Miyazaki, N., Tsuchiya, Y., Tachibana, T., Ohshita, Y., Arafune, K., & Ogura, A. (2012, July). EBIC Study on Metal Contamination at Intra Grain Defects in Multicrystalline Silicon for Solar Cells. In *Materials Science Forum* (Vol. 725, pp. 129-132).
- ⁵ C. Donolato, *Optik* 52 (1978) 19.
- ⁶ Williams, D. B., & Carter, C. B. (1996). *The Transmission Electron Microscope* (pp. 3-17). Springer Us.
- ⁷ Reimer, L. (2000). Scanning electron microscopy: physics of image formation and microanalysis. *Measurement Science and Technology*, 11(12), 1826.
- ⁸ Giannuzzi, L. A., & Stevie, F. A. (Eds.). (2005). *Introduction to focused ion beams: instrumentation, theory, techniques and practice*. Springer.
- ⁹ Volkert, C. A., & Minor, A. M. (2007). Focused ion beam microscopy and micromachining. *MRS bulletin*, 32(05), 389-399.
- ¹⁰ Melngailis, J. (1987). Focused ion beam technology and applications. *Journal of Vacuum Science & Technology B*, 5(2), 469-495.
- ¹¹ Giannuzzi, L. A., Geurts, R., & Ringnalda, J. (2005). 2 keV Ga⁺ FIB milling for reducing amorphous damage in silicon. *Microscopy and Microanalysis*, 11(S02), 828-829.
- ¹² Thompson, K., Gorman, B., Larson, D., van Leer, B., & Hong, L. (2006). Minimization of Ga induced FIB damage using low energy clean-up. *Microscopy and Microanalysis*, 12(S02), 1736-1737.
- ¹³ Thompson, K., Lawrence, D., Larson, D. J., Olson, J. D., Kelly, T. F., & Gorman, B. (2007). In situ site-specific specimen preparation for atom probe tomography. *Ultramicroscopy*, 107(2), 131-139.
- ¹⁴ Bas, P., Bostel, A., Deconihout, B., & Blavette, D. (1995). A general protocol for the reconstruction of 3D atom probe data. *Applied Surface Science*, 87, 298-304.
- ¹⁵ Kvande, R., Geerligs, L. J., Coletti, G., Arnberg, L., Di Sabatino, M., Øvrelid, E. J., & Swanson, C. C. (2008). Distribution of iron in multicrystalline silicon ingots. *Journal of applied physics*, 104(6), 064905.
- ¹⁶ Buonassisi, T., Istratov, A. A., Peters, S., Ballif, C., Isenberg, J., Riepe, S., & Weber, E. R. (2005). Impact of metal silicide precipitate dissolution during rapid thermal processing of multicrystalline silicon solar cells. *Applied Physics Letters*, 87(12), 121918.
- ¹⁷ Macdonald, D., & Geerligs, L. J. (2004). Recombination activity of interstitial iron and other transition metal point defects in p-and n-type crystalline silicon. *Applied Physics Letters*, 85(18), 4061-4063.
- ¹⁸ Miller, M.K. (2000). *Atom Probe Tomography: Analysis at the Atomic Level*. New York: Kluwer Academic/Plenum, 161.

3 The development of preferential etching

Table of Contents

3.1	Introduction	- 69 -
3.2	Defect requirements	- 69 -
3.3	Methodology	- 71 -
3.3.1	Dislocation pit diameter measurement methods	- 72 -
3.3.2	Defect depth measurement method	- 72 -
3.4	Experimental errors	- 72 -
3.5	Investigation of different preferential etchants	- 74 -
3.3.3	Conclusion	- 76 -
3.6	Sirtl etch	- 76 -
3.7	Secco etch	- 78 -
3.3.4	Introduction	- 78 -
3.3.5	Dislocation pit diameter measurement programs	- 79 -
3.3.6	Optimising etch conditions	- 85 -
3.3.7	Repeat etching	- 88 -
3.3.8	Etch pit depth measurement	- 89 -
3.3.9	Conclusion	- 90 -
3.8	Determining the propagation direction of defects in mc-Si	- 90 -
3.3.10	A line of dislocation pits	- 91 -
3.3.11	Grain boundaries	- 92 -
3.3.12	Propagation of defects through the sample thickness	- 93 -
3.3.13	Conclusion	- 95 -
3.9	Chapter summary	- 95 -
3.10	References	- 96 -

3.1 Introduction

This chapter describes the experimental work as regards the selection of the preferential etchant, and the optimisation of the etch parameters for APT specimen fabrication in the Nvision. These parameters were then used as described in Section 3.7.5 to determine the propagation direction of dislocations and grain boundaries through the thickness of mc-Si samples.

The project initially prioritised isolated dislocations over grain boundaries because these are considered to be the most detrimental to solar cell performance. Hence, the experiments described in Section 3.5 to most of Section 3.7 focus mainly on dislocation pits. However, the new APT specimen fabrication approach developed as described in Chapter 4 made fabrication of APT specimens from grain boundaries much easier than fabrication of APT specimens from dislocations due to the etch pit being visible at the triangular surface of the wedge (see Section 4.5.1.2 for more detail). Hence, the experiments described in Section 3.7.5 include both dislocations and grain boundaries. It is important to note that the APT specimen fabrication method described in Section 2.7.4.2 and those which were developed as described in Chapter 4 have different requirements as regards the geometry of the etched defects. These requirements are described in Section 3.2.

3.2 Defect requirements

The fabrication methods can be separated into two types according to the orientation of the specimen relative to the defect. For the first type, the specimen was fabricated such that the defect runs along the long axis of the specimen, as illustrated in Figure 3-1(a). This was the approach adopted by the APT specimen fabrication method described in Section 2.7.4.2. It was used in the early part of Chapter 4 to assess the effectiveness of two of the defect-marking techniques. The figure indicates that the likelihood of fabricating an APT specimen containing a dislocation depends on the dislocation pit having a similar diameter and shape to the specimen's apex. A typical APT specimen has a circular shaped apex, with a diameter of about 100nm¹. Hence, the requirements for

this method are that the dislocation pits must have a circular geometry and an average dislocation pit diameter, referred to hereafter as d_{avg} , of about 100nm.

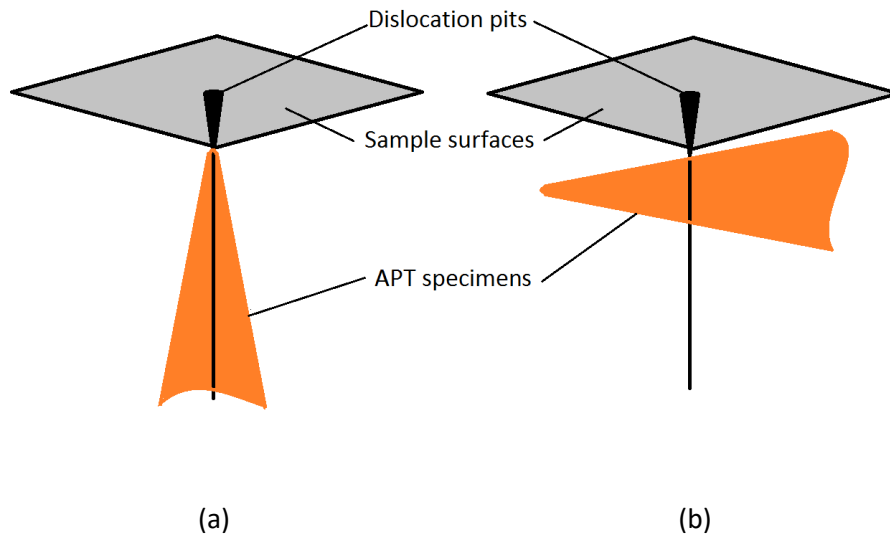


Figure 3-1. Schematic illustrations of the APT specimen position relative to a defect, which, in this case, is a dislocation pit, in (a) the initial and (b) the final APT fabrication methods.

The other two methods were developed as described in Chapter 4 after it was discovered that the defects in mc-Si samples do not run perpendicular to the surface. In these methods, the APT specimen axis is normal to the propagation direction of both dislocations and grain boundaries, as illustrated in Figure 3-1 (b). This was achieved by performing annular milling normal to the triangular surface of the specimen wedge instead of the original sample surface (which is where the defect etch pit is located), as in the previous method. It is therefore essential that the depth of the etch pit be not so large as to extend to the other surfaces of the wedge, otherwise the fabricated APT specimen would contain a hole that would be the cross-section of the etched pit. The maximum depth was calculated based on the schematic in Figure 3-2. The orange area indicates possible directions at which the defect can propagate. The maximum depth is given by the shortest distance between the defect and the edge, d_{max} . Using this approach, d_{max} was determined to be about 1.4 μm . The maximum depth of the etch pit should be considerably less than d_{max} in order to account for the gallium-implanted layer and surface oxides, both of which can lead to premature fracture

during APT analysis. Maximum depth was set at $1\mu\text{m}$. In addition, the depth of the etch pit has to be at least the same as its width, i.e., 100nm , in order to be distinguishable from other surface features (i.e., artefacts and contaminants). In conclusion, the fabrication methods developed as described in Chapter 4 require defects with a depth of between 100nm and 1000nm .

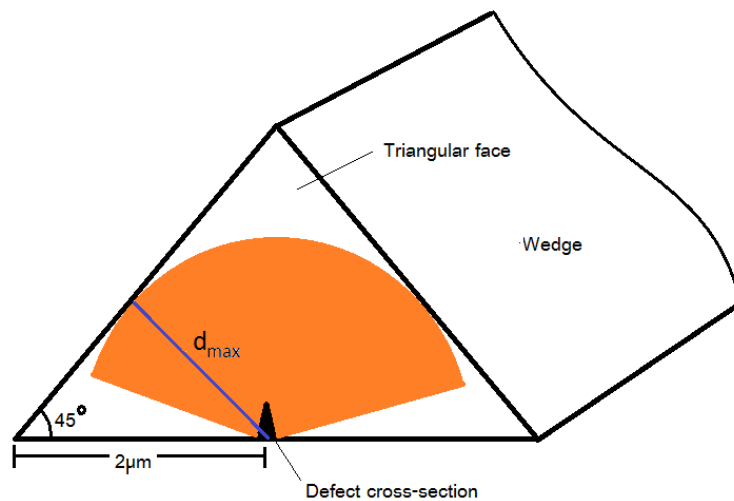


Figure 3-2. A schematic showing the triangular face of a wedge containing the cross-section of a defect. The orange area signifies possible propagation directions of the defect while d_{max} indicates the smallest distance between the defect and the edge of the wedge.

3.3 Methodology

All the etching experiments were carried out in the set-up described in Section 2.6.2. The instruments used to image the samples were an Olympus BH2 optical microscope equipped with a Nikon CCD camera, the Nvision, and the JEOL 2000FX TEM. Various methods were used to measure the dimension of defects. As described in Section 3.5 and 3.6, “ImageJ” software was used to measure the dislocation pit diameters. As described in Section 3.7, Matlab programs were employed to measure dislocation pit diameters. As described in Section 3.7.5, the depths of etched grain boundary grooves and dislocation pits were measured using the method described below.

3.3.1 Dislocation pit diameter measurement methods

The average defect size in the preferential etching experiments described in Section 3.5 and 3.6 was determined by the average dislocation pit diameter, due to the inconsistency of the grain boundary width. The dislocation pit diameter was initially measured using the ImageJ software. However, this approach provides limited accuracy as it is subject to large human errors and is extremely time-consuming.

Automated Matlab programs were developed as described in Section 3.7 to determine average defect size from a much larger sample size. These programs were used in the optimisation of etch conditions for the Secco etch.

3.3.2 Defect depth measurement method

Depth measurements were performed as described in Section 3.7.5 on both dislocation pits and grain boundaries. A single pass vertical trench was milled across the defect, during which SEM images were taken at regular intervals. For dislocations, the depth was measured using the image with the deepest profile. The same method was employed for grain boundaries, but the milling distance of the vertical trench was limited to 2 microns. Since the measurements were carried out at 54°, the obtained depths, H_m , were converted into true depths, H_t , by:

Equation 3-1
$$H_t = \frac{H_m}{\sin \theta} \quad (\theta = 54^\circ)$$

3.4 Experimental errors

This section summarises the various sources of errors in regard to the experiments described in this chapter. Regarding chemical concentration, the accuracy is limited by the measurement implements for mixing the solution, i.e. the measuring cylinder ($\pm 0.05\text{ml}$) and the weighing scale ($\pm 0.05\text{g}$). The chemical variation was determined by:

Equation 3-2
$$C_{error} = M_{max} - M_{expect}$$

Chapter 3- The development of preferential etching

where $M_{\max}$ and M_{expect} is the molar concentration with the maximum measurement errors and the expected value, respectively. The molar concentration can be determined using the equation:

Equation 3-3
$$M_i = \frac{m}{V * MW}$$

where m is the mass of the solute in grammes (potassium dichromate powder), V is the solvent volume in litres and MW is the molar mass of the solute in g/mol (294.184g/mol). Note that in Secco etch experiments, V is kept at 7ml. For example, if M_{expect} is 0.05M then, using Equation 3-3, the amount of potassium dichromate needed is 0.1g. $M_{\max}$ can then be calculated to be 0.07M using the same equation but with maximum errors added to the measurements, i.e., $m = 0.10 + 0.05 = 0.15\text{g}$ and $V = 7 + 0.5 = 7.5\text{ml}$ or 0.0075litre. Equation 3-2 then determines the error to be $\pm 0.02\text{M}$.

The accuracy of the etch time is limited by the time taken to stop the reaction, which includes removing the sample from the etchant and, subsequently, rinsing the surface with distilled water. In order to account for the variation in the etch time, a sample was etched five times. The time taken to remove and rinse the sample was recorded each time. The average time taken to perform these tasks was determined to be 1.5sec.

The temperature variation was also measured by monitoring changes in the temperature of the etchant over the period of one minute. This was performed at varying temperatures from 20°C to 35°C. The results are summarised in Table 3-1.

Temperature (°C)	Variation (°C)
20	0.2
25	0.4
30	0.5
35	0.8

Table 3-1. Temperature variation at four different temperatures.

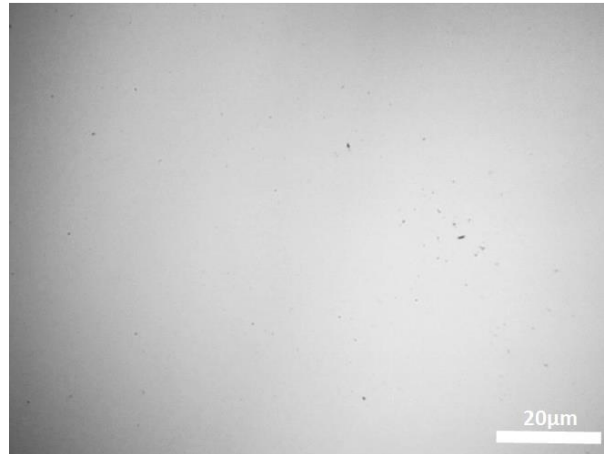
3.5 Investigation of different preferential etchants

As described in this section, three etchants were explored: Dash, Secco and Sirtl. The compositions and etch rates of the etchants are given in Table 3-2. A mc-Si sample was etched in each etchant. The temperature of the solutions and the etch time were kept at 20°C and 5min, respectively. The samples were then observed in the optical microscope at 1000x magnification.

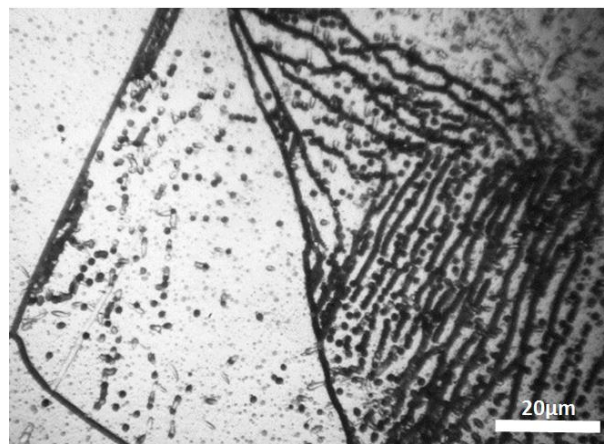
Etchant	Chemical composition	Etch rate ($\mu\text{m}/\text{min}$)
Dash	HF(49%): O_3 (70%): CH_3COOH (100%), ratio: 1:3:10	0.05-0.13 [2]
Sirtl	HF(40%): CrO_3 (0.3M), ratio: 4:5	3.0 [3]
Secco	HF(40%): $\text{K}_2\text{Cr}_2\text{O}_7$ (0.3M), ratio: 2:1	1.5 [4]

Table 3-2. Table giving the chemical compositions and etch rates of the potential etchants.

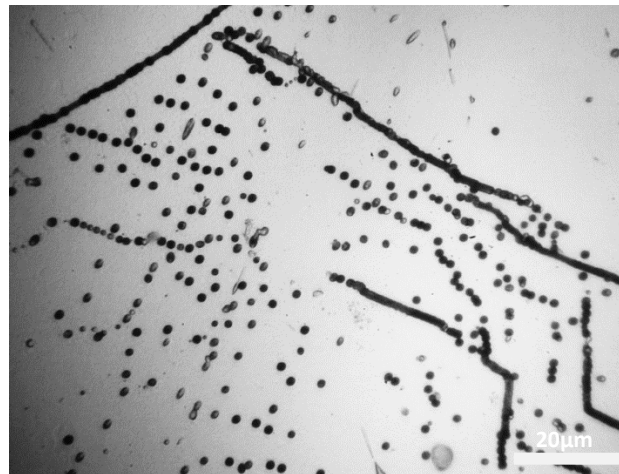
Figure 3-3 (a) shows no observable defect pattern in the Dash-etched sample. The sample was given an additional etch time of 55min, to compensate for the low etch rate, resulting in a total etch time of one hour. Despite the extended etch time, the sample surface remained unchanged. In contrast, Figure 3-3 (b) illustrates that Sirtl etch produces distinctive defect patterns and most dislocation pits are circular. Surface artefacts were also observed, in the form of small stain-like dots. Nonetheless, the defects are easily distinguishable from these dots since they are significantly larger. However, d_{avg} of $1.5\mu\text{m}$ is larger than the optimum diameter of 100nm, at which point surface artefacts could potentially limit the visibility of the defects once their size has been optimised. This was investigated further as described in Section 3.6. Secco also produced a distinctive defect pattern and mostly circular dislocation pits, with no visible surface artefacts, as shown in Figure 3-3 (c). d_{avg} of the sample of $1.1\mu\text{m}$ is larger than the optimum diameter.



(a) Dash-etched sample



(b) Sirtl-etched sample



(c) Secco-etched sample

Figure 3-3 (a)-(c). Optical images of mc-Si samples etched in various etchants at 20°C for 5min.

3.3.3 Conclusion

The Dash etch failed to produce visible defects even after one hour etch time. Although this could potentially be resolved with a longer etch time, the process would be extremely time-consuming. Hence, the etchant was discarded. On the other hand, Sirtl and Secco etches both produced distinctive defect patterns and most dislocation pits were circular. However, surface artefacts observed in the Sirtl-etched sample could limit the visibility of dislocations once their diameters have been optimised. Hence, further assessment was conducted to verify this hypothesis.

3.6 Sirtl etch

This section investigates the effect of surface artefacts found in the Sirtl-etched mc-Si sample described in Section 3.5 on the visibility of the dislocation pits once the diameter of the pits has been reduced to 100nm.

The investigation begins with the optimisation of the etch parameters to produce the required dislocation pit diameter: a set of samples was subjected to Sirtl etching at 20°C for etch times varying from 3sec to 300sec. Figure 3-4 shows an increase in d_{avg} with etch time. Each data point represents measurements on 100 dislocation pits.

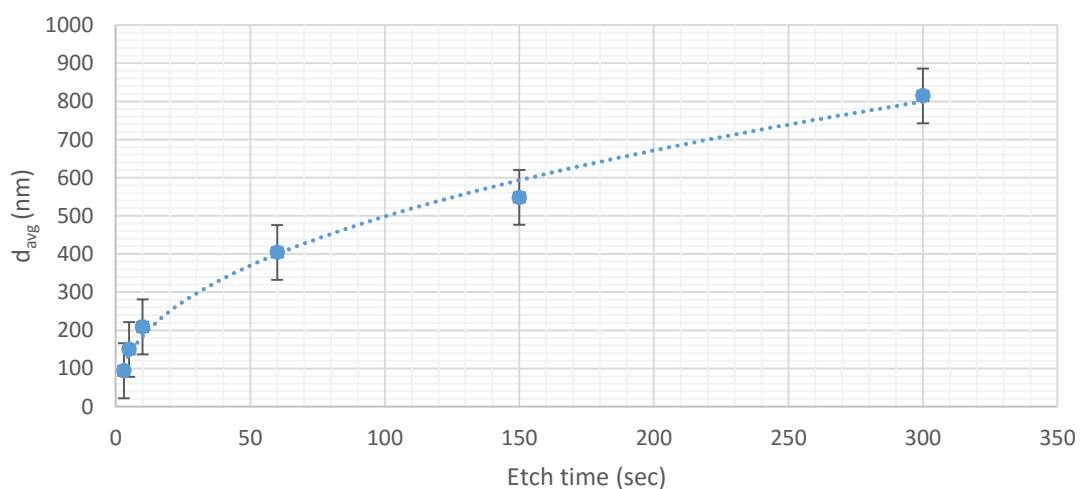


Figure 3-4. The graph shows d_{avg} as a function of etch time. The samples were etched in Sirtl solution at 20°C.

d_{avg} was found to be less than 100nm in the sample etched for three seconds. However, surface analysis of the sample in the SEM reveals dislocations having circular pits in some grains while appearing to be heavily distorted in others. The former were generally found on uniform surfaces, as shown in Figure 3-5. In contrast, the latter were accompanied by shallow pits, the density of which was found to vary significantly from one grain to another. These pits could be surface artefacts that are formed due to the anisotropic etching behaviour of the etchant.^{5,6}

These results indicate that only when dislocation pits are present on grains with uniform surfaces are they suitable for use as location markers for the fabrication of APT specimens. Since it is beneficial to maximise the number of analysable dislocations, this etchant was not considered suitable.

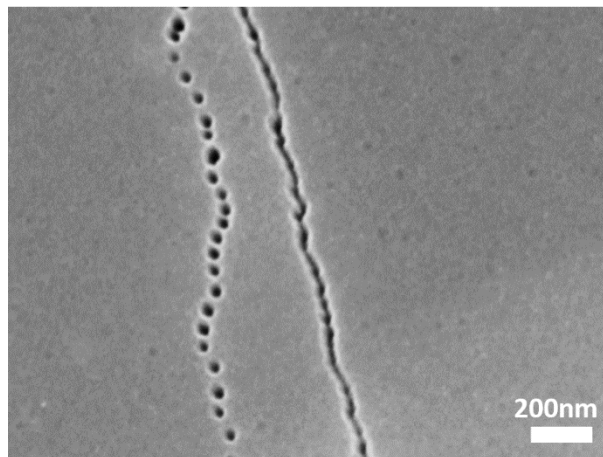


Figure 3-5. An SEM image showing the uniform surface region of Sirtl-etched mc-Si sample for 3sec at 20°C. The dislocation pits are easily distinguishable from the surface.

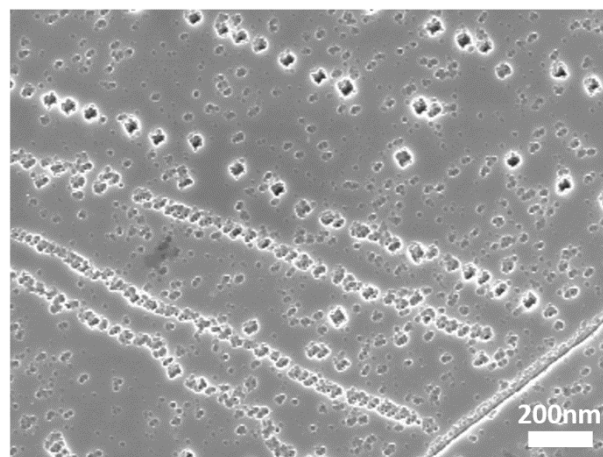
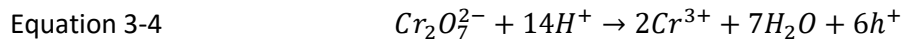


Figure 3-6. An SEM image showing the irregular surface region of an mc-Si sample Sirtl etched for 3sec at 20°C. In some cases it is ambiguous as to whether a pit is due to a dislocation or the other shallow surface features.

3.7 Secco etch

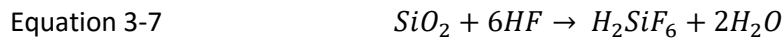
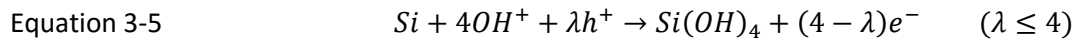
3.7.1 Introduction

The Secco etch is effective on all crystallographic planes and produces circular dislocation pits.^{6,7,8} Similar to other preferential etchants, it comprises oxidising and oxide-dissolving components, which are potassium dichromate ($K_2Cr_2O_7$) and hydrofluoric acid, respectively. The reaction kinetics of the HF- $K_2Cr_2O_7$ -H₂O system, described by Seo et. al.⁹, begin with the generation of holes on the sample surface:

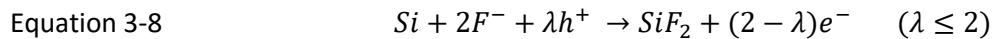


This is followed by two possible reaction routes depending on the HF concentration:

For low HF concentration:



For high HF concentration:



Both reaction routes show the dependence of the etch rate on hole concentrations, which in turn can be influenced by the concentration of potassium dichromate. In addition, other factors that affect result reproducibility are the concentration of impurities at the defects and localised stirring caused by the releasing of hydrogen gas in the high HF concentration regime. In order to minimise

these effects, the samples were etched with the polished surface facing up, to allow hydrogen gas to escape. A study by H. Idrisi et al.¹⁰ has shown that the etch rates of dislocations were significantly enhanced when either copper or lithium were introduced into the material. This work strongly suggests that dislocation pit diameters are dependent on the concentration of impurities at the defect. Unfortunately, it is extremely difficult to control this factor since the local concentration of impurities can vary depending on a number of factors, such as defect density and the environmental factors during ingot fabrication—i.e., liquid-solid segregation during ingot solidification and solid-state in-diffusion from crucible walls during the cooling down stage.

3.7.2 Dislocation pit diameter measurement programs

Up to this point, the diameter of dislocation pits was measured using the ImageJ software. This involved manually fitting a circle around each dislocation pit, from which its diameter was obtained. Despite its simplicity, the method is subject to large human errors and requires the sample size to be limited, since it is time-consuming. In order to overcome these limitations, two Matlab programs were developed for optical and SEM images. The program codes can be found in the Appendix.

3.7.2.1 *Dislocation selection criteria*

Surface analysis of the samples using both the SEM and the optical microscope reveal two types of dislocation pits, with observable difference in the diameter, as shown in Figure 3-7 (a)-(b). This could be due to the differences in the impurity composition at dislocations and/or their type (e.g. edge and screw dislocations).

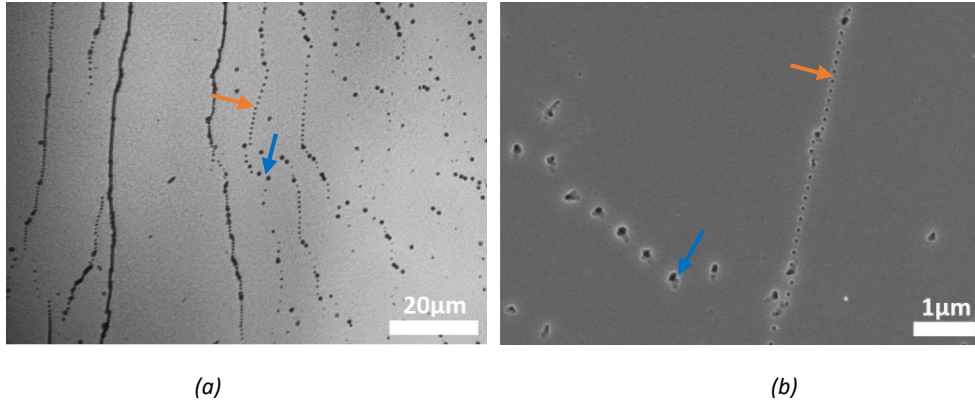


Figure 3-7. Images of Secco-etched samples taken using (a) the optical microscope and (b) the SEM show two types of dislocation pits with an observable difference in diameter. The larger pits and smaller pits are indicated by blue and orange arrows, respectively.

It is clear that d_{avg} will vary depending on the relative number of small and large dislocation pits in the dataset. In order to avoid this problem, only the diameters of large dislocation pits were measured. This selection criterion was implemented in both Matlab programs. The selection methods are described in the subsequent sections.

3.7.2.2 Optical images

A typical optical image of a Secco-etched sample is shown in Figure 3-8. The figure shows that the dislocation pits are mostly circular. Hence, the program works by searching for circular objects. Once found, circles are fitted around the object and their radii, r , are calculated. The radii are then converted into dislocation pit diameters, D , using the equation:

Equation 3-11
$$D = 2rC_{opt}$$

where C_{opt} is the unit conversion factor (pixel/nm) and can be determined using the ImageJ software.

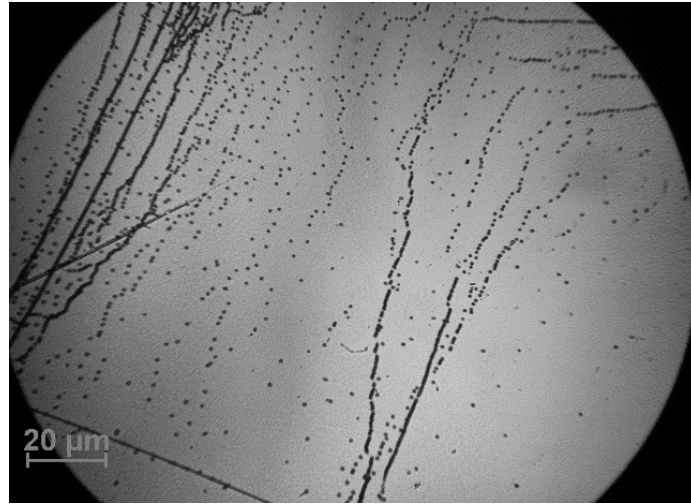


Figure 3-8. A typical optical image of a Secco-etched sample.

The detection sensitivity and the diameter range were optimised for each sample, to exclude artefacts and small dislocation pits while maximising the number of identified dislocation pits. Figure 3-9 shows the defect pattern in Figure 3-8 after dislocation pit diameter measurements were taken using the program; the dislocation pits identified by the program are marked by blue circles.

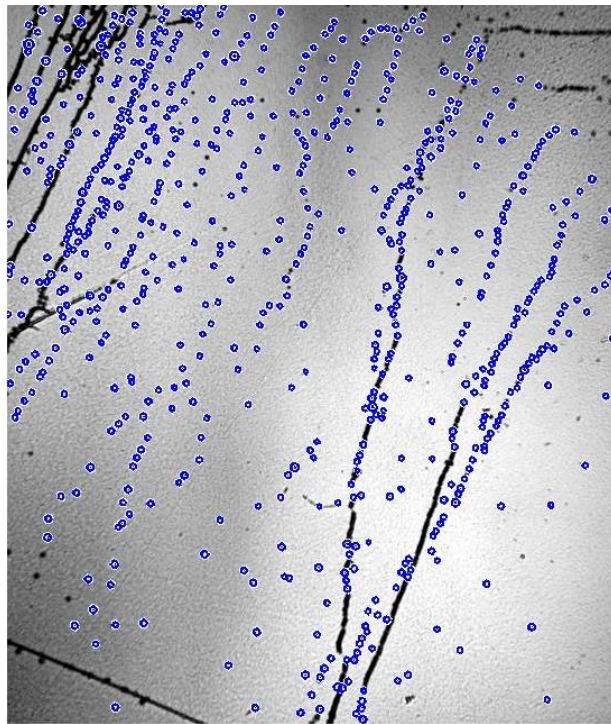


Figure 3-9. The optical image in Figure 3-8 after having measured dislocation pit diameters using the Matlab program. Note that blue circles mark the dislocation pits identified by the program.

3.7.2.3 SEM images

The geometry of dislocation pits in SEM images are different to those in optical images, in that the higher resolution available shows that, when seen in detail, they are not quite circular. Dislocation “trails” of varying length and orientation were also observed in some regions of the samples, as illustrated in Figure 3-10. There are two possible explanations for the formation of these trails: one is caused by a dislocation intersecting the sample surface at an inclined angle. This leads to a “memory effect” of the position at which the dislocation intersects the surface as progressively more surface material is etched away. Another is due to impurities or other defects left behind by the dislocation lines as they propagate through the sample during the ingot-cooling stage. These “residuals” might then be preferentially etched by the etchant, forming the trails. This will be discussed further in Section 3.8. In any case, it is still possible to distinguish the dislocation pit component from the trail component by differences in the depth profile.

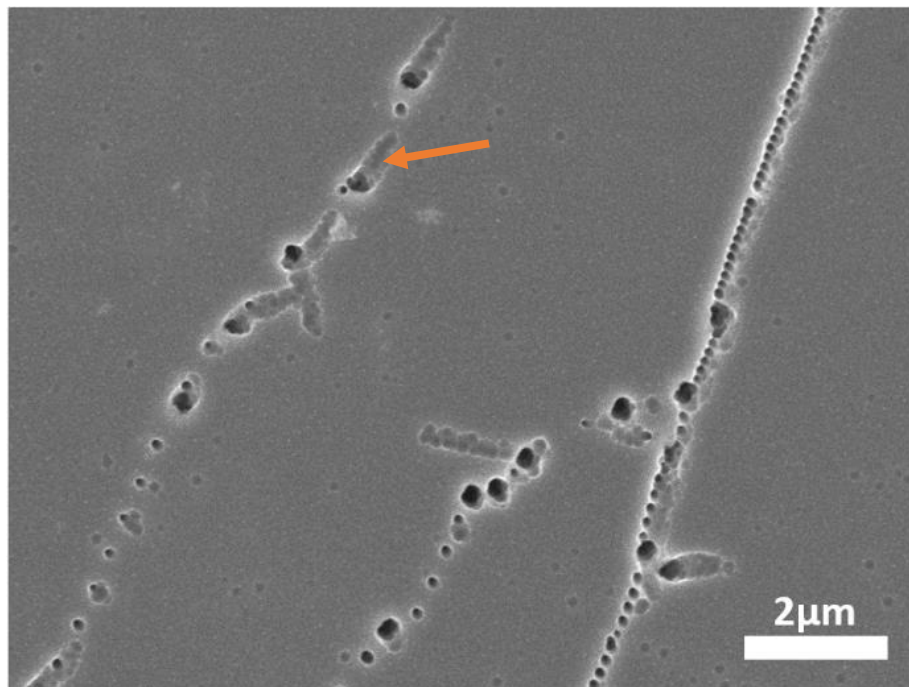


Figure 3-10. An SEM image of an mc-Si sample etched in dilute Secco solution for 60sec at 20°C. The figure shows trails attaching to some of the dislocations, as indicated by the orange arrow.

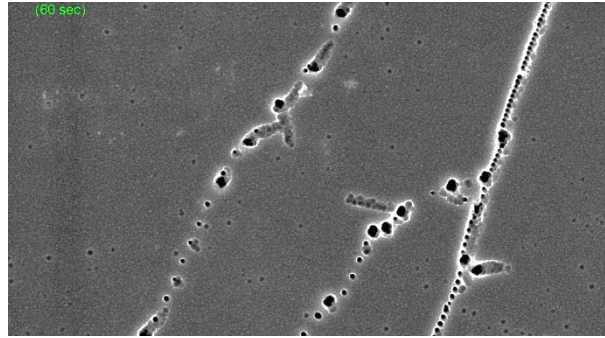
The principle of the method developed for dislocation pits in SEM images is to take into account only the section of the pits where the depth profile cannot be observed.

The method is demonstrated in the SEM image in Figure 3-10. The first step was to maximise the dislocation contrast by performing image normalisation in the ImageJ software. The process involves stretching the contrast histogram such that the pixels with extreme contrast values become saturated. The image after normalisation is shown in Figure 3-11 (a). In the second step, dislocation pits were isolated from the rest of the sample by converting the image into a binary image with a contrast threshold of one, i.e., pixels with intensity values other than zero become 0 (black) while those with pixel values equal to zero become white (255). The resulting image in Figure 3-11 (b) still contains undesirable features, such as small dislocation pits and surface artefacts. These features were removed by introducing a cluster threshold, A_{min} . The optimum A_{min} was determined by systematically increasing the value until all the undesirable features were removed. Figure 3-11 (c) shows the final binary image with $A_{min} = 90$ pixels. The fourth step was to determine the area of the white pixel clusters, i.e. dislocation pits. In the last step, the areas were converted into diameters using:

Equation 3-12

$$d = \frac{\sqrt{A}}{\pi} * 2 * C_{SEM}$$

where C_{SEM} is the unit conversion factor (pixel/nm), which can be determined using the ImageJ software.



(a) Normalised image



(b) Binary image ($A_{min}=1$)



(c) Binary image ($A_{min}=90$)

Figure 3-11. Shown here are various stages of image processing performed by the program to measure the diameter of dislocation pits in SEM micrographs: (a) is the normalised image; and (b) and (c) are the binary images at $A_{min} = 1$ pixel and $A_{min} = 90$ pixels, respectively.

There were occasions where undesirable features could not be removed using A_{min} . The most common case was overlapping of dislocation pits with a combined pixel value normally exceeding A_{min} . These features could lead to overestimation of d_{avg} . They were removed using a similar Matlab program that employs the same measurement method to the previous one, but that allows the user

to select a specific dislocation pit, from which its diameter was determined. The dislocation pit with the same diameter in the dataset was discarded. It should be noted that this approach discarded measurements from the “small” type of etch pits.

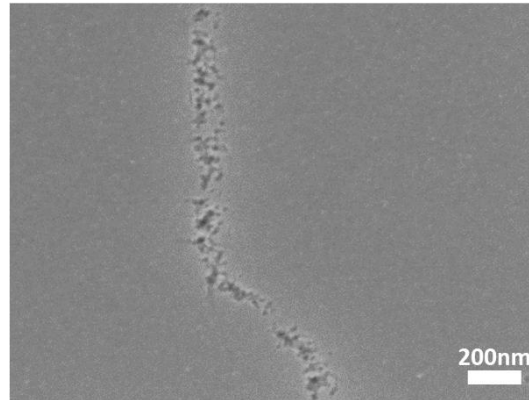
3.7.3 Optimising etch conditions

Three sets of samples were etched in Secco solution at various potassium dichromate concentrations, temperatures and time. The first set of samples was etched in Secco solution at potassium dichromate concentrations varying from 0.05M to 0.30M. The temperature and the etch time were kept constant at 20°C and 60sec, respectively. The second set of samples was etched at a variety of temperatures from 20 to 30°C. Other etch parameters remained the same, i.e., 0.05M potassium dichromate concentration and 60sec etch time. In the last set of samples, the etch time was varied from 10sec to 60sec. The solution temperature and the potassium dichromate concentration remained the same at 20°C and 0.05M, respectively.

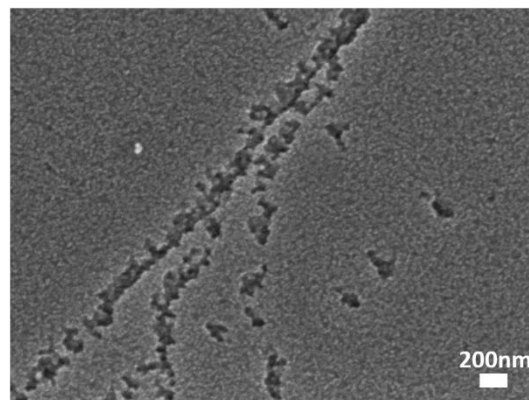
Samples were imaged using the optical microscope, with the exception of those etched for varying times. These samples were imaged in SEM because the dislocation pits were smaller than the resolution limit of the optical microscope. Matlab programs developed as described in Section 3.7.2 were employed to measure the diameters of 2000 dislocation pits for each sample, from which d_{avg} was calculated. Note that it is not possible to compare the values obtained from different imaging modes, i.e., optical images and SEM images, due to the differences in the lateral and depth resolutions, and the defect size measurement methods.

The results are summarised in Figure 3-13 to Figure 3-15. The error bars were determined using the methods described in Section 3.4. Each data point contains about 2000 dislocation pits. All the figures show a linear increase in d_{avg} , with an increase in all three parameters, i.e., the potassium dichromate concentration, the temperature and the etch time. Note that the d_{avg} was not determined for the samples etched for 10 and 20sec because the shape of the dislocation pits in both samples was too distorted to be used for APT specimen fabrication. In addition, the latter also

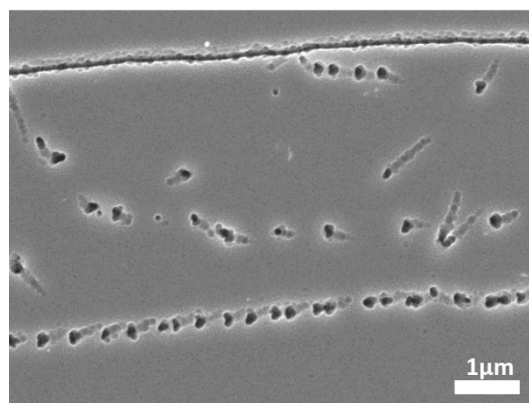
contained surface irregularities, which could reduce the visibility of defects. The only sample with d_{avg} close to 100nm was etched at a 0.05M potassium dichromate concentration, a 20°C temperature and a 30sec etch time. Hence, these parameters were used for the next experiment.



(a) $t=10\text{sec}$



(b) $t=20\text{sec}$



(c) $t=30\text{sec}$

Figure 3-12. SEM images of mc-Si samples etched in diluted Secco solution at 20°C for (a) 10sec, (b) 20sec and (c) 30sec.

Chapter 3- The development of preferential etching

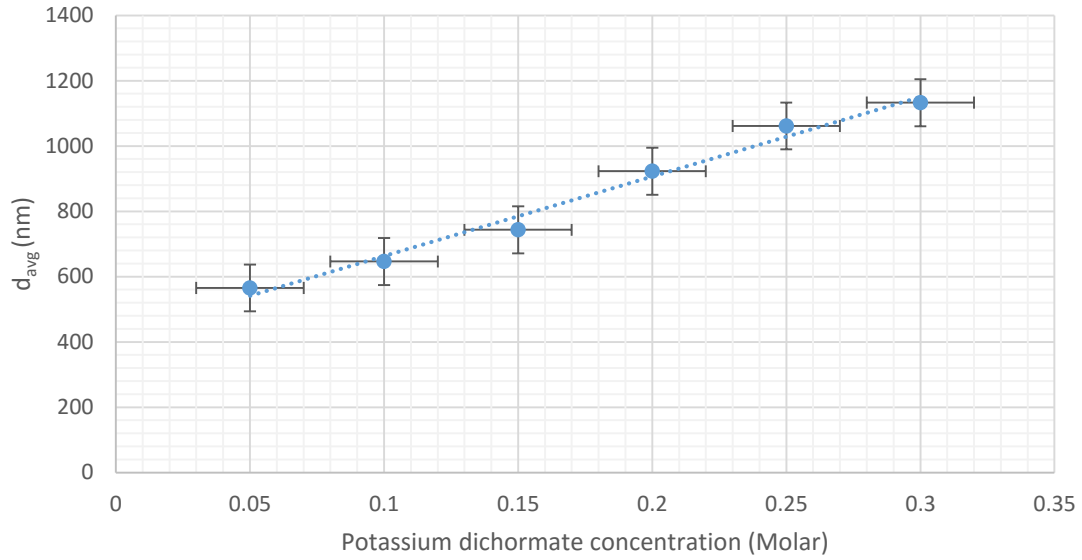


Figure 3-13. The graph shows d_{avg} as a function of potassium dichromate concentration. The temperature and the etch time were kept constant at 20°C and 60sec, respectively. The data were obtained from optical images.

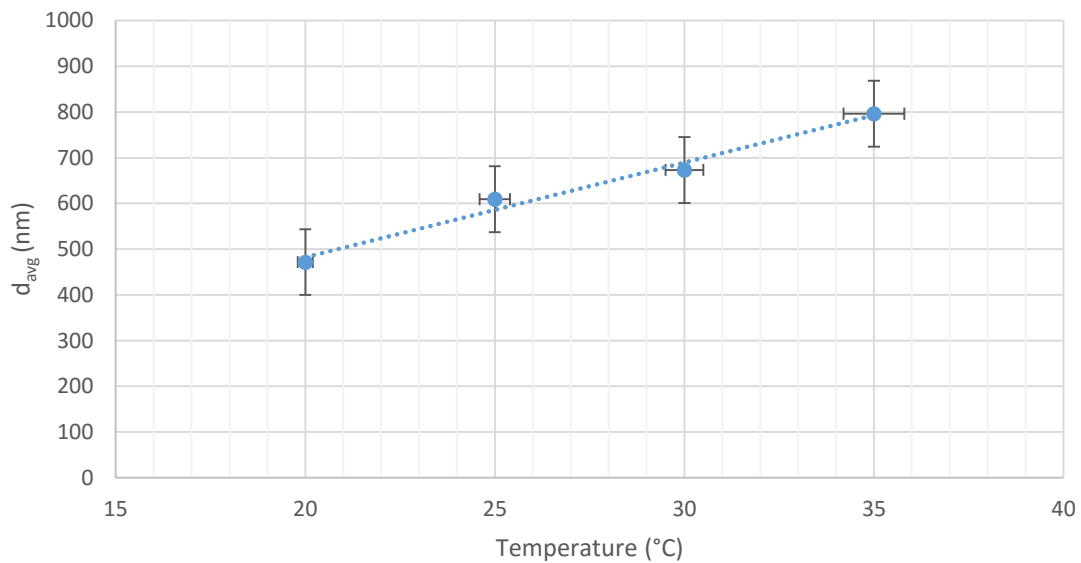


Figure 3-14. The graph shows d_{avg} as a function of temperature. The potassium dichromate concentration and the etch time were kept constant at 0.05M and 60sec, respectively. The data were obtained from optical images.

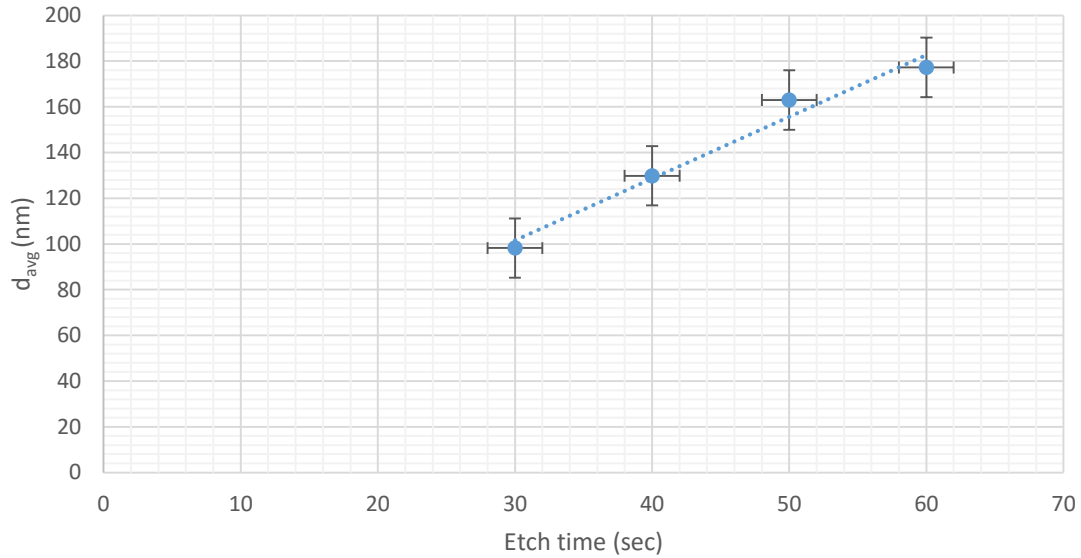


Figure 3-15. The graph shows the d_{avg} as a function of etch time. The potassium dichromate concentration and the temperature were kept at 0.05M and 20°C, respectively. The data were obtained from SEM images.

3.7.4 Repeat etching

The etch parameters obtained from these experiments were used to etch five samples to determine whether similar d_{avg} would be obtained. The result is summarised in Figure 3-16. Each bar contains measurements from 2000 dislocation pits. The average d_{avg} over all the samples was 100nm. The difference between the smallest and the largest diameters was 11nm. The variations in the d_{avg} between the samples could be due to combinations of experimental errors and factors associated with the sample mentioned in Section 3.4 and 3.4, respectively. From this work the reproducibility of etch pit diameters was considered satisfactory in terms of locating the dislocation locations for APT specimen fabrication.

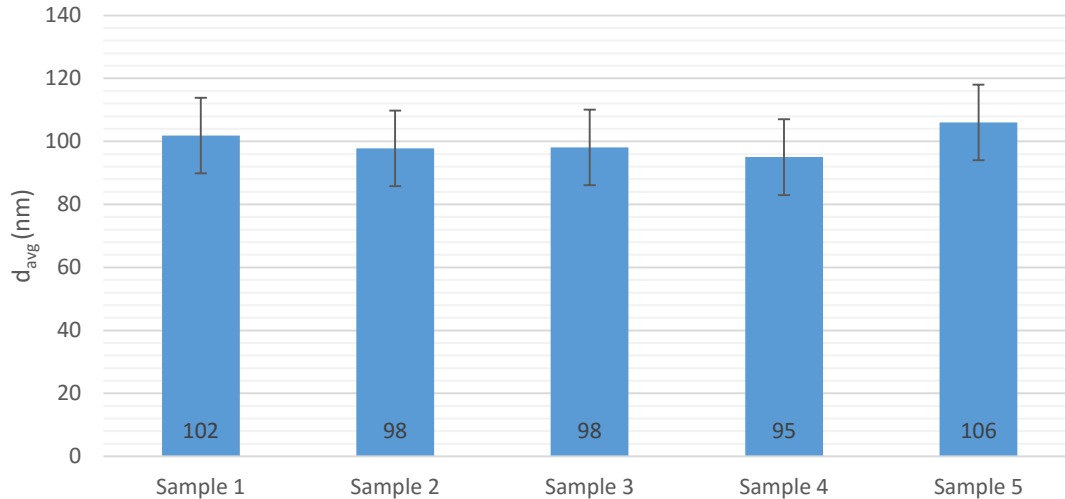


Figure 3-16. The graph shows d_{avg} of five mc-Si samples etched in Secco containing 0.05M potassium dichromate concentration for 30sec at 20°C.

3.7.5 Etch pit depth measurement

This experiment in this section was conducted to determine whether the etch parameters obtained as described in Section 3.7.5 could still be used with the APT fabrication methods developed in Chapter 4. Depth measurements were performed on the same samples from Section 3.7.4 using the method described in Section 3.3.2.

The result is summarised in Figure 3-17. Each bar contains measurements from 20 dislocation pits and 20 grain boundaries. The average defect depth was 170nm, which is within the required range (100nm–1000nm). Hence, the following etch parameters were also used for the APT specimen fabrication methods developed as described in Chapter 4.

It was not possible to determine whether there was a correlation between the depth and the height, due to the small sample size and the fact that it was difficult to perform accurate depth measurement on dislocation pits that did not run normal to the surface.

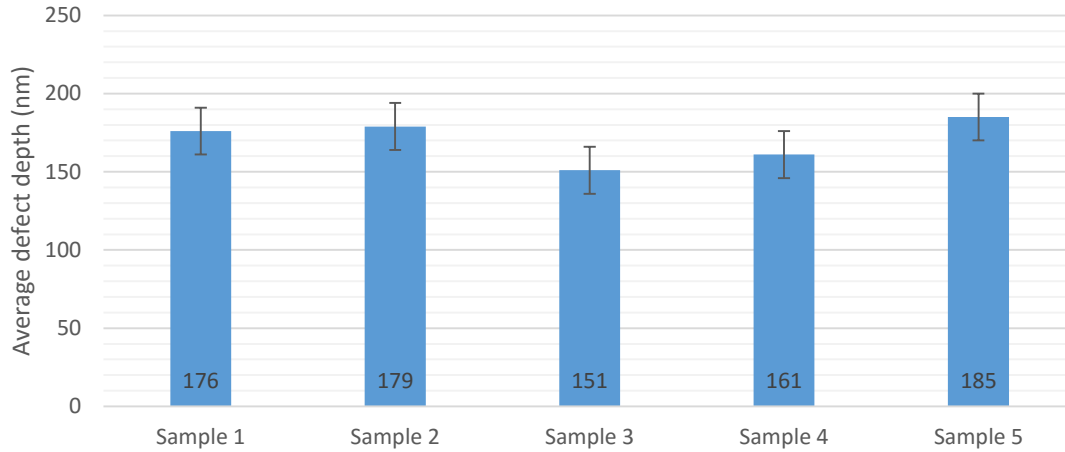


Figure 3-17. The graph shows average defect depths of five mc-Si samples etched in Secco containing 0.05M potassium dichromate concentration for 30sec at 20°C.

3.7.6 Conclusion

The results showed approximately linear dependence of d_{avg} on all three etch parameters: namely, the potassium dichromate concentration, the temperature and the etch time. The etch parameters that produced dislocation pits with d_{avg} of about 100nm were 0.05M potassium dichromate concentration, 20°C temperature and 30sec etch time. These parameters were able to consistently produce similar d_{avg} in five samples. Defect depth measurement indicates that the parameters can also be used for the APT specimen fabrication methods described in Section 2.7.4.2. Hence, these parameters were used to etch mc-Si samples throughout the rest of this work.

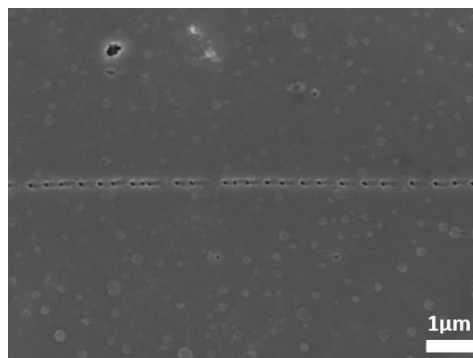
3.8 Determining the propagation direction of defects in mc-Si

The APT specimen fabrication method described in Section 2.7.4.2 was developed based on the assumption that all defects run normal to the sample surface. However, TEM analysis of the specimens in Section 4.5.1.1 shows that they did not contain extended defects despite having the marker at the tip. Consequently, experiments were conducted to investigate the propagation behaviour of defects through the sample thickness. All the experiments were performed on as-grown mc-Si samples taken from the top section of a directionally-solidified ingot. The samples were etched in Secco using the parameters established in Section 3.7.5.

3.8.1 A line of dislocation pits

The first experiment investigates the propagation behaviour of dislocations through the sample thickness as well as the trails attached to the dislocations.

A line of dislocations with trails aligned along the direction of the line in Figure 3-18 (a) was fabricated into a TEM specimen using the method described in Section 2.7.4.3. The TEM image of the specimen in Figure 3-18 (b) shows that all dislocation lines do not run normal to the sample surface. Instead, they propagate at very similar inclined angles ranging from 10° to 12° . The other important feature is that the dislocation lines incline towards the trails, which is the opposite of what would be expected if these trails were formed simply by the memory effect described in Section 3.7.2.3. Hence, the trail structure cannot simply be explained by the inclined dislocations. This means that etching of impurities or other defects left behind by advancing dislocation lines is a better explanation for the formation of these trails.



(a)

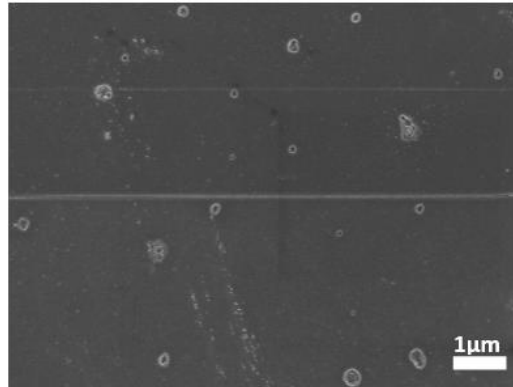


(b)

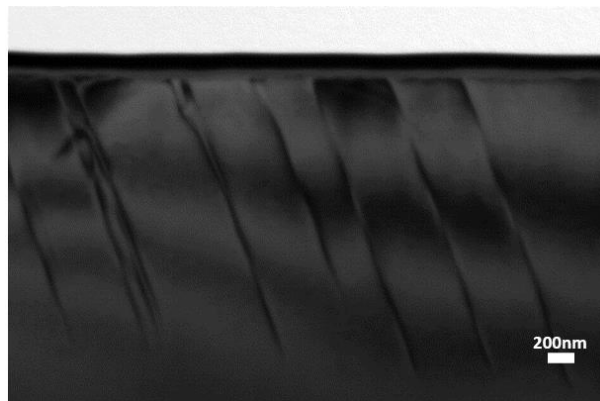
Figure 3-18. (a) An SEM micrograph of a line of dislocations in a Secco-etched mc-Si sample; and (b) a TEM image showing a cross-section of the dislocation lines. Note that the two notches on the right-hand side, indicated by the orange arrows, were created during TEM specimen fabrication to ensure that the position of the TEM image relative to the location on the original plan view sample surface is known.

3.8.2 Grain boundaries

In the second experiment, the propagation behaviour of the grain boundary shown in Figure 3-19 (a) was investigated. Similar to the previous experiment, the defect was fabricated into a TEM specimen and then observed in the TEM. Figure 3-19 (b) reveals dislocation lines contained within the grain boundary. These dislocations were found to propagate at inclined angles of between 20 and 25°.



(a)



(b)

Figure 3-19. (a) An SEM micrograph of a grain boundary in a Secco-etched mc-Si sample; and (b) a TEM image showing a cross-section containing the grain boundary.

Similar behaviour was also observed for some grain boundaries while undertaking depth measurements as described in Section 3.3.2. Figure 3-20 shows a cross-sectional image of a grain boundary taken at 54° relative to the sample surface. The boundary was filled with tungsten to differentiate it from the rest of the sample. The tilting angle of the grain boundary plane was 22° relative to the surface normal.

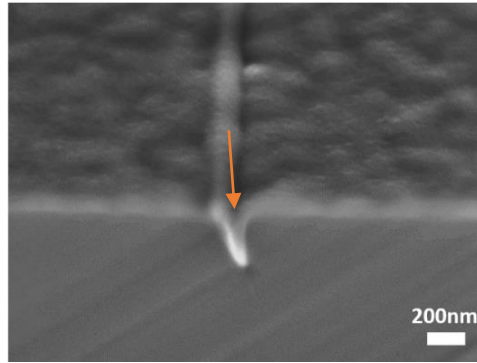


Figure 3-20. An SEM image of an etched grain boundary filled with tungsten, as indicated by the orange arrow. The image was taken at 54° relative to the sample surface.

3.8.3 Propagation of defects through the sample thickness

Previous experiments have shown that defects in mc-Si samples do not run perpendicular to the surface. However, since the wafers are only 200microns thick, it was thought that it might be possible to predict the propagation direction of defects throughout the entire thickness of a wafer by comparing the positions on a wafer where they intersected the top and bottom surfaces. If the defects were found to run in straight lines in between, this would allow the direction of propagation to be inferred.

The top and the bottom surfaces of the sample were etched in Secco using the parameters established in Section 3.7.6. SEM images of the same region of the sample were then taken from both surfaces. The images were then patched together to form two large images of the region. The image of the bottom surface was inverted and then merged with the image of the top surface. The final image is shown in Figure 3-21. These processes were carried out using the Adobe Photoshop CS6 software. The coincident point of the two images was the grain boundary in Figure 3-21 (a). The defects at the top and the bottom surfaces are displayed in white and black, respectively. Figure 3-21 (b) shows random misalignment between the dislocations at the top and the bottom surfaces. Similar behaviour was also observed for the grain boundary: this is marked by orange arrows, in Figure 3-21 (c). These misalignments meant it was not possible to identify individual etch pits on the top and bottom surfaces with the same defect and this approach was therefore discontinued.

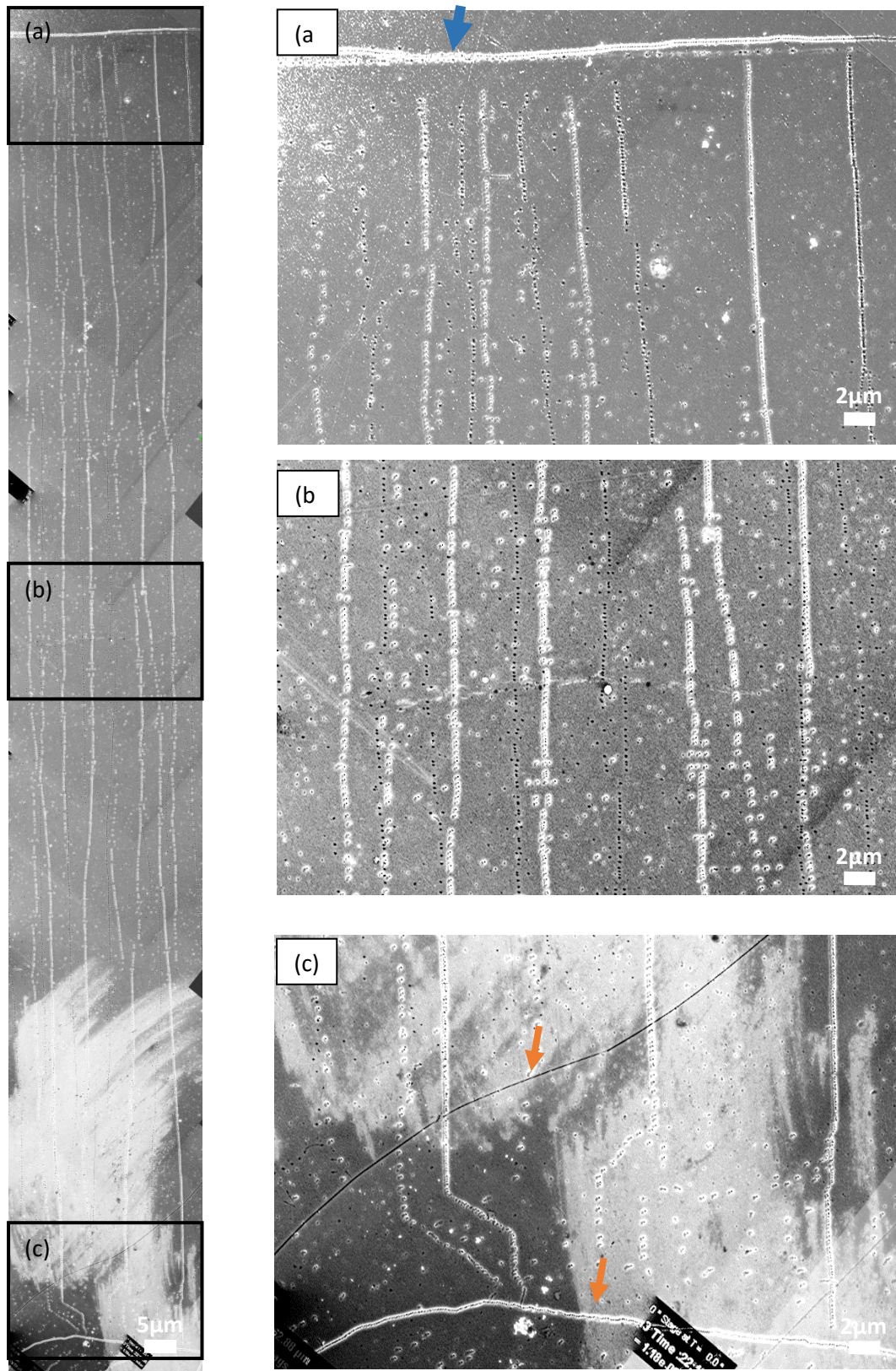


Figure 3-21. Merged SEM images of a Secco-etched mc-Si sample. (a) to (c) are high magnification images of three selected regions. Note that the defects at the top and bottom surfaces are white and dark, respectively. The coincidence point is the grain boundary in (a) indicated by the blue arrow. The orange arrows in (c) indicate the position of the grain boundary at the top surface relative to the bottom surface.

3.8.4 Conclusion

The studies of the propagation behaviours of defects in mc-Si samples show that most defects do not run perpendicular to the sample surface but instead are inclined, with angles typically in the range of 10° to 25°. The propagation direction of these defects through the sample thickness appears to be random. This makes it difficult (with the equipment available) to predict the propagation direction of a particular defect without using TEM or performing cross-sectional characterisation using FIB.

3.9 Chapter summary

This chapter has explored three potential etchants for defect delineation: namely, Dash, Sirtl and Secco—from which Secco was selected. Three parameters of the Secco etch process were then optimised to produce circular dislocation pits with d_{avg} of about 100nm. The optimum parameters were 0.05M potassium dichromate concentration, 20°C temperature, and 30sec etch time. Repeat etching on five samples has shown that dislocations with similar d_{avg} can be produced. Hence, the parameters were used for the APT specimen fabrication method described in Section 2.7.4.2. Depth measurement results show that the average defect depth was 170nm across five samples, which is within the 100nm to 1000nm range required for APT specimen fabrication, and, thus, these etch parameters were used to etch samples for the APT specimen fabrication methods developed as described in Chapter 4. The optimum parameters were also used to study propagation behaviours of defects through the sample thickness. The investigated defects were found to propagate at inclined angles to the surface normal, and their propagation directions were found to be unpredictable.

3.10 References

- ¹ Miller, M. K., Russell, K. F., Thompson, K., Alvis, R., & Larson, D. J. (2007). Review of atom probe FIB-based specimen preparation methods. *Microscopy and Microanalysis*, 13(06), 428-436.
- ² W. C. Dash, *J. Applied Physics*, 27, 1193 (1956).
- ³ E. Sirtl and A. Adler, *Z. Metallkunde*, 52, 529 (1961).
- ⁴ F. Secco d'Argona; *J. Electrochemistry Society*, 948–951 (1972).
- ⁵ Schimmel, D. G. (1979). Defect etch for < 100 > silicon evaluation. *Journal of the Electrochemical Society*, 126(3), 479-483.
- ⁶ Jenkins, M. W. (1977). A new preferential etch for defects in silicon crystals. *Journal of the Electrochemical Society*, 124(5), 757-762.
- ⁷ Yang, K. H. (1984). An etch for delineation of defects in silicon. *Journal of the Electrochemical Society*, 131(5), 1140-1145.
- ⁸ d'Aragona, F. S. (1972). Dislocation etch for (100) planes in silicon. *Journal of the Electrochemical Society*, 119(7), 948-951.
- ⁹ Seo, Y. H., Nahm, K. S., Hahn, Y. B., & Kim, C. B. (1994). Reaction kinetics of silicon etching in HF-K₂Cr₂O₇-H₂O solution. *Korean Journal of Chemical Engineering*, 11(2), 89-95.
- ¹⁰ Idrisi, H., Sinke, T., Gerhardt, V., Ceglarek, D., & Kolbesen, B. O. (2011). Decoration and preferential etching of crystal defects in silicon materials: influence of metal decoration on the defect etching process. *physica status solidi (c)*, 8(3), 788-791.

4 The development of the APT specimen fabrication method

Table of Contents

4.1	Introduction	98
4.2	Materials and sample preparation	98
4.3	Methodology.....	99
4.3.1	Instrumentation	99
4.3.2	APT specimen holders.....	99
4.3.3	Dimensional measurement methods for marker components	99
4.3.4	Experimental errors	100
4.4	Defect-marking techniques.....	100
4.4.1	FIB-milled line-marking technique	100
4.4.2	Electron beam-induced deposition dot-marking technique.....	105
4.4.3	FIB-deposited line-marking technique.....	129
4.5	The development of APT specimen fabrication method	132
4.5.1	Novel approach to APT specimen fabrication.....	132
4.5.2	APT specimen holders.....	146
4.5.3	Summary of the APT specimen fabrication methods	151
4.5.4	References	152

4.1 Introduction

APT specimen fabrication methods reported in the literature^{1,2,3,4} lack the spatial accuracy to select a specific defect, such as a dislocation. Hence, this chapter describes the development of new APT specimen fabrication methods. The chapter can be separated into three major parts: (a) defect-marking techniques; (b) the APT specimen fabrication approach; and (c) APT specimen holders.

The defect-marking techniques for dislocations described in Sections 4.4.1 and 4.4.2 were developed for dislocations and for the early APT fabrication method described in Section 2.7.4.2. However, the experiments described in Section 3.8 and 4.5.1.1 have shown that the fabrication method cannot be used to fabricate APT specimens containing a single, selected dislocation. An alternative approach to APT specimen fabrication is postulated in Section 4.5.1.2: in this section, two APT specimen fabrication methods are described for dislocations and grain boundaries. Due to the late incorporation of grain boundaries into this work, the marking technique for grain boundaries described in Section 4.4.3.2 was developed especially for the later fabrication method described in Section 4.5.1.2.

Three types of holders were also used at different stages, as described in this chapter, to mount and fabricate APT specimens. These holders are described in Section 4.5.2.

4.2 Materials and sample preparation

Two types of samples were employed, as described in this chapter: cz-Si samples and mc-Si samples. The former were used (after RCA-cleaning) to optimise various instrumental parameters associated with the marking techniques.

The latter were polished, RCA cleaned, and, subsequently etched in the Secco etch, which contained a 0.05M potassium dichromate concentration, for 30sec at 20°C. These parameters were those obtained from the experiments described in Chapter 3 to produce dislocation pits with an average diameter of 100nm and defects with an average depth of 170nm. They were used to evaluate the

effectiveness of the marking techniques, as described in Section 4.4, and the APT specimen fabrication methods described in Section 4.5.1.

4.3 Methodology

4.3.1 Instrumentation

Two instruments were employed, as described in this chapter: the Nvision and Jeol 2000FX TEM. The Nvision was used in the development of the marking techniques and APT specimen fabrication methods, and the fabrication of tungsten posts. All SEM images were taken in “InLens” mode, at 5kV accelerating voltage and 120 μ m objective aperture size. FIB milling and deposition were performed using the parameters mentioned in Section 2.7.3, unless stated otherwise. The presence of defects in APT specimens was confirmed in the TEM. TEM images were taken in “BF” mode.

4.3.2 APT specimen holders

APT specimens were fabricated on three different types of platforms. Silicon coupons containing an array of 36 highly-doped silicon posts were employed throughout, as described in Section 4.4. TEM analyses were performed on APT specimens attached to tungsten posts, as described in Section 4.5.1.3. The lift-out grids were then used with the “parallel surface methods” described in Section 4.5.1.2.

4.3.3 Dimensional measurement methods for marker components

The dimensions of various components of the marking techniques developed as described in Section 4.4 were determined by taking an average of five measurements. It is important to note that the thickness or the height of a component was determined with the component tilted at an angle of 54° relative to the surface normal. Hence, Equation 3.1 was used to determine the actual height or thickness of the component.

A problem encountered when measuring the thickness of the material strip was that the sharpness of the strip edges was insufficient to allow the thickness to be accurately determined. Hence, a sharp

cross-section of the strip was created prior to the height measurement, by milling a vertical trench close to the strip at a milling current of 3nA. This was followed by milling a second trench that overlapped the first trench and part of the strip at a milling current of 300pA. The first trench provided a sink for sputtered materials to redeposit when milling the second trench. The second trench was milled at lower beam energy to produce strips with a sharp cross-sectional surface.

4.3.4 Experimental errors

This section summarises possible sources of errors associated with the experiments described in this section. The human errors associated with the dimensional measurement methods, e_m , is taken to be the standard deviation of five measurements. In the case of thickness and height measurements, measurement errors also accounted for the fact that the sample was tilted by 54°. This was achieved by:

Equation 4-1
$$e_t = \frac{e_m}{\sin 54^\circ}$$

4.4 Defect-marking techniques

4.4.1 FIB-milled line-marking technique

The FIB-milled line-marking technique was the first technique to be developed in this project, but it was not incorporated into the final APT specimen fabrication method due to problems with reproducibility and limited accuracy as a defect-marker. This section provides a summary of the development of the marking technique.

The technique was used for marking the position of a line of dislocation pits. The fabrication procedure of the technique is shown schematically in Figure 4-1. The first step was to deposit a material strip over the line of dislocations, with the latter running along the centre and parallel to length of the former. The strip served two functions, which were: (a) to outline the size of the wedge component to aid with the cantilever fabrication; and (b) to protect dislocation pits from the ion beam during the application of the line pattern and subsequent APT specimen fabrication process.

Carbon was used for the outline strip because it is the most common material used in the Nvision to protect the feature of interest from FIB irradiation. The length and the width of the outline strip were $15\mu\text{m}$ and $4\mu\text{m}$, respectively. The second step was to mark the location of the line by milling a line pattern directly over it. Both steps were performed using the FIB. The length of the milled line was the same as that of the strip, in order to maximise the number of APT specimens that could be fabricated from a single wedge.

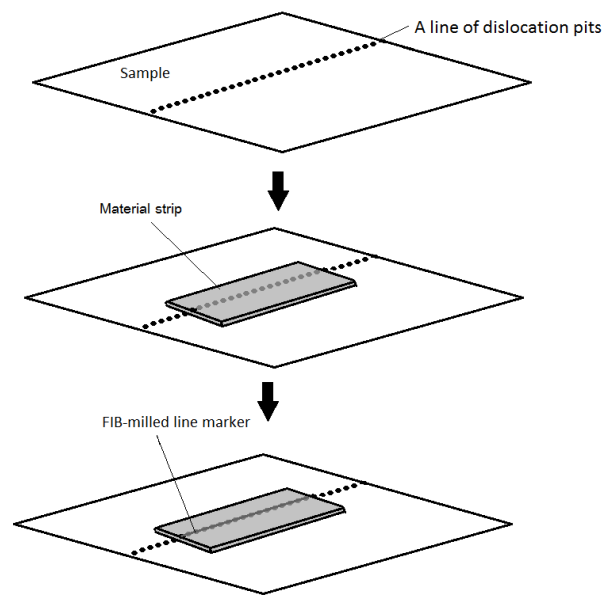


Figure 4-1. A schematic of the FIB-milled line-marking technique.

An important parameter that influences the effectiveness of the milled line maker is its width, since a wider line would increase the location uncertainty of marked defects. It was therefore necessary to minimise the width of the line. The line width is dependent on the diameter of the ion beam, which changes with the beam current. Hence, the effect of the beam current on the width of the milled line-marker was investigated by measuring the width of five lines milled at different milling beam currents: 1pA, 10pA, 40pA, 80pA and 150pA. The milling time was kept constant at 10sec. Figure 4-2 shows an increase in line width with higher beam current. This can be explained by the fact that the

ion beam current in the FIB column is decreased by reducing the objective aperture size. Since the objective was to minimise the line width, the lowest beam current (i.e, 1pA) was selected.

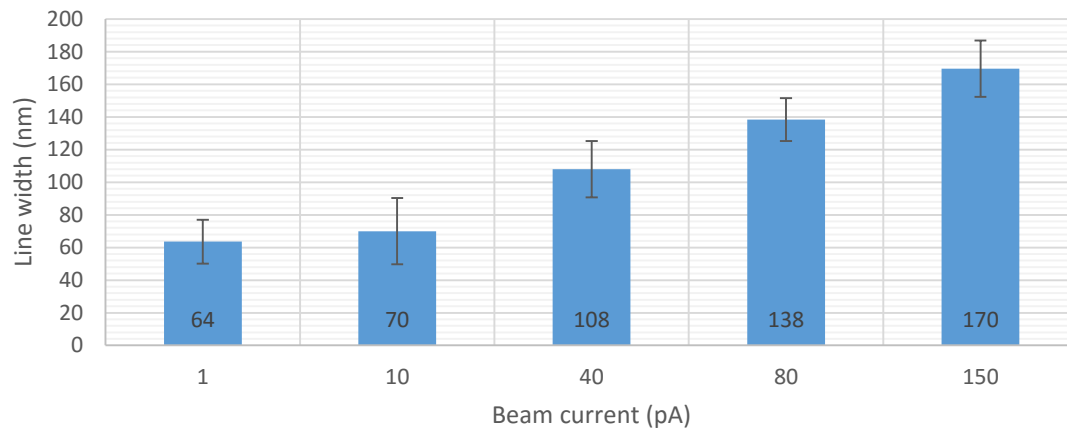


Figure 4-2. Average width of 10µm long lines milled at five different beam currents with a milling time of 10sec.

The marking technique was applied to four lines of closely-spaced dislocation pits. The deposition time of the carbon strip was kept the same at 90sec. In order to determine the optimum milling time for the marker, the time was varied from 5sec to 20sec, at 5sec intervals. The markers were then fabricated into APT specimens using the method described in Section 2.7.4.2.

Three specimens were successfully attached to s-Si posts for each marker milling time. However, only one specimen was fabricated into an APT specimen. The milling time of the line-marker for this specimen was 10sec. Figure 4-3 (a) to (d) shows that the line-marker from a trial along the side of the specimen could only be observed up to the last few stages of the annular milling process. It was therefore difficult to unambiguously determine the effectiveness of the marking technique without TEM or APT analysis. Furthermore, TEM analysis could not be performed on the specimen because the specimen was attached to a post on a Si coupon, which was specifically designed to be used for APT. Consequently, the specimen was analysed for APT. The results did not show visible segregation of chemical species in the specimen, and thus there was no indication of a dislocation having been present in the APT specimen.

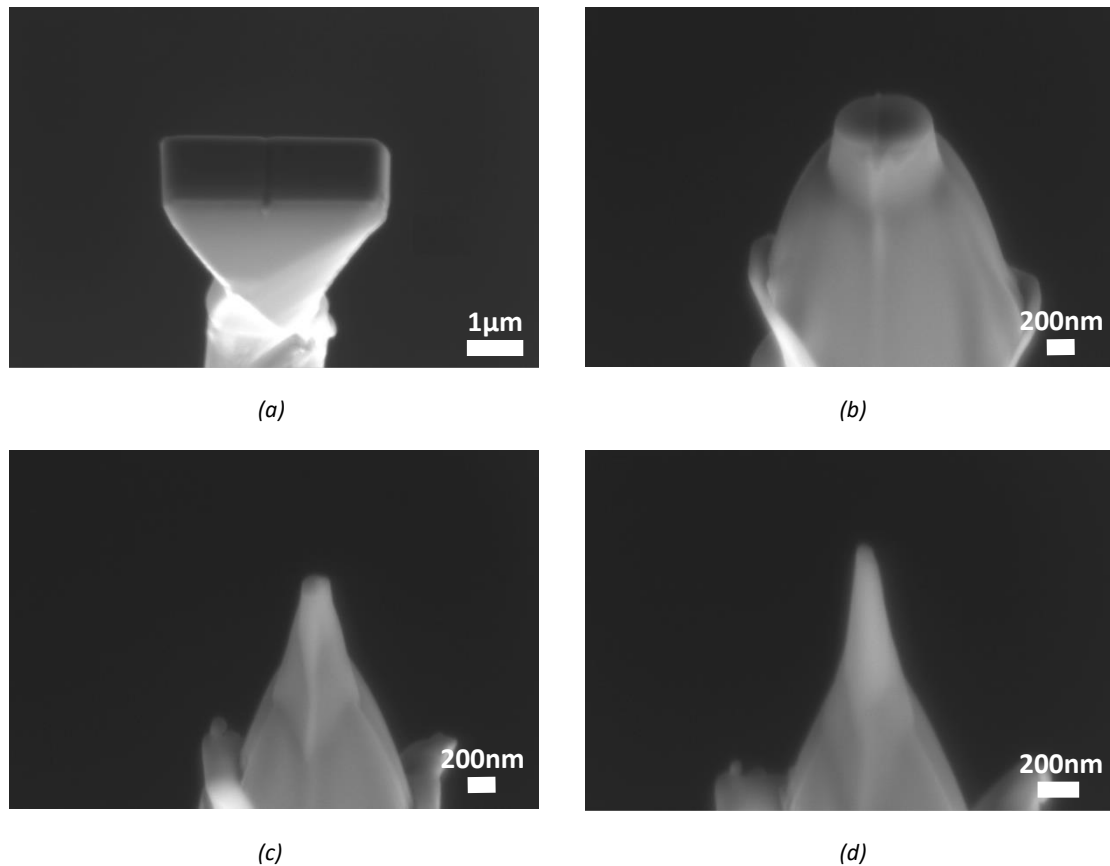


Figure 4-3 (a)–(d). SEM images show four stages of the annular milling process of the specimen, containing a line of dislocations marked using the FIB-milled marking technique.

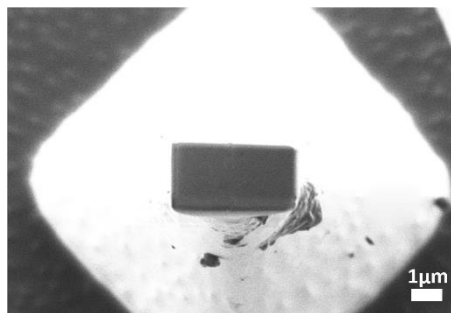
The APT specimen fabrication process could not be completed if the marker failed during the sharpening step. The failures can be separated into three main types.

The first type of failure occurred when the line-marker was applied at 5sec milling time: the markers were gradually removed from the carbon surface to the point where they were indistinguishable from the carbon strip's surface. Figure 4-4 (a) shows a specimen with the marker having been removed right after it was attached to the silicon post.

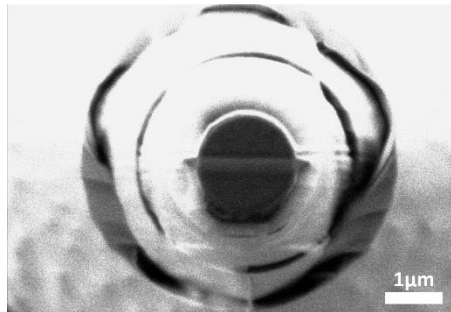
The second type of failure took place at 10sec and 15sec marker milling time. The width of the markers increased with longer exposure to FIB irradiation. The extent of this broadening effect varies depending on the stages in the sharpening step: i.e., the exposure of the marker to FIB irradiation. Figure 4-4 (b) shows a specimen where the marker had a width as large as 350nm. If the width of the marker exceeds 100nm, which is the apex diameter of a typical APT specimen, the

chances of fabricating an APT specimen with a defect running along its core are significantly reduced.

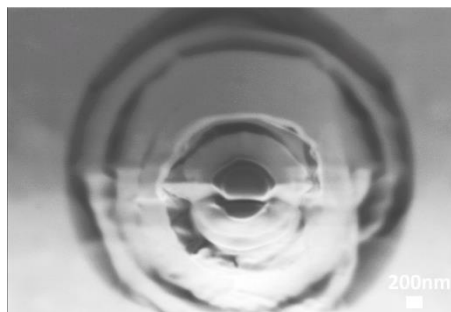
The third type of failure occurred at marker milling times of 15sec and 20sec. A broadening effect was observed. Although this was not as severe as in the previous type of failure, the markers caused the specimens to split into two segments, as illustrated in Figure 4-4 (c). This is perhaps due to the fact that the markers had penetrated the carbon layer, thus exposing the underlying dislocation pits to FIB irradiation.



(a)



(b)



(c)

Figure 4-4 (a)–(c). FIB images showing three types of marker failure behaviours, which are: marker (a) removal; (b) broadening; (c) splitting.

4.4.1.1 Conclusion

The evaluation of an FIB-milled line-marking technique revealed two major issues: one was the inability to reproduce APT specimens from the wedge segments with the same marker milling time. The other was the fact that the line pattern did not offer sufficient accuracy in relation to marking the location of a single dislocation. Although this can be overcome by using a different pattern to mark a specific dislocation, i.e., a cross-pattern, reproducibility issues would remain unresolved. Consequently, an alternative marking technique was needed.

4.4.2 Electron beam-induced deposition dot-marking technique

An alternative marking technique was developed to overcome the problems associated with the previous technique. This technique, shown schematically in Figure 4–5, consisted of two steps: first, a material strip was deposited to outline the size of the wedge. The length and the width of the strip were kept the same as those used in the previous technique: i.e., 15 μ m and 4 μ m, respectively. Second, a material dot was then applied directly over the dislocation pit to mark its location, as well as to define the diameter of the APT specimen's tip. The dot was deposited by switching the SEM to spot mode and focusing the beam, which is shown in the instrument software as a green crosshair, at a fixed position. The reasons why the electron beam was used instead of the ion beam were because (a) electrons do not cause sputtering of sample atoms, which would lead to the removal of dislocation pits; and (b) the electron beam can produce smaller dots than the ion beam because the former can be focused to a smaller diameter than the latter.

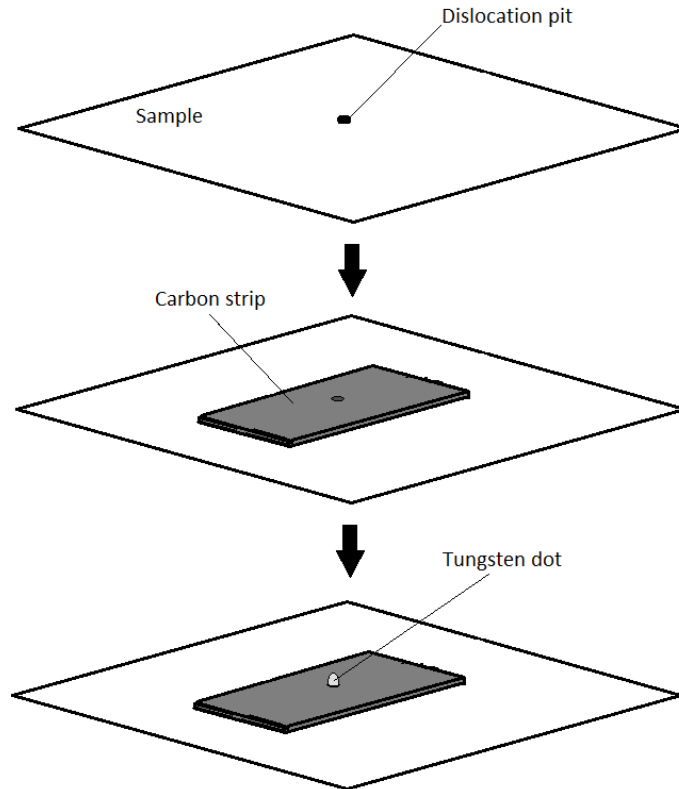


Figure 4–5. A schematic of the electron beam-induced deposition (EBID) dot-marking technique.

4.4.2.1 Material selection for the dot-marker

The visibility of tungsten and carbon on the Cz-Si sample surface was compared in order to select a material for the dot-marker. The visibility of each material was determined by its contrast value relative to that of the sample surface, which will be referred to as “differential contrast value”.

A rectangular pattern was employed instead of a dot pattern to avoid the influence of the edge effect – local enhancement of SE yield brought about by changes in surface topography – on their contrast values. The deposition was carried out using the FIB instead of the SEM because pattern deposition can only be done in the FIB. This is due to the limitation of the instrument’s software.

4.4.2.1.1 Surface irregularities of the tungsten strip

Surface irregularities were observed on a tungsten strip when it was deposited using the FIB parameters described in Section 2.7.3. A study by Jenkins et al.⁵ has shown that uniform strips can be obtained when the ion beam current is sufficiently low. Hence, tungsten strips were deposited at four different beam currents: 1pA, 10pA, 40pA and 80pA. The deposition time was kept constant at 300sec. Strip uniformity was obtained at ion beam currents of 40pA or less, as shown in Figure 4-6. Non-uniform deposition behaviours were observed at beam currents of 80pA. This can be explained by the removal of the native silicon oxides in the scanning direction of the FIB beam and subsequent nucleation of tungsten on the exposed silicon surfaces. Cross-sectional images of the strips, Figure 4-7, show an increase in the strip thickness with higher ion beam currents, compared with when the beam current is between 1pA and 40pA. This can be explained by the fact that the deposition rate is limited by the dissociation rate of the precursor gas molecules, which increases with the beam current.

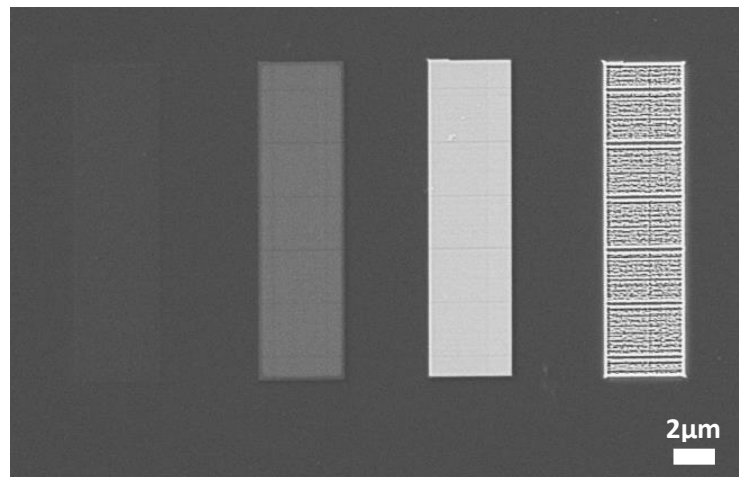


Figure 4-6. Top-view images of tungsten strips deposited at four different beam currents: 1pA, 40pA, 80pA and 150pA (from left to right).

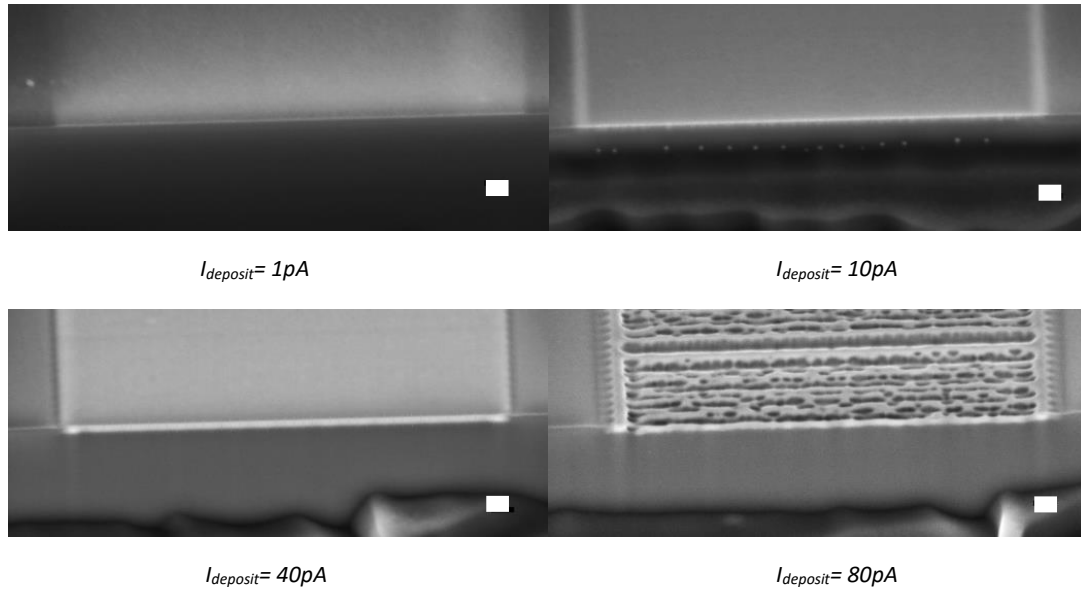


Figure 4-7. Cross-sectional images of tungsten strips deposited at four different beam energies. The scale bars are 200nm.

It was decided that the best beam current for depositing tungsten dots was 40pA, because this current has the highest deposition rate among the beam currents that produce uniform strips.

4.4.2.1.2 Strip thickness calibration

After having resolved the problem regarding surface irregularities of tungsten dots, the next step was to perform a thickness calibration in respect of both materials (carbon and tungsten) in order to produce strips with the same thickness. This was necessary because the contrast value is affected by the thickness of the strip. This is illustrated in Figure 4-8, which shows the contrast value of the strip at time t (C_t) relative to that of the strip deposited at 20sec deposition time (C_{20}), which was expressed mathematically by Equation 4-2, in the SEM in InLens mode and in SE mode.

Equation 4-2

$$\Delta C = \left(\frac{C_t}{C_{20}} * 100 \right) - 100$$

Another notable feature of this graph is that ΔC increases with longer deposition time for tungsten while the opposite relationship was observed for carbon. This indicates that tungsten and carbon become, respectively, brighter and darker with longer deposition times.

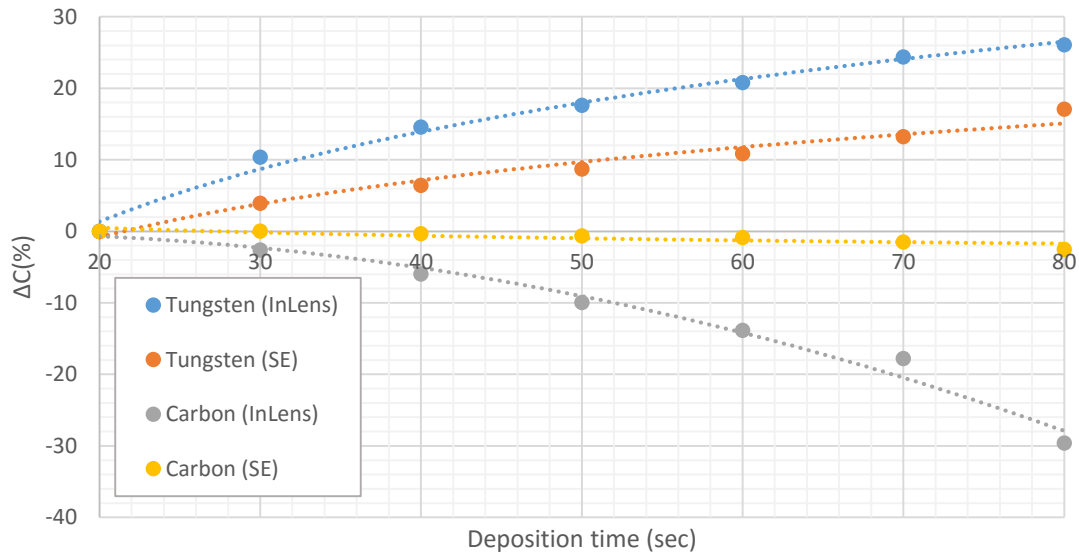


Figure 4-8. Graph showing changes in the contrast value of the carbon and tungsten strips relative to that deposited at 20sec for two imaging modes: SEM in InLens mode and in SE mode. The lines are guides for the eyes only.

Figure 4-9 shows strip thickness as a function of deposition time for carbon and tungsten. Note that all the tungsten strips were deposited at the beam current of 40pA in order to maintain surface uniformity. The experimental data points for carbon and tungsten can be described by linear equations:

Equation 4-3
$$T_{carbon} = 1.1t_{strip} + 35.3 \text{ (for carbon)}$$

Equation 4-4
$$T_{tungsten} = 0.5t_{strip} + 13.2 \text{ (for tungsten)}$$

where T_{carbon} and $T_{tungsten}$ are the thickness of carbon and tungsten in nm, respectively, and t_{strip} is the deposition time in sec. The equations indicate that the vertical growth rate of carbon is higher than that of tungsten, which is confirmed in the cross-sectional images of the strips in Figure 4-7, respectively. It is worth pointing out that, according to these equations, the thickness of both material strips is not zero at zero deposition time, indicating that the equations lose validity at short deposition times. This could be due to the fact that the vertical growth rate is very fast at deposition times below 10seconds and this is not accounted for in the equations.

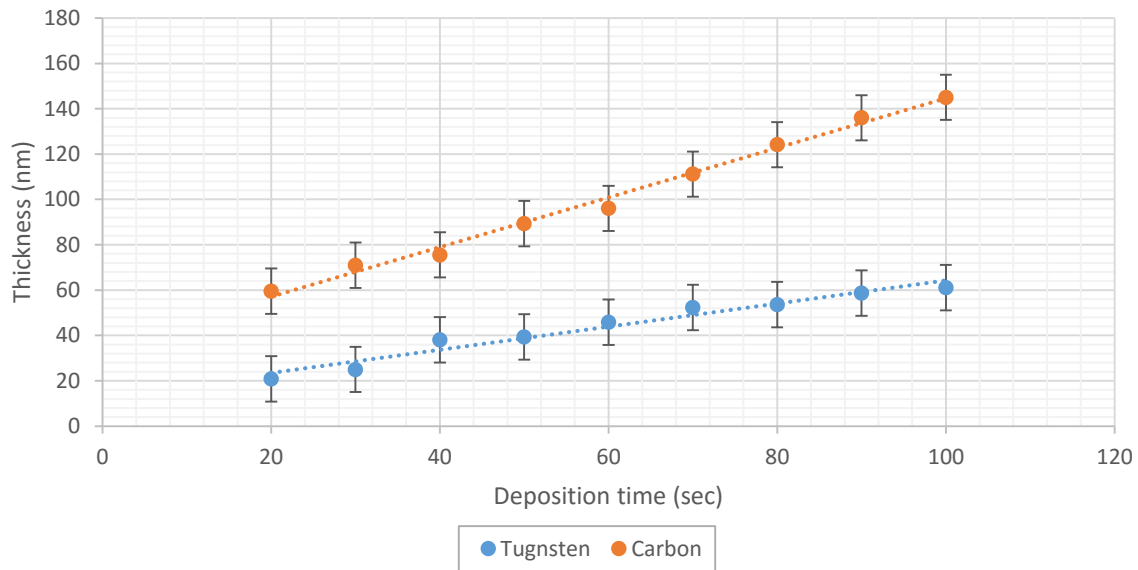


Figure 4-9. Strip thickness as a function of deposition time for carbon (orange dots) and tungsten (blue dots).

4.4.2.1.3 Comparing differential contrast between tungsten and carbon strips

Carbon and tungsten strips were deposited next to each other in order to expose both strips to the same imaging conditions. This is particularly important for FIB imaging, where the contrast value of the strips changes with FIB exposure time. Equation 4-3 and Equation 4-4 were then used to determine the deposition time needed to deposit 60nm thick carbon and tungsten strips, respectively. Other deposition parameters were kept the same as those used in Section 4.4.2.1.2. The gas nozzle was outgassed with the precursor gas of the material to be deposited, to minimise cross-contamination between carbon and tungsten precursor gases. The process was carried out with the stage lowered to 20mm working distance, in order to minimise the number of gas molecules reaching the sample surface and the strip.

The strips were imaged in four modes: SEM and FIB in SE and in InLens modes. The images were taken at two tilting angles: 0° and 54°. These angles were chosen because they are the most common tilting angles used in the APT specimen fabrication process. Note that the contrast values of the sample surface were taken from a region close to the deposition site. The contrast value of each strip was obtained from the central region of the strip in order to avoid the edge effect.

Table 4-1 (a) and (b) contain differential contrast values for tungsten and carbon taken at two tilting angles: 0° and 54°. For each angle, images were taken using four different modes: SEM in SE and in InLens modes, and FIB in SE and in InLens modes. It is important to note that it was not possible to standardise the contrast and brightness settings for all imaging modes, owing to the variation in the electron intensity being detected, which is affected by the imaging source, the detection efficiency of the detectors and the tilting angle of the sample relative to the detectors.

	SEM		FIB	
DETECTOR	SE	InLens	SE	InLens
TUNGSTEN	95.413	59.814	81.232	19.008
CARBON	-5.855	-54.686	-37.451	-3.754

(a) 0° tilt

	SEM		FIB	
DETECTOR	SE	InLens	SE	InLens
TUNGSTEN	74.554	46.325	54.923	59.673
CARBON	-15.782	-19.634	1.441	13.581

(b) 54° tilt

Table 4-1. Differential contrast value of 50nm tungsten strips taken from four imaging modes. The images used to obtain the contrast values in (a) and (b) were taken at tilting angles of 0° and 54° relative to the column axis of the SEM, respectively.

The differential contrast values of tungsten were higher than those of carbon in all the imaging modes and tilting angles, despite the former having high carbon content due to the use of a lower beam current (40pA as opposed to 80pA). This means that tungsten always has higher visibility than carbon. Another important point is that the values for carbon were mostly negative, while the tungsten always remained positive. This indicates that tungsten always appears brighter than the silicon surface. In contrast, carbon appears darker, except in the FIB images taken at a 54° tilt.

4.4.2.1.4 Conclusion

Tungsten was found to have larger differential contrast values than carbon for all the imaging modes and tilting angles, indicating that the former has better visibility than the latter. On the other hand, the maximum depositing beam current of tungsten was limited to 40pA, due to issues with surface uniformity at higher beam currents, resulting in a significantly slower deposition rate than that for carbon. It was therefore decided to use tungsten and carbon for the rest of this work, for the dot-marker and the outline strip, respectively.

4.4.2.2 Addressing problems associated with the deposition behaviours of the tungsten dot

Two problems associated with the deposition behaviours of the tungsten dot were encountered when attempting to optimise the geometry of the dot. These problems could potentially reduce the effectiveness of the dot at marking dislocation pits and, hence, they were addressed prior to the optimisation step.

4.4.2.2.1 Cross-sectional shape of the tungsten dot

Initially, tungsten dots often had elliptical-like cross-sections, as illustrated in Figure 4-10 (a). An SEM image taken at the tilting angle of 54° relative to the dot axis (Figure 4-10 (b)) reveals a dendrite-like structure. These features indicate that the electron beam was distorted during the deposition process.

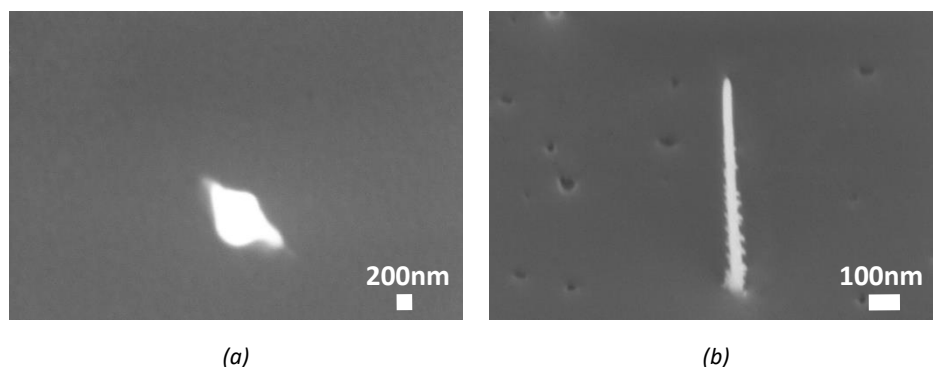


Figure 4-10. SEM images of a tungsten dot viewed (a) from the top and (b) at 54° relative to the dot axis. The deposition was performed using the SEM in spot mode at 10sec deposition time, 5kV accelerating voltage and 30μm objective aperture size. The gas injector was in the inserted position.

The likely cause of this distortion is the gas nozzle, because the nozzle induced distortion in the SEM image when it was in the inserted position. Two possible solutions were proposed: the first solution was to perform aperture alignment and stigmatism correction after the insertion of the gas injector. The second solution was to carry out tungsten dot deposition with the gas injector in the retracted position, whereby the gas nozzle is positioned at one side of the SEM column and is not visible in the SEM image. The relative positions of the gas nozzle to the scanning area of the SEM column in the inserted and the retracted positions are shown in Figure 4-11 (a) and (b), respectively.

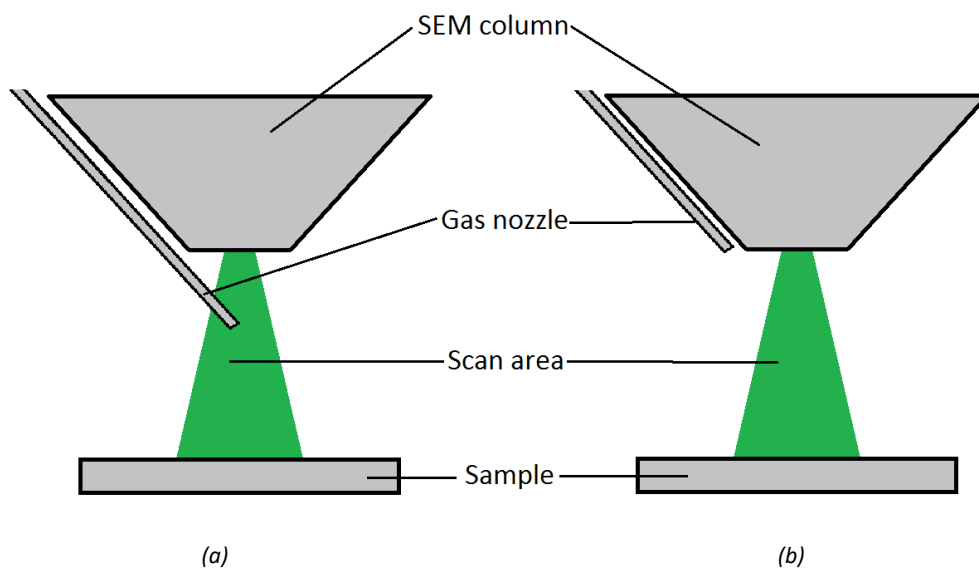


Figure 4-11. Schematics illustrating the relative positions of the gas nozzle to the scan area of the SEM column when the former is in (a) the inserted and (b) the retracted positions.

The first solution did not lead to significant improvements in SEM image quality and the geometry of the tungsten dot. In contrast, the latter solution was able to produce a circular tungsten dot, as shown in Figure 4-12 (a). The dot was deposited with the gas nozzle retracted using the same SEM parameters as those summarised in Figure 4-10: i.e., 10sec deposition time, 5kV accelerating voltage and 30 μ m objective aperture size. Figure 4-12 (b) also shows that the dot is shorter than that being deposited with the gas injector in the extended position. This is due to an observed reduction in the deposition rate because of an increase in the distance between the gas nozzle and the sample,

resulting in a lower replenishing rate in respect of the precursor gas molecules in the electron-irradiated region of the sample.

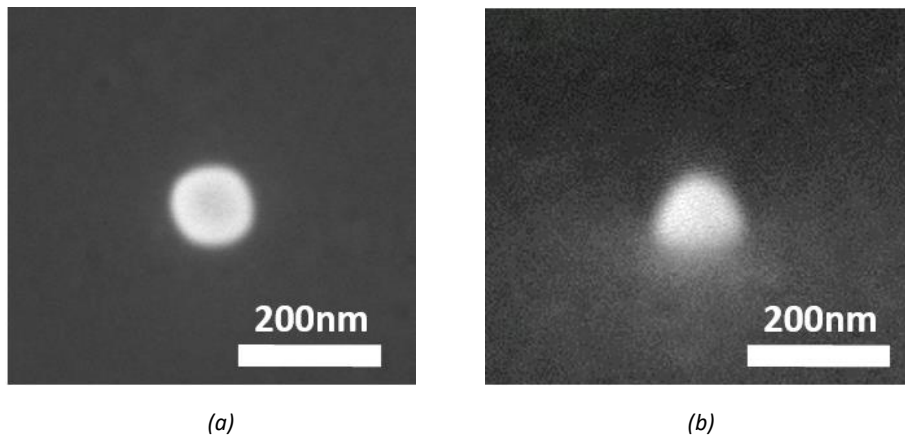


Figure 4-12. SEM images of a tungsten dot viewed (a) from the top and (b) at 54° relative to the dot axis. The deposition was performed using the SEM in spot mode at 5kV accelerating voltage and 30μm objective aperture size. The gas injector was in the retracted position.

4.4.2.2.2 Electron beam drift during tungsten dot deposition

One other problem was that the electron beam had a tendency to drift away from the initial location during the deposition. The problem was not resolved even with the gas injector in the retracted position, implying that the interference of the gas injector when in the extended position is not a major factor causing electron beam drift. Figure 4-13 shows an inclined tungsten dot as a result of this effect.

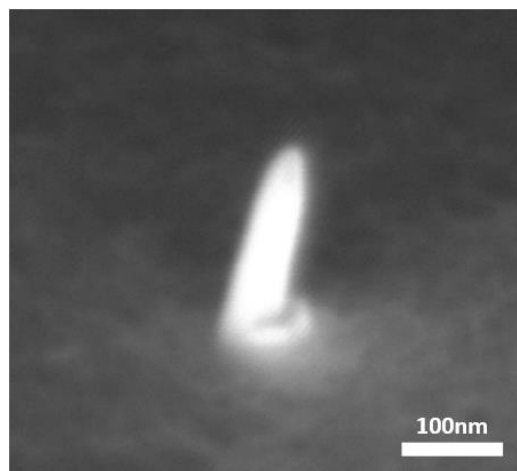


Figure 4-13. The effect of electron beam drifts causes the tungsten marker to tilt away from its base. The marker was deposited at 60sec deposition time, 1kV accelerating voltage and 30μm objective aperture size. The image was taken at 54° relative to the surface normal.

The drifting effect could be due to (a) thermal expansion caused by differences in the temperature of the sample and the specimen chamber; and (b) surface charging due to prolonged exposure of the surface to the stationary electron beam. The relative importance of these factors was investigated.

A sc-Si sample was left in the specimen chamber for about two hours to allow the temperature of the sample to reach that of the specimen chamber. A crosshair pattern, Figure 4-14 (a), was then milled onto the sample surface using the FIB at 1pA milling current and 200sec milling time (i.e. 100sec milling time per line). In SEM imaging mode, the crosshairs were aligned with those introduced by the instrument software, as illustrated in Figure 4-14 (b). The sample was then exposed to SEM imaging at a frame rate of 377msec/frame for five minutes. Figure 4-14 (c) shows misalignments between the two crosshairs, indicating that the electron beam has drifted away from its original position. In addition, the crosshair regions after prolonged exposure to the SEM appeared darker than the surrounding regions. Since the temperature of the sample should be similar to that of the specimen chamber, surface charging is likely to be the cause of the electron beam drift during deposition.

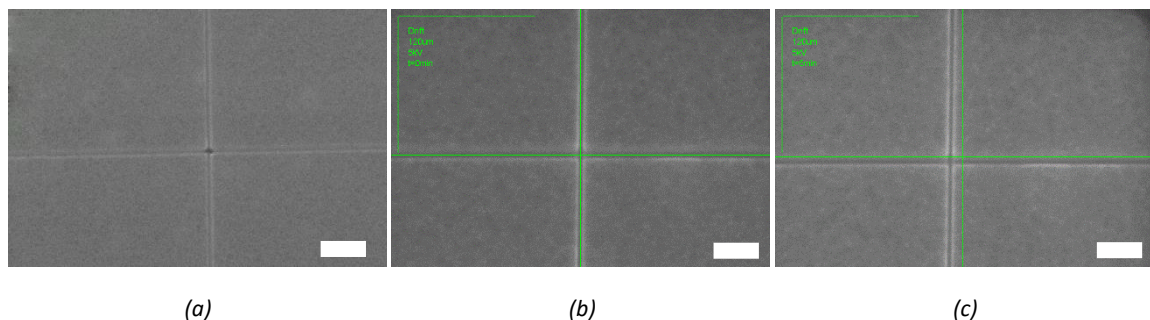


Figure 4-14. SEM images showing (a) the position-marker on the sample surface; (b) the position-marker aligned with that introduced by the instrument's software; and (c) changes in the position of the software-marker relative to that of the sample after exposing the sample to SEM for five minute. The scale bars are one micron.

An attempt was made to reduce the surface charging effect by decreasing the accelerating voltage from 5kV to 1kV. The same experiment was repeated, but no significant improvement was observed.

An alternative approach was to correct the position of the electron beam during deposition. This was achieved by briefly switching from spot mode to imaging mode to capture the image of the tungsten

dot. The position of the electron beam was then corrected in spot mode by aligning the beam crosshairs with the centre of the tungsten dot. After having repeated this process on five tungsten dots, it was decided that it should be repeated every 10sec because the magnitude at which the electron beam had drifted within this time was not significantly large (about 5nm in most cases), while attempting to minimise the disruption caused by switching of the SEM mode to the dot deposition process.

4.4.2.2.3 Summary of the tungsten dot deposition procedure

The final deposition procedure is as follows:

1. Obtain an SEM image of the selected dislocation pit.
2. Switch from imaging mode to spot mode and move the beam position to a corner of the imaging screen to prevent unintentional deposition of the tungsten dot near the dislocation pit.
3. Switch from spot mode to imaging mode.
4. Release the precursor gas with the gas nozzle in the retracted position and wait for about 5sec, to ensure that the gas reaches the sample surface.
5. Switch from imaging mode to spot mode.
6. Move the beam position over the dislocation pit.
7. Switch from spot mode to imaging mode to capture the image of the tungsten dot.
8. Switch from imaging mode to spot mode.
9. Correct the position of the electron beam (small crosshairs) by aligning it with the centre of the tungsten dot.

Steps 7 to 9 are repeated every 10sec to correct the position of the electron beam during the deposition. It is also worth noting that the tungsten dot will not be visible after a deposition time of 10sec when marking the position of a dislocation pit (see Section 4.4.2.4.1). In this case, the beam needs to be aligned with the centre of the pit.

4.4.2.3 *Optimisation of tungsten dot geometries*

4.4.2.3.1 Optimising tungsten dot diameter

The aim is to produce a tungsten dot with a diameter close to but not exceeding the diameter of a typical APT specimen apex: i.e., 100nm. This is because the dot is not only used to locate selected dislocation pits, but also to define the diameter of the specimen tip. The diameter should not exceed 100nm as this would result in a large specimen apex diameter, which would require higher electric fields to induce field evaporation and, in turn, increase the chance of premature fracture.

It was decided that the best approach for changing the diameter of the tungsten dot was to adjust the objective aperture size, since the latter has a direct effect on the size of the electron probe and, in turn, the dot size. The accelerating voltage was kept the same as that used for SEM imaging – i.e., 5kV – because changes in the accelerating voltage will affect the penetration depth of incident electrons and, in turn, the diameter of dislocation pits.

One additional factor that must also be optimised in conjunction with diameter is the quality of the SEM. This is due to the fact that the technique introduced in Section 4.4.2.2 for correcting the position of the electron beam during the dot deposition process requires the SEM to switch periodically between the imaging and the spot modes. It is therefore important to keep the SEM parameters – i.e., the accelerating voltage and the objective aperture size – the same for both modes, in order to avoid significant beam shift when switching between the modes.

Figure 4-15 (a)–(e) shows SEM images of etched defects in a Secco-etched mc-Si sample taken at five different objective aperture sizes: 10 μ m, 20 μ m, 30 μ m, 60 μ m and 120 μ m. The figure shows an increase in the background noise with smaller aperture sizes. This is due to a reduction in the beam current and, in turn, the signal generated by PE-sample interactions. It can be concluded that the largest possible aperture size should be used, in order to minimise background noise.

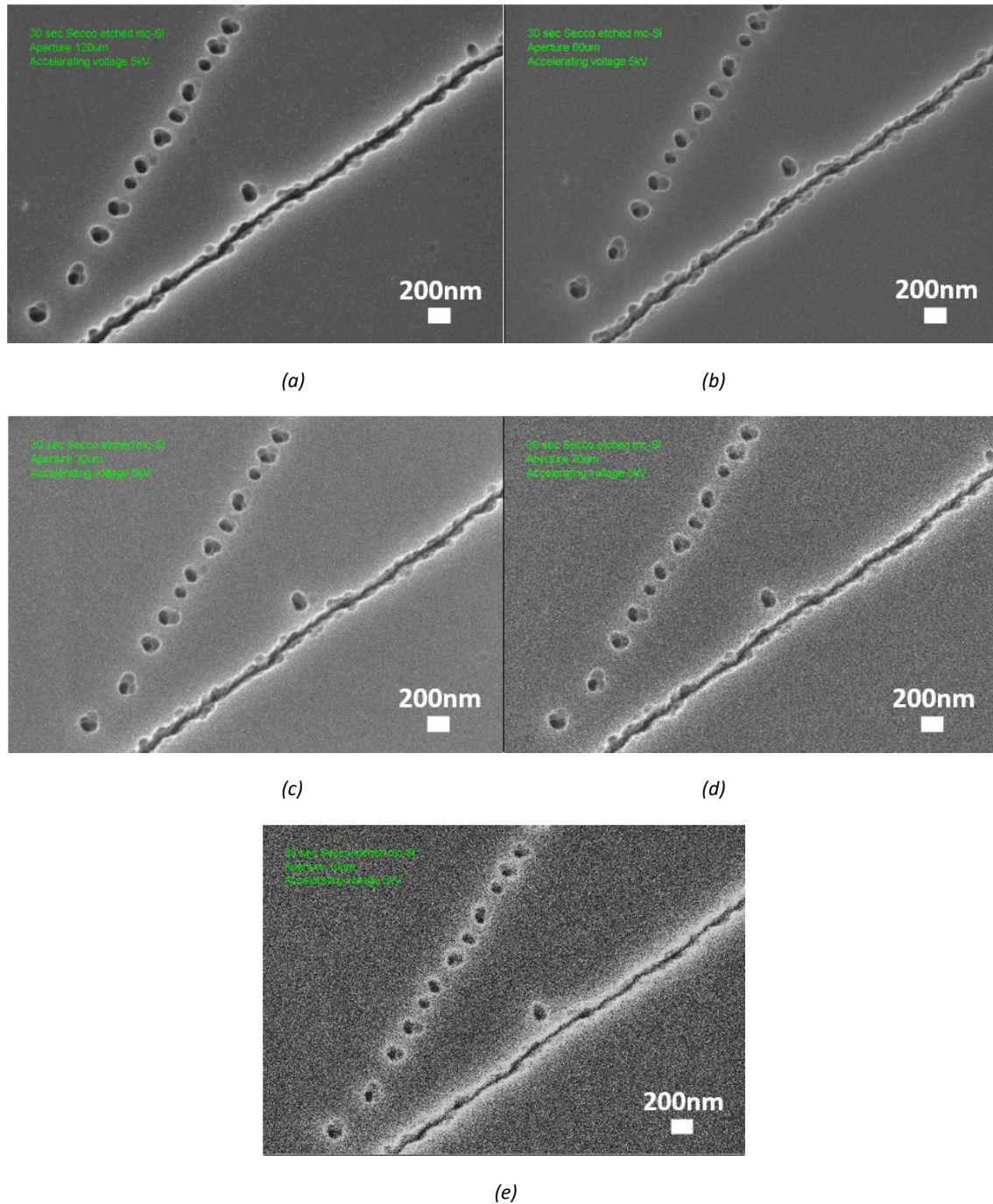


Figure 4-15. SEM images of a region of a mc-Si wafer that was preferentially etched in Secco for 30sec. The images were taken using the SEM at various aperture sizes: (a) 120μm; (b) 60μm; (c) 30μm; (d) 20μm; and (e) 10μm. The accelerating voltage of the electron beam was kept constant at 5kV. The frame refreshing rate was 377msec/frame.

Tungsten dots were deposited at five different aperture sizes: 10 μ m, 20 μ m, 30 μ m, 60 μ m and 120 μ m. The accelerating voltage and the deposition time were kept constant at 5kV and 60sec, respectively. Figure 4-16 shows an increase in tungsten dot diameter with an increase in the objective aperture size. This can be explained by the fact that the dissociation area of precursor gas molecules increases proportionally with the square of the diameter of the electron beam.

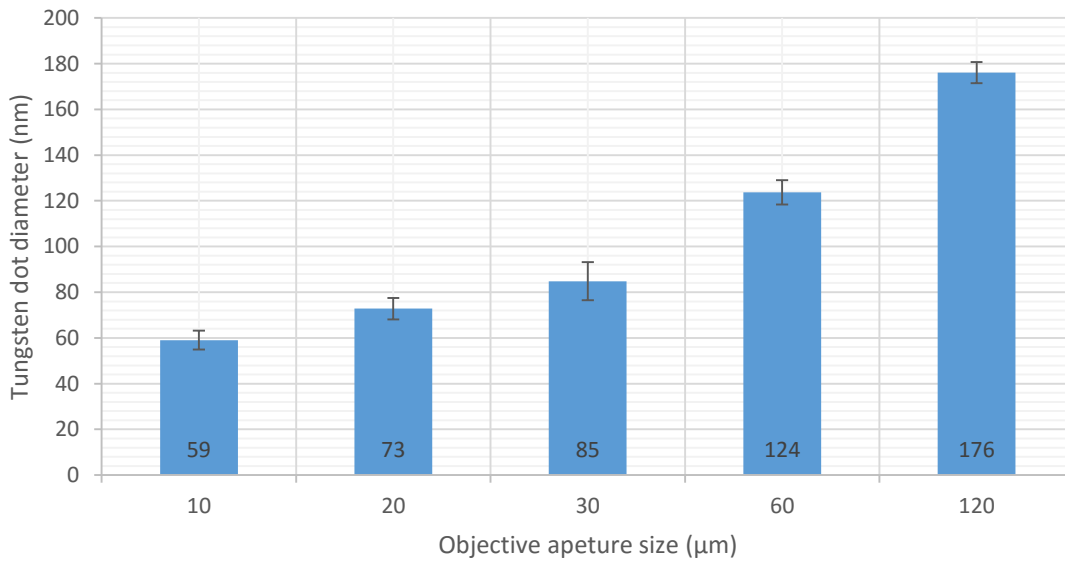


Figure 4-16. Diameter of the tungsten dots deposited at five different objective aperture sizes. The accelerating voltage and the deposition time were kept constant at 5kV and 60sec, respectively.

Figure 4-17 shows tungsten dot diameter as a function of deposition time. The dots were deposited at 5kV accelerating voltage and 30 μ m objective aperture size. An initial increase in the diameter with increases in the deposition time was observed. Diameter then reaches a plateau at 30sec deposition time. This trend can be explained by the relative size of the tungsten dot to that of the dissociation region of the precursor gas—the diameter of the electron beam plus twice the diffusion length of SEs. At the early stage of the deposition, the dot is much smaller than the dissociation region and, thus, lateral growth can occur. However, the growth rate becomes negligible once their sizes are comparable. It can therefore be concluded that the diameter of the tungsten dot will not exceed 100nm regardless of the deposition time.

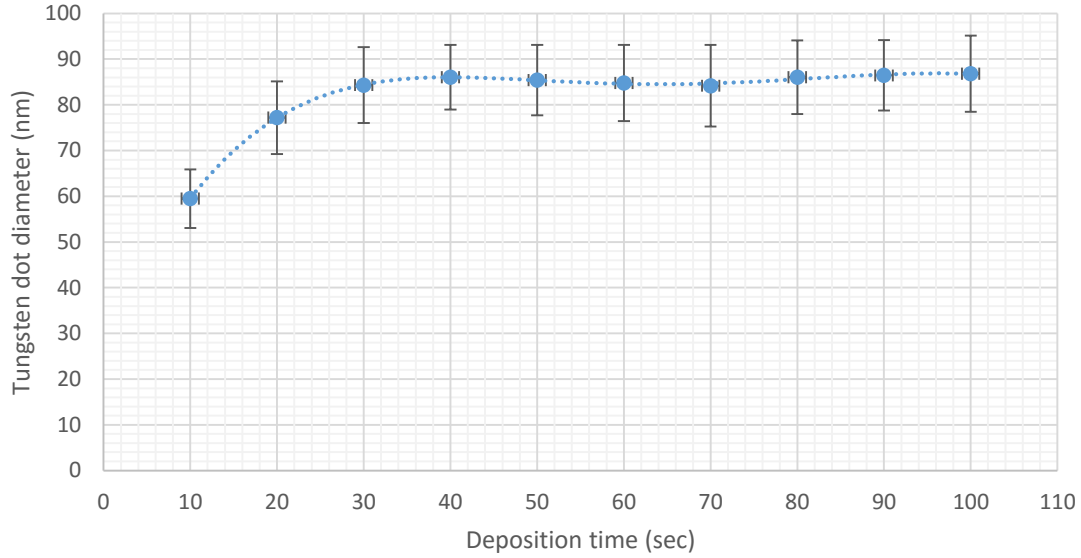


Figure 4-17. A graph showing tungsten dot diameter as a function of deposition time. All the tungsten dots were deposited at 5kV accelerating voltage and 30 μ m objective aperture size.

The objective aperture size that produced a tungsten dot with the diameter closest to, but not exceeding, 100nm was 30 μ m. Hence, the tungsten dot deposition parameters used for the rest of this work are 5kV accelerating voltage and 30 μ m aperture size.

4.4.2.3.2 Optimising tungsten dot height

The height of the dot must be able to withstand FIB irradiation during the APT specimen fabrication process.

Figure 4-18 shows the relationship between the true tungsten dot height, h_{true} (nm), and the deposition time, t_{dot} (sec). This can be described by a linear fit with the equation $h_{true} = 3.3t_{dot} + 32.5$. Hence, the deposition time t_{dot} required to produce a tungsten dot with a true height of h_{true} is given by:

Equation 4-5

$$t_{dot} = \frac{h_{true} - 32.5}{3.3}$$

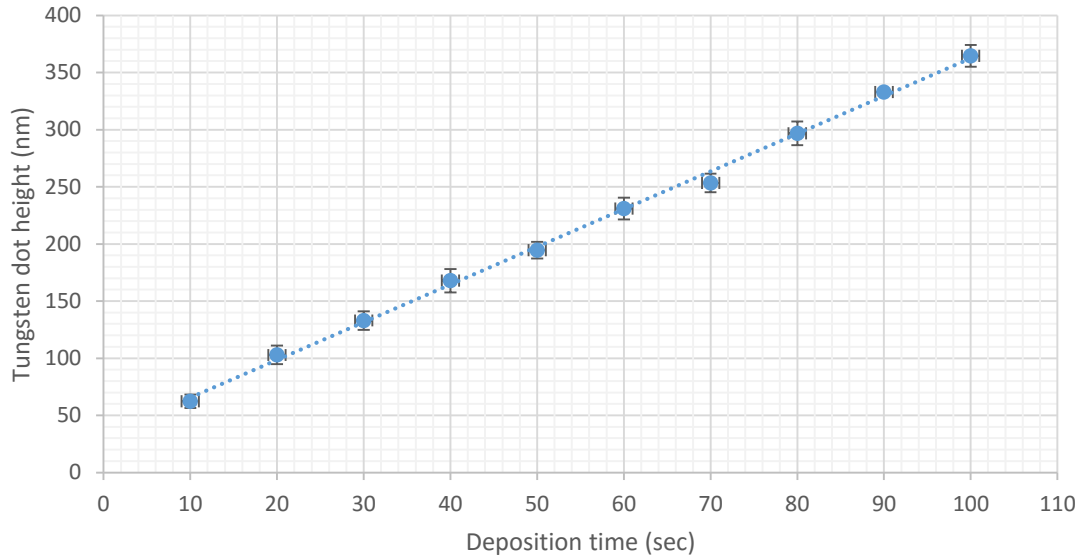


Figure 4-18. A graph showing tungsten dot height as a function of deposition time. All the tungsten dots were deposited at 5kV accelerating voltage and 30 μ m objective aperture size.

The removal rate of the tungsten dot by FIB imaging was investigated to determine the minimum height of the tungsten dot necessary to withstand FIB irradiation during the APT specimen fabrication process. A tungsten dot was deposited using the SEM in spot mode for 100sec at 5kV accelerating voltage and 30 μ m objective aperture size. The height of the tungsten dot was about 375nm.

The dot was then exposed to FIB imaging, with the imaging plane normal to the dot axis, at an image scanning speed and magnification of 377msec/frame and 110k times, respectively. These FIB parameters were chosen to mimic the exposure conditions of the tungsten dot to FIB imaging during the specimen sharpening stage, where highest height removal rate was expected. SEM images of the dot were taken at 30sec intervals. Figure 4-19 shows that the relationship between h_{true} (nm) and FIB exposure time, t_{FIB} (sec), can be described by a linear fit with the equation:

Equation 4-6
$$h_{true} = -1.5t_{FIB} + 640.9$$

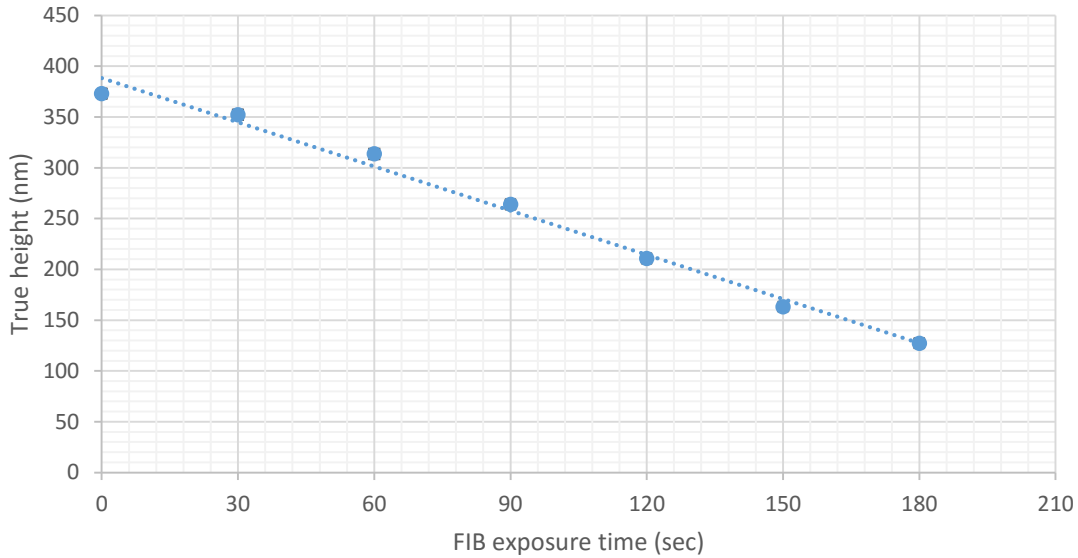


Figure 4-19. A graph showing tungsten dot height as a function of exposure time to FIB irradiation.

The equation indicates a removal rate of 1.5nm/sec. The minimum tungsten dot height, h_{min} , required to withstand FIB exposure time t_{FIB} is therefore given by:

Equation 4-7
$$h_{min} = 1.5t_{FIB}$$

By combining Equation 4-7 with Equation 4-5 the t_{dot} required for a given t_{FIB} can be directly determined using:

Equation 4-8
$$t_{dot} = \frac{1.5t_{FIB} - 32.5}{3.3}$$

The longest FIB exposure time during the annular milling process, based on my experience, was about 100sec. The minimum t_{dot} was determined, using Equation 4-8, to be 40sec. An additional 10sec was added to the deposition time to ensure that the dot could withstand the FIB. Consequently, the selected deposition time was 50sec, which produces a tungsten dot with a height of about 200nm.

4.4.2.4 Marking technique assessment

4.4.2.4.1 Inconsistency in the tungsten dot height

A tungsten dot was deposited over a dislocation pit at 50sec deposition time, 5kV accelerating voltage and 30 μ m objective aperture size. However, a tungsten dot was not observed, as shown in Figure 4-20. This is probably due to the additional depth of the dislocation pit.

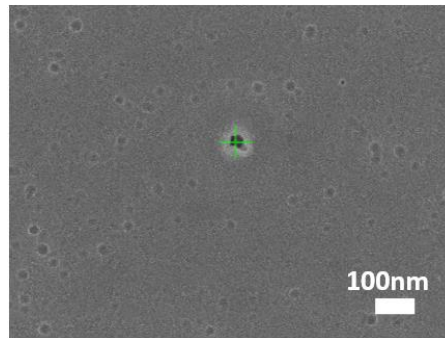


Figure 4-20. SEM images showing tungsten dot deposition over a dislocation pit at a deposition time of 50sec. The accelerating voltage and the objective aperture were 5kV and 30 μ m, respectively.

The evolution of the tungsten dot when deposited over a dislocation pit was investigated by taking a series of SEM images during the deposition process. At the initial stage of the deposition, the diameter of the dislocation pit decreased as tungsten filled the cavity, as shown in Figure 4-21 (a). The tungsten dot, protruding above the specimen surface, then formed when the pit was no longer visible, see Figure 4-21 (b).

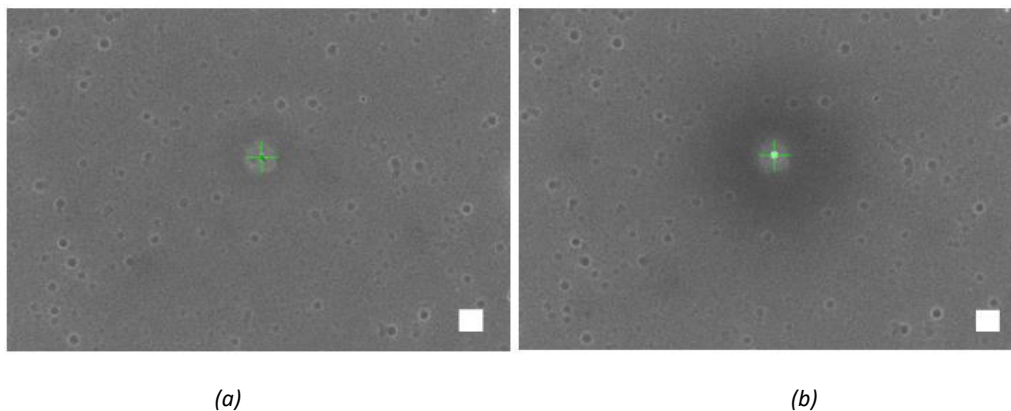


Figure 4-21. SEM images showing two stages of tungsten dot deposition over a dislocation pit: (a) the diameter of the dislocation pit decreases with the deposition time; (b) the formation of the tungsten dot after the pit is no longer visible. The scale bars are 100nm. Note that the green crosshairs are the position of the electron beam when the SEM is set to spot mode.

It was decided that the best solution was to start the deposition time when the tungsten dot was observed in the SEM. Figure 4-22 shows the diameter and the height of tungsten dots deposited using this technique over five randomly selected dislocation pits. The frequency at which the SEM was switched between the imaging mode and spot mode was increased to every 3sec at the stage where the dislocation pit was almost invisible, in order to minimise the lag time between the nucleation of the tungsten dot and when it was observed in the SEM.

The diameter of the tungsten dots remained the same at about 88nm. This is because that diameter had reached the saturation point, beyond which further increase in the deposition time only affects the vertical growth.

The average dot height was 210nm, which is slightly higher than the height calculated using Equation 4-5. This can be explained by the fact that the deposition time could have started sometime after the formation of the tungsten dot. Nonetheless, height variation between the dots does not have a significant effect on the accuracy of the marker, since they are all above the required height of 200nm.

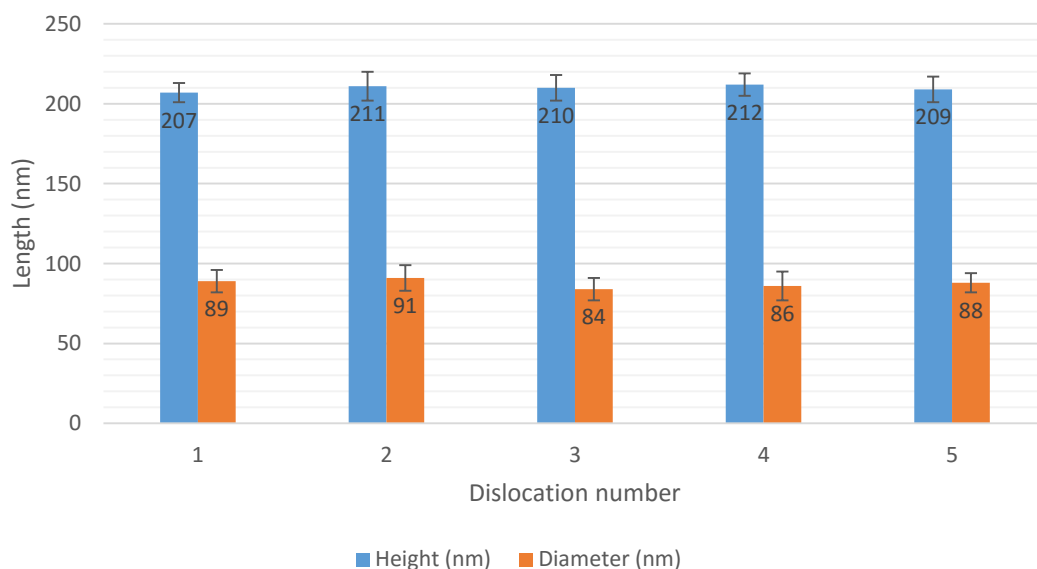


Figure 4-22. True height of five tungsten dots deposited over dislocation pits. The deposition was carried out using the SEM in spot mode at 5kV accelerating voltage and 30 μ m objective aperture size. The deposition time was 50sec after the mark

4.4.2.4.2 Stability of tungsten dot under angular FIB imaging

During the APT specimen fabrication process, tungsten dots were regularly exposed to FIB imaging at an inclined angle to the dot axis. This section, therefore, investigates the effect of angular FIB exposure on the stability of the tungsten dot.

A vertical tungsten dot was deposited at 80sec deposition time, 5kV accelerating voltage and 30 μ m aperture. The dot was then exposed to FIB imaging for 60sec at a 54° tilt relative to the dot axis. This particular tilt angle was chosen because it was the most common angle used in the early APT specimen fabrication method. Figure 4-23 shows that the dot has tilted towards the FIB column, denoted by the orange arrow, with the angle between the surface normal and dot axis being 45°. Since the tungsten dot was vertical before the experiment, the tilting rate of the dot was determined to be about 0.75°/sec. It is surprising that the tungsten dot tilted towards, instead of away from, the FIB imaging direction. The most probable explanation is that the base of the tungsten dot was being progressively removed by the FIB, causing the dot to topple forward towards the beam direction.

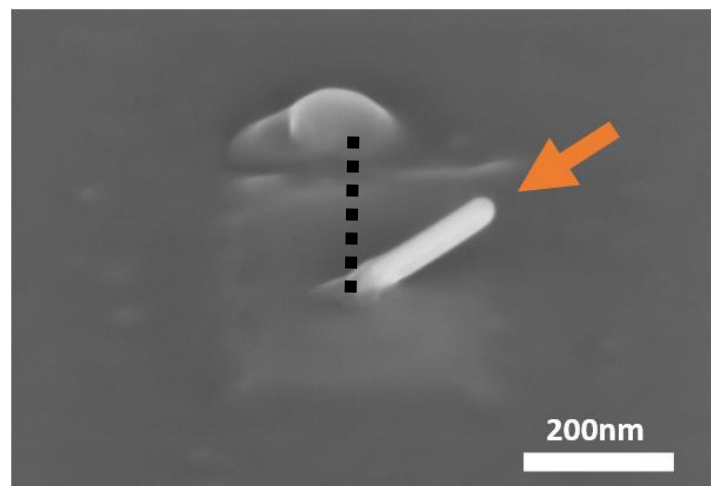


Figure 4-23. SEM images of a tungsten pillar after FIB imaging at 54° to the wafer surface normal for 60 seconds. The orange arrow indicates the FIB imaging direction while the original position of the pillar is marked by the black dotted line. The standard imaging current and accelerating voltage were used: i.e., 30kV 40pA.

It is clear that the tungsten dot does not have sufficient mechanical stability to withstand prolonged angular exposure to FIB imaging. Two possible solutions were proposed.

The first solution was to develop an alternative APT fabrication method, with the aim of minimising the fabrication steps that required angular FIB imaging. This proposed method is similar to the device-specific or feature-specific lift-out method described in [6], whereby a feature of interest is isolated from the rest of the sample by milling a moat around it using FIB. The only change made to the technique was that the APT specimen had to be partially fabricated prior to the lift-out. Ideally, the shape of the specimen should be similar to the one in Figure 4-24. In this way, the tungsten dot would no longer be needed since the tip of the specimen would be sufficiently small for it to be located in the FIB. This method removes the cantilever fabrication step and, hence, provides a reduction in the time for which the tungsten dot's side is exposed to FIB imaging.

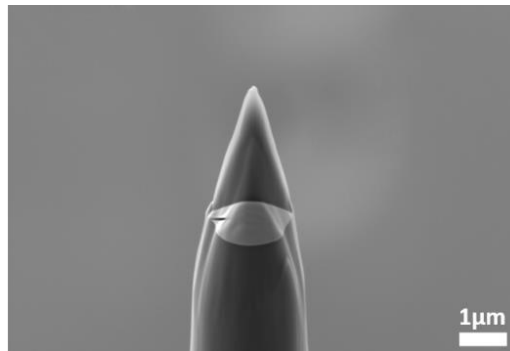


Figure 4-24. The ideal shape of the APT specimen before the lift-out.

When this method was applied to a dislocation pit, it was found that some of the material that had sputtered during the annular milling process had accumulated at the tungsten dot, see Figure 4-25 (a)–(c). This reduces the accuracy of the marker and, in turn, the likelihood of successful APT specimen fabrication. Hence, this method was discarded.

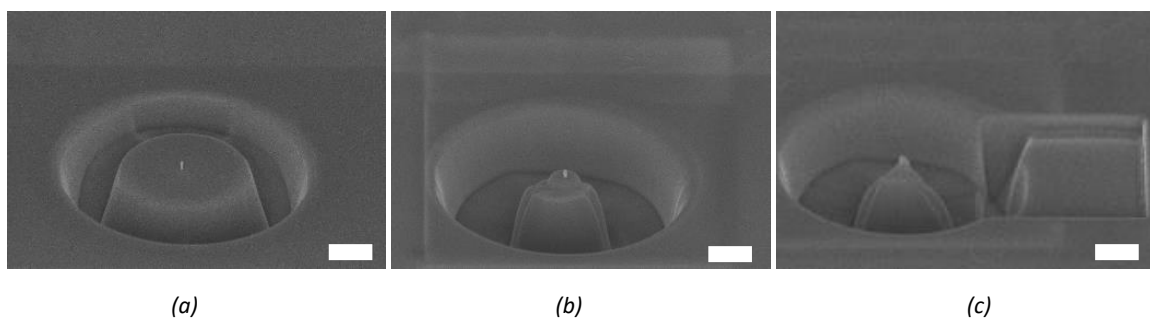


Figure 4-25. SEM images showing three annular milling stages of the annular milling process performed on a dislocation pit marked by a tungsten dot. The scale bars are 1 μm.

The second solution was to reinforce the tungsten dot by encapsulating it in the carbon dome. In other words, the marking steps were reversed. The modified technique is schematically illustrated in

Figure 4-26.

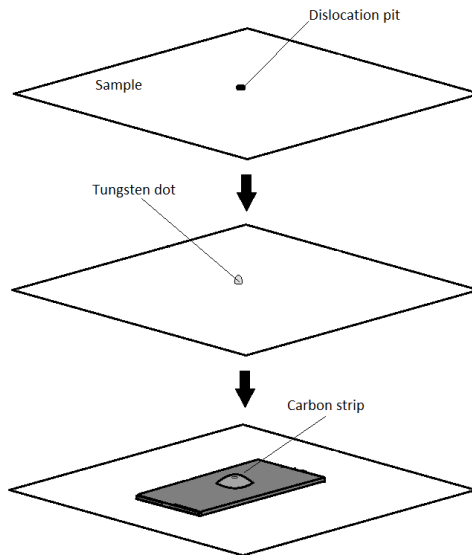


Figure 4-26. A schematic of the modified EBID dot-marking technique.

Figure 4-27 shows a dislocation pit marked using the modified marking technique. The deposition times for the tungsten dot and the carbon strip were 40sec and 90sec, respectively. The marker comprised of a tungsten dot at the centre, surrounded by a mixture of carbon and tungsten. The carbon acts as a support for the tungsten dot, which should allow the structure to withstand FIB radiation from all viewing directions.

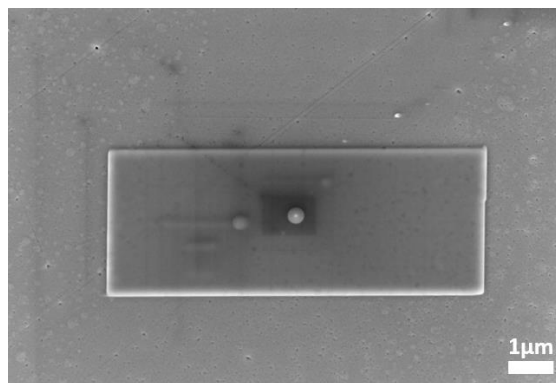


Figure 4-27. An SEM image of the revised EBID dot-marking technique. The scale bar for the inset is 100nm.

4.4.2.4.3 Annular milling approach

The diameter of the carbon dome was always larger than the apex diameter of the APT specimen, i.e., 100nm. Since FIB cannot distinguish the tungsten dot from the carbon dome, due to the lack of back-scattered electrons, the tungsten dot was no longer able to serve as an outline for the diameter of the specimen apex. Figure 4-28 shows that the tungsten dot is located at the centre of the dome. This problem was overcome by aligning the centre of the annular pattern with that of the dome at the specimen sharpening stages when the inner diameter of the annular pattern is either similar to or less than the diameter of the dome. In order to prevent unnecessary beam shift, the same ion beam energy (i.e., 30kV 40pA) was used for both FIB imaging and milling. Image magnification was also kept the same. Figure 4-29 shows the final APT specimen, with the marker being clearly visible at the tip.

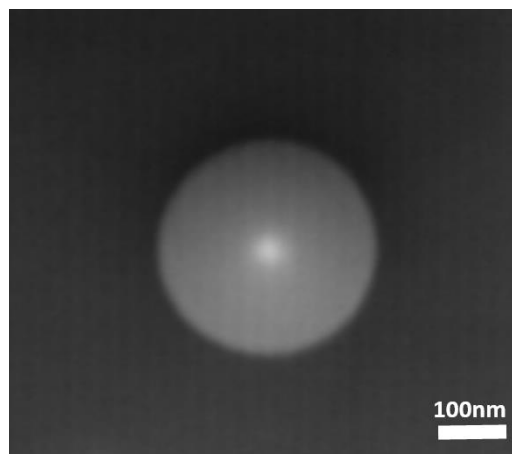


Figure 4-28. SEM image showing the tungsten dot-marker encapsulated within the carbon dome.

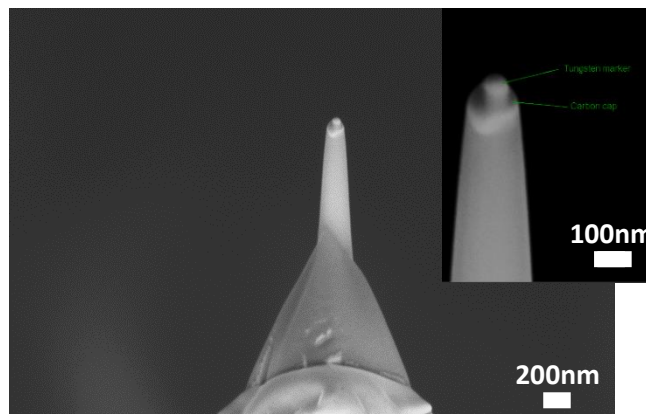


Figure 4-29. The final APT specimen and inset showing a high resolution image of the tip.

4.4.2.5 *Summary of the marking technique*

A tungsten dot is deposited over the selected defect – i.e., a single dislocation or a specific point on a grain boundary – using EBID at 5kV accelerating voltage and 30 μ m objective aperture size. The deposition time is the time taken for the tungsten dot to fill the cavity plus 50sec deposition time to produce a tungsten dot with a height of about 200nm. A 15 μ m by 4 μ m carbon strip is then deposited over the tungsten dot using the FIB at 90sec deposition time. The misalignments between the crosshairs in spot mode and the tungsten dot in the image are corrected by moving the crosshairs to the centre of the dot. This process is performed every ten seconds.

4.4.3 FIB-deposited line-marking technique

This marking technique was introduced after the introduction of the new APT specimen fabrication method described in Section 4.5.1.2 and was used for marking grain boundaries. Similar to the previous techniques, it is a two-step process—both steps being carried out using the FIB. In the first step, a tungsten line is deposited over a section of the selected grain boundary to mark its location. In the second step, a 15 μ m long and 4 μ m wide rectangular carbon strip is then applied over the line to mark the wedge component of the cantilever. The deposition time for the carbon strip was kept constant at 20sec. The length and the deposition time for the tungsten line varied significantly from one grain boundary to another. The length depends on the length of the selected section of the grain boundary, while the deposition time depends on the time taken for the line to become visible in the SEM. Other deposition parameters are discussed in Section 2.7.3.

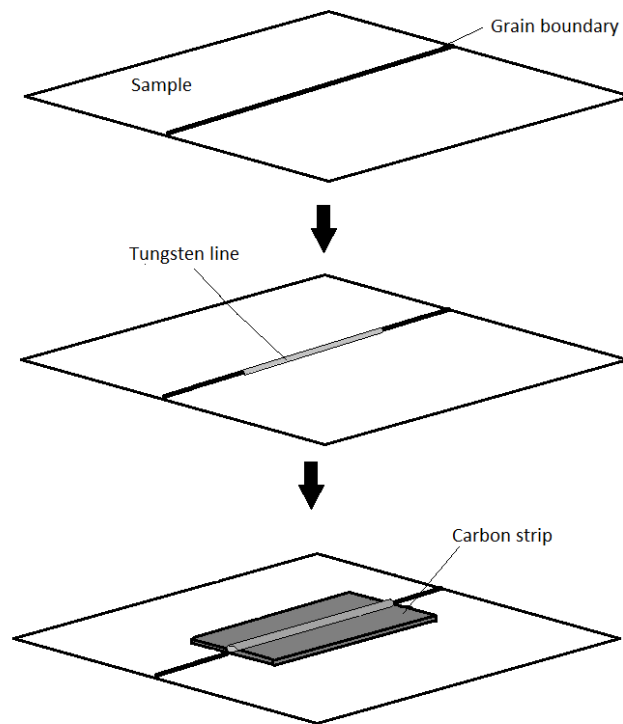


Figure 4-30. A schematic illustration of FIB line-marking technique.

4.4.3.1 Marker optimisation

This section investigates the ability of tungsten line to fill the entire etched depth of the grain boundary, in accordance with the requirement in respect of the APT specimen fabrication method developed as described in Section 4.5.1.2.

Five tungsten lines were deposited along a straight grain boundary at four different ion beam currents: 1pA, 10pA, 40pA and 80pA. The lines were then dissected and imaged using the SEM. The cross-sectional images of the lines are shown in Figure 4-31 (a)–(d). The grain boundary was completely filled only at 1pA, while higher depositing beam currents formed cavities at the bottom of the grain boundary groove. This could be due to the fact that tungsten was deposited at the side walls of the groove instead of just at the bottom of the groove. As the deposition process

progresses, tungsten gradually builds up in these regions, until they merge some distance above the bottom of the groove, leaving behind cavities.

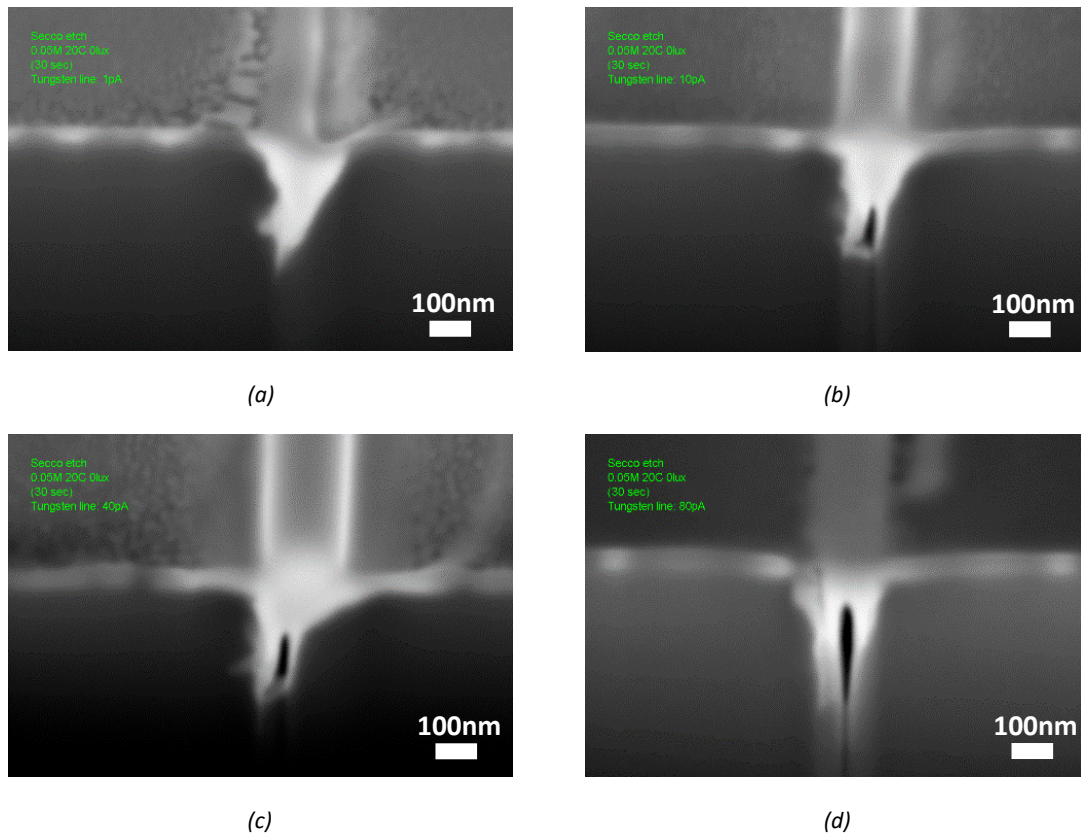


Figure 4-31. Tungsten line deposition over a grain boundary. The deposition was performed at an ion beam current of (a) 1pA, (b) 10pA, (c) 40pA and (d) 80pA.

4.4.3.2 Summary of the marking technique

A tungsten line is deposited over the grain boundary using the FIB at 1pA beam current. The length of the tungsten line can be adjusted depending on the length of the grain boundary to be analysed. The deposition time can also vary depending on the depth of the etched grain boundary. The general idea is to continue to deposit until the tungsten line is observed. A carbon strip, 15 μ m long and 4 μ m wide, is then applied over the tungsten marker using the FIB for a 20sec deposition time.

4.5 The development of APT specimen fabrication method

4.5.1 Novel approach to APT specimen fabrication

4.5.1.1 *The limitations of the lift-out method*

Three APT specimens were fabricated at positions marked by dislocation etch pits in a Secco-etched mc-Si sample using the marking technique developed as described in Section 4.4.2, followed by the APT specimen fabrication method described in Section 2.7.4.2. The specimens were attached to tungsten posts using the method described in Section 4.5.2.1. The specimens were then observed in the TEM.

Figure 4-32 (a)–(c) shows that not all of the specimens contained a dislocation line, despite having the tungsten marker at the tip. This suggests that extended defects in mc-Si samples do not run perpendicular to the sample surface, which is in contrast to the statement in [7]. This was confirmed by the experiments described in Section 3.8, which show that defects in mc-Si samples run at angles inclined to the surface normal, usually ranging from 10° to as much as 25°. The lift-out method requires the angle between the selected dislocation line and the APT specimen axis to be less than the specimen's shank angle (about 7°) in order for the dislocation line to lie inside the specimen. Hence, a different APT specimen fabrication approach was required.

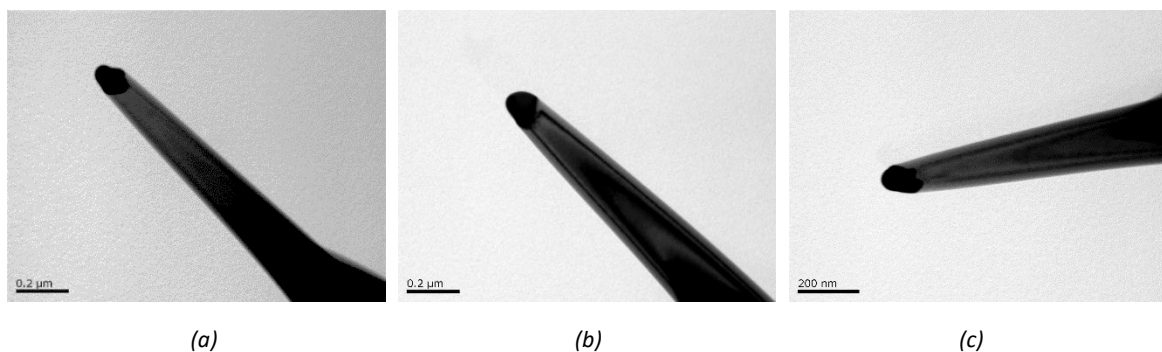


Figure 4-32 (a)–(c). TEM images of atom probe specimens that were made using the standard lift-out and annular milling method. Tungsten marker was present on both specimens, but no grain boundary was observed.

4.5.1.2 Alternative APT specimen fabrication approach

The atom probe fabrication method described in Section 2.7.4.2 can be viewed as a top-down approach—i.e., an APT specimen is fabricated with its axis normal to the sample surface. An alternative approach was to determine the propagation direction before or during the specimen sharpening process and to take this into account during the APT specimen fabrication process. This approach led to the development of two different APT specimen fabrication methods for dislocations as well as grain boundaries. Figure 4-33 (a) and (b) demonstrates the position and the orientation of the APT specimen relative to the defect for dislocations and grain boundaries, respectively.

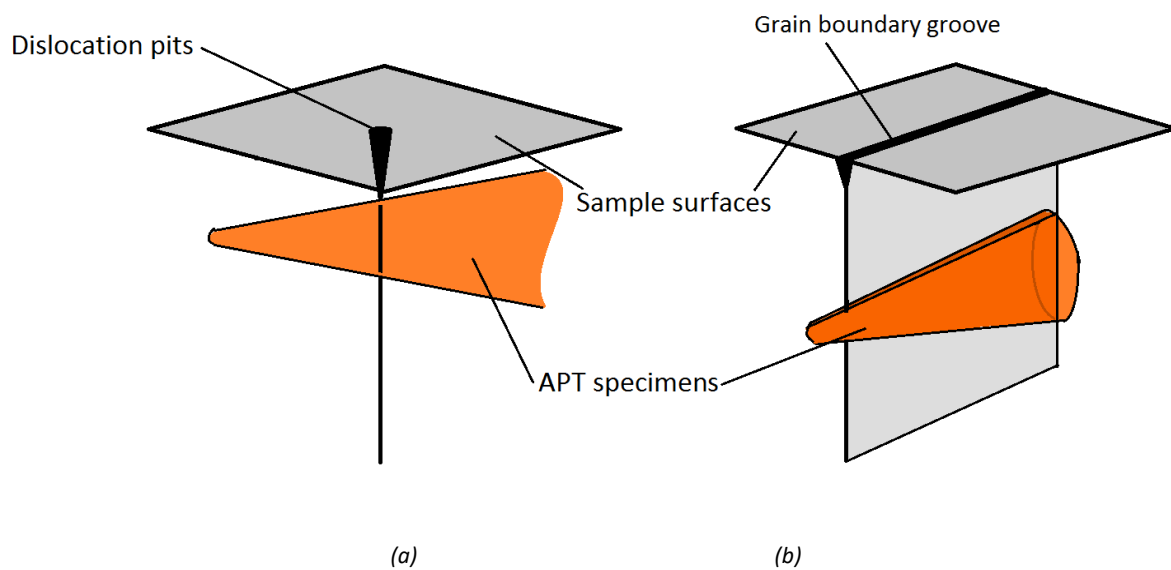


Figure 4-33. Schematic illustrations of parallel APT specimen fabrication method for (a) dislocations and (b) grain boundaries.

Both methods follow the same procedure:

- 1) Defect marking;
- 2) Cantilever fabrication;
- 3) Wedge lift-out;
- 4) Wedge attachment;
- 5) Wedge preparation; and
- 6) Specimen sharpening.

The marking techniques for dislocation pits and grain boundaries are summarised in Section 4.4.2.5 and 4.4.3.2, respectively, and will not be repeated here.

Copper lift-out grids containing five copper posts were employed in both fabrication methods to attach wedges and perform specimen sharpening. Due to the limitations of the specimen stage, the grid was arranged into two configurations for different stages of the APT fabrication process. These stages are described in more detail in Section 4.5.2.2.

4.5.1.2.1 Cantilever fabrication

A similar method to that described in Section 2.7.4.1 was used to fabricate cantilevers. However, two small changes were made to the dimensions of the wedge.

First, the length of the wedge was increased in order to ensure that the specimen could be observed in the APT, as well as to prevent interference from the Cu post on AP signals during the analysis. Initially, the length was increased to 50 μm . However, wedges of this length had the tendency to become detached from the copper posts of the lift-out grid during transfer between instruments. Consequently, the length of the wedge was reduced to 30 μm . The specimens made from 30 μm wedges often survived specimen transfer and APT analysis.

A 4-5 μm gap was left between the overhanging edge of the wedge and the marker. There are two reasons for this: one reason was to accommodate the micromanipulator for lift-out; the second was to allow room for the gap to be adjusted for APT specimen fabrication. The latter issue will be explained in more detail in Section 4.5.1.2.4. Figure 4-34 (a) and (b) shows typical cantilevers fabricated from a grain boundary and a dislocation, respectively.

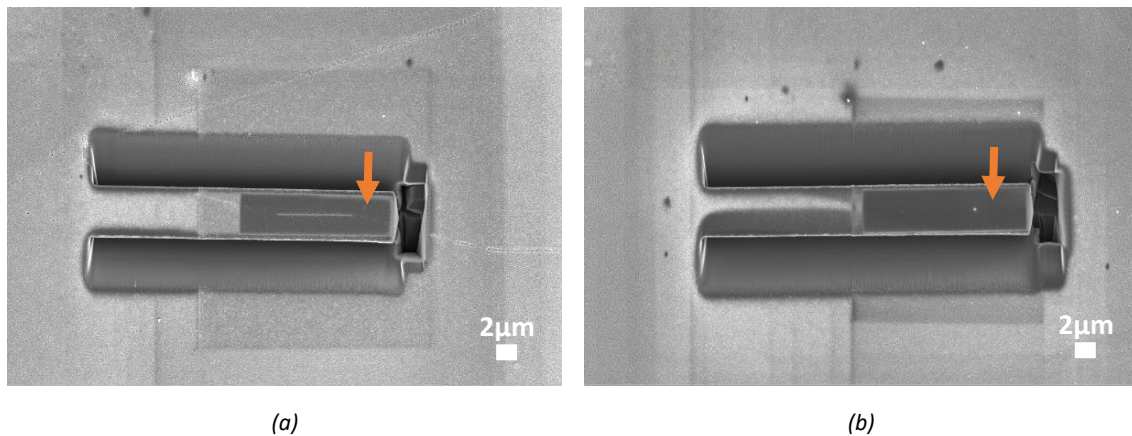


Figure 4-34. SEM images showing cantilevers containing (a) grain boundaries and (b) dislocations. Orange arrows indicate the 4-5 μm gaps between the defect-marker and the overhanging edge.

4.5.1.2.2 Wedge lift-out

Although no modification was made in the wedge lift-out step, it is worth illustrating the orientation at which the wedge was attached to the micromanipulator. Figure 4-35 (a) and (b) shows the wedge lift-out for grain boundaries and dislocations, respectively. Note that a 2 μm wide gap was left between the micromanipulator and the defect-marker for the reasons mentioned in Section 4.5.1.2.1.

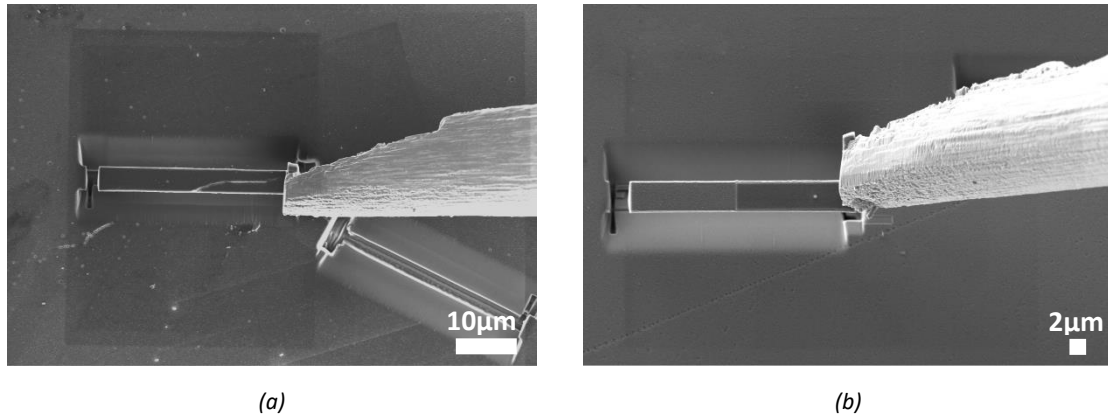


Figure 4-35. SEM images showing the attachment orientation of the micromanipulator to the wedge for (a) grain boundaries and (b) dislocations.

4.5.1.2.3 Wedge attachment

In order to perform annular milling on the triangular surface of the wedge the wedge has to be attached to the copper post such that the axes of the wedge and the post are parallel to each other. Initially, the method for attaching the specimen to the copper post was to rest the lower section of the wedge over the flat end of the copper post, as illustrated in Figure 4-36 (a). The wedge was then attached to the post by depositing a tungsten strip that overlapped both the wedge and the copper post. The wedge-post attachment was reinforced by milling rectangular patterns at three different locations, as demonstrated in Figure 4-36 (b). The milling current was 300pA and the milling time was about 10–15sec. These pits were then filled with tungsten using the FIB, see Figure 4-36 (c).

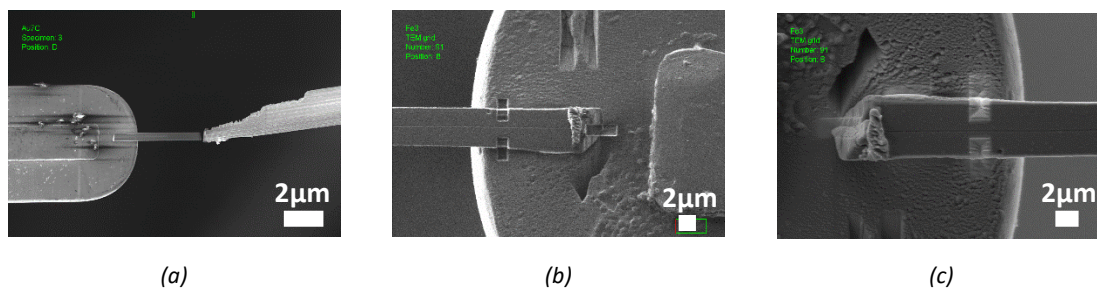


Figure 4-36. An illustration of the wedge attachment technique: (a) the lower part of the wedge was lowered to the back of the Cu post; (b) three attachment points were prepared by FIB milling at 300pA; and (c) tungsten was deposited at the attachment points to secure the wedge to the post.

However, this attachment method directly exposed tungsten reinforcements at the sides of the wedge to the ion beam during the specimen sharpening stage, resulting in a number of specimens becoming detached from the posts, as illustrated in Figure 4-37 (a).

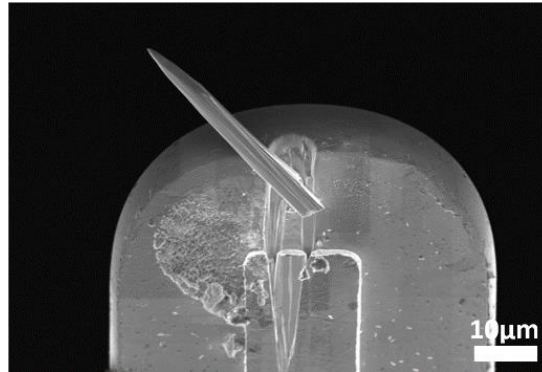


Figure 4-37. The image shows the detachment of the post during the annular milling stage of the atom probe fabrication process.

An alternative attachment method was developed to overcome this problem. All the steps were performed using the FIB. The attachment procedure is illustrated in Figure 4-38 (a)–(f).

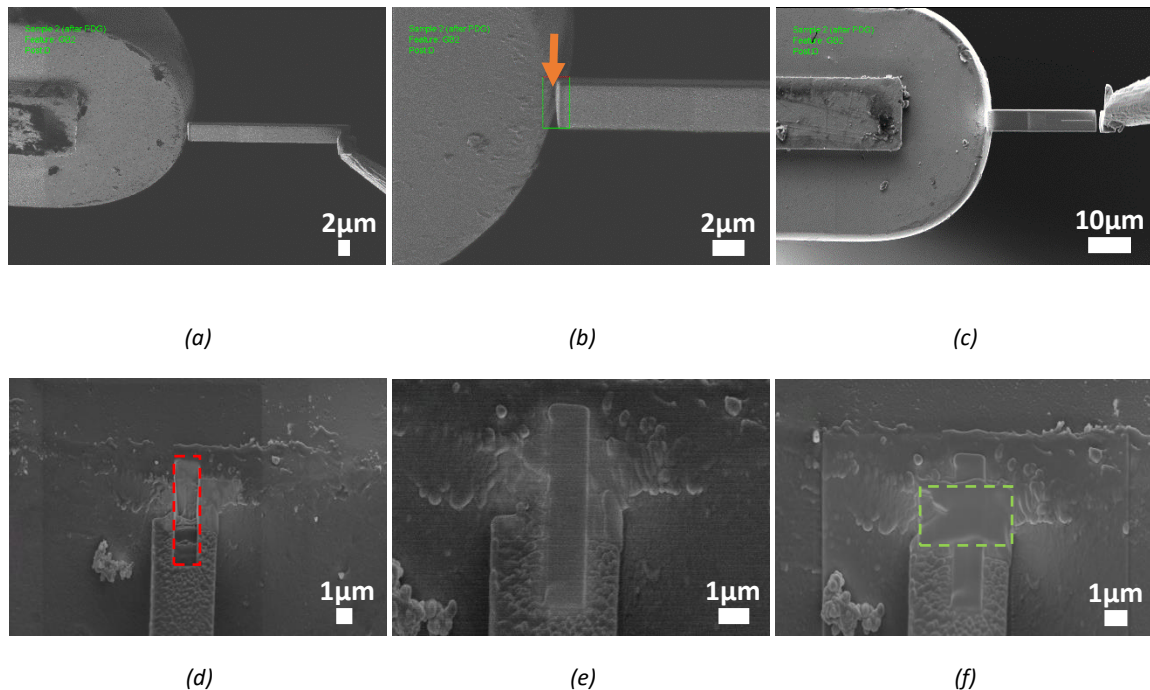


Figure 4-38 (a)–(f). Illustration of the final wedge-copper post attachment method: (a) the end of the wedge is positioned end-to-end with the copper post; (b) the wedge is attached to the post by depositing tungsten at the interface between the two components, as indicated by the orange arrow; (c) the wedge is detached from the micromanipulator; (d) a rectangular hole is partially milled at the interface between the wedge and the post, marked by the dashed red rectangle; (e) the hole is filled with tungsten by FIB deposition; and (f) a tungsten bar is FIB-deposited parallel to the interface, marked by the dashed green rectangle.

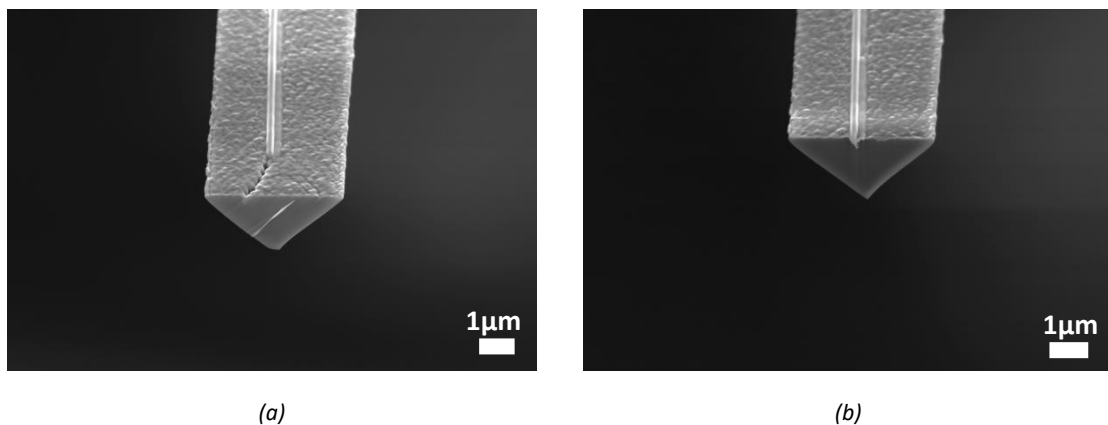
First, the triangular face of the wedge furthest away from the micromanipulator was placed over the very tip of the copper post. Second, a tungsten strip was deposited over the wedge–copper post interface to mount the wedge onto the post. Third, the wedge was detached from the micromanipulator. Fourth, a rectangular trench was milled between the specimen and the holder, after which the trench was filled with tungsten. Fifth, a smaller rectangular tungsten strip was deposited inside the milled trench, normal to the previous one, to fill small gaps between the wedge and the post. Lastly, a rectangular strip was deposited at the wedge–copper post interface with its length normal to that of the first strip. The entire process usually takes about ten minutes to perform.

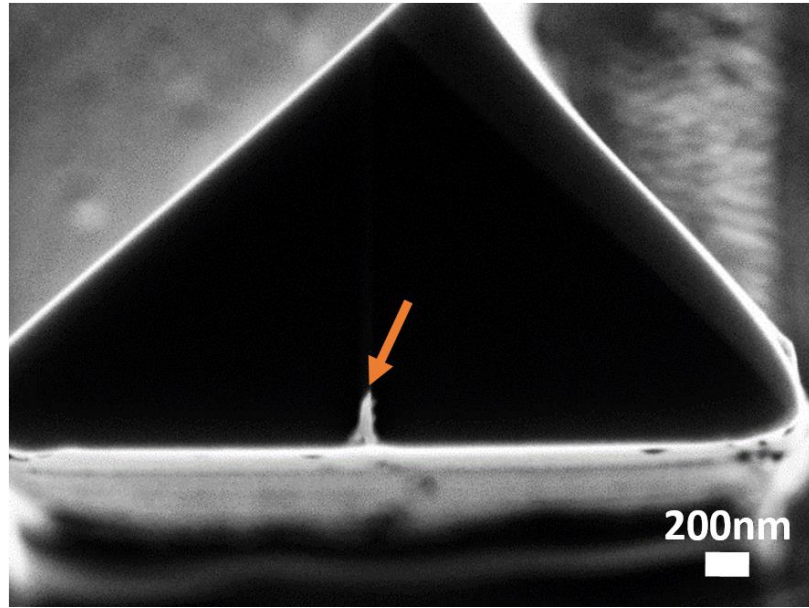
4.5.1.2.4 Wedge preparation

After having firmly attached the wedge to the copper post, excess height was removed from the wedge—the amount of excess height removed depends on the defect type, as described below.

4.5.1.2.4.1 Grain boundaries

The top section of the wedge was removed until it reached the tungsten line-marker, as illustrated in Figure 4-39 (a)–(c).



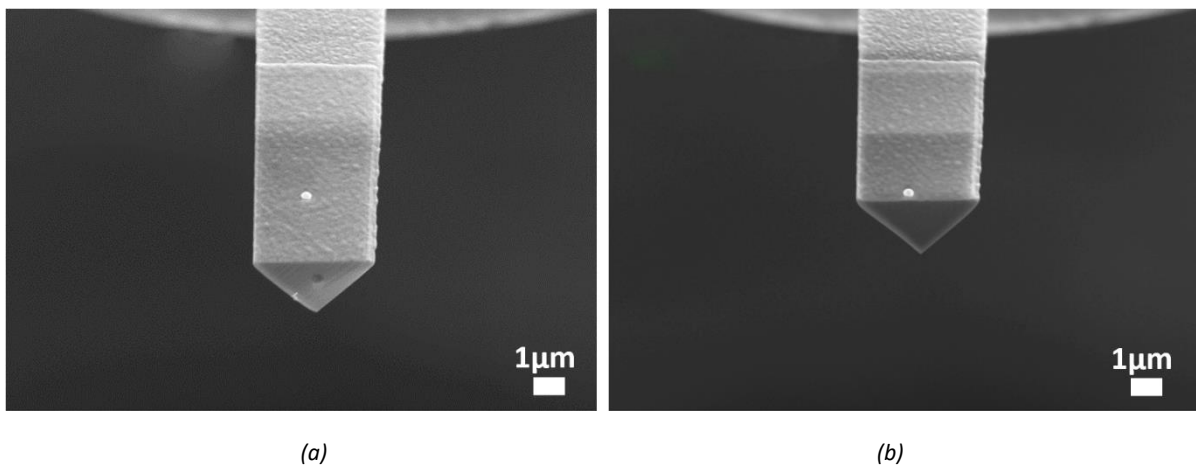


(c)

Figure 4-39. SEM images showing a wedge containing a grain boundary, with a section marked by a tungsten line (a) before and (b) after excess height was removed. (c) shows the triangular surface of the wedge with the grain boundary highlighted by the tungsten line, as indicated by the orange arrow.

4.5.1.2.4.2 Dislocations

The height of the wedge was reduced until the edge reaches about 300–400nm from the centre of the marker, to allow room for the dislocation pit if it were to propagate towards the tip. Figure 4-40(a) and (b) shows the wedge before and after the removal process, respectively.



(a)

(b)

Figure 4-40. SEM images showing a wedge containing a marked dislocation pit (a) before and (b) after excess height was removed.

4.5.1.2.5 Specimen sharpening

The specimen sharpening stage was performed at a 54° tilt such that the specimen's triangular surface was facing the FIB. Due to the differences in the geometry of grain boundaries and dislocations, a sharpening method was developed for each defect type.

4.5.1.2.5.1 Grain boundaries

The specimen sharpening method for grain boundaries was developed based on the fact that the angle at which the grain boundary propagates through the wedge can be observed on the triangular surface of the wedge. The fabrication procedure is shown schematically in Figure 4-41.

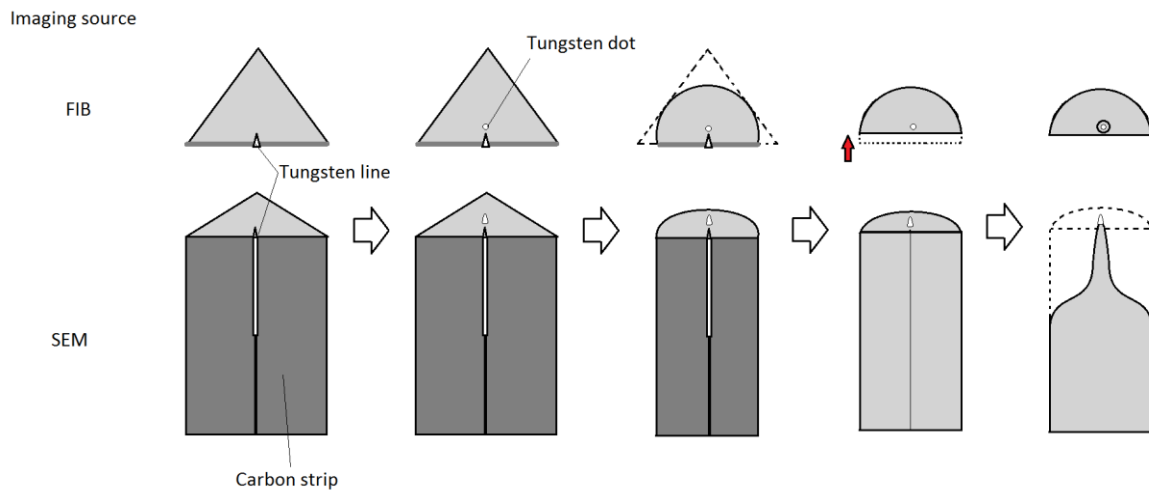


Figure 4-41. A schematic illustrating the sharpening method for grain boundaries. First, a tungsten dot was deposited a small distance from the bottom of the grain boundary groove, to mark the position of the APT specimen's tip. Second, the edges of the wedge were removed by annular milling. Third, defect-marking components were removed by milling a rectangular pattern parallel to the marker surface. Fourth, the APT specimen was fabricated by applying a series of annular milling patterns at various beam currents, with their centres aligned with the tungsten dot.

First, a tungsten dot was deposited a small distance away from the end of the grain boundary groove to mark the position of the APT specimen. This required the triangular surface of the wedge to face the SEM column: i.e., the specimen stage needed to be at a 0° tilt. The dot was deposited using SEM in spot mode at 5kV accelerating voltage, 30µm objective aperture size and 50sec deposition time. A small gap was left between the dot and the end of the grain boundary groove since the depth of the etched pit can vary along the length of the grain boundary groove.

Second, the specimen stage was tilted to 54° so that the triangular surface of the wedge was facing the FIB column. The edges of the wedge were removed by annular milling at an ion beam current of 3nA. The centre of the annular pattern was aligned with the tungsten dot, in order to produce a symmetrical APT specimen.

Third, the defect-marking components – i.e., the tungsten line and the carbon strip – were removed, to avoid non-uniform milling, see Figure 4-42. This was achieved by milling a rectangular pattern parallel to the marker surface using FIB at a 300pA beam current.

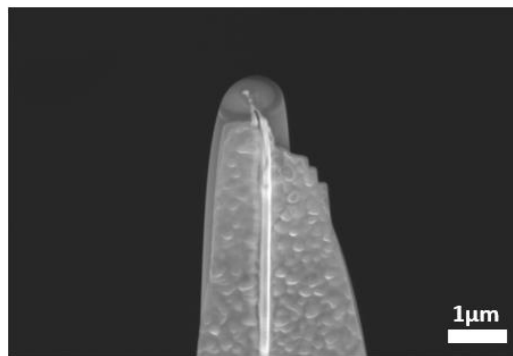


Figure 4-42. An SEM image showing the remaining carbon strip and the tungsten line-marker attached to the side of the specimen.

Fourth, the wedge was sharpened into an APT specimen by applying a series of annular milling patterns. The centre of the annular milling patterns was always aligned with the tungsten dot, which was applied in the first step to mark the position of the APT specimen's tip, throughout the sharpening process. Similar to the early APT specimen fabrication method described in Section 2.7.4.2, the beam current was systematically decreased from 3nA to 40pA as the inner diameter of the annular pattern decreased. It is also worth noting that, during the last few stages of the specimen sharpening step (i.e., when the diameter of the specimen is at about 500–1000nm) the FIB image must be kept at the same magnification, and the same ion beam current must be used for annular milling and imaging, in order to avoid misalignments between the intended and the actual milling positions. The final APT specimen should have a tungsten marker at the tip, as shown in Figure 4-43.

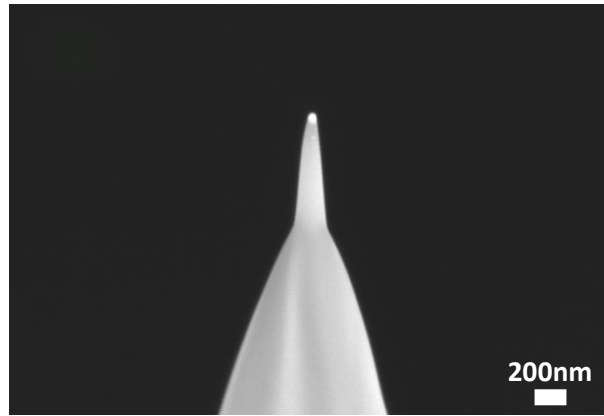


Figure 4-43. An SEM image of an APT specimen containing a grain boundary, with a tungsten dot at the tip.

4.5.1.2.5.2 Dislocations

A major challenge when sharpening a specimen containing an isolated dislocation was that its propagation direction could not be observed on the triangular surface of the wedge, unlike in the grain boundary in Figure 4-39(c). The sharpening method developed for dislocations was based on that for grain boundaries, with small modifications being made in order to determine the propagation direction of the dislocation before sharpening the wedge into an APT specimen. The sharpening procedure is schematically illustrated in Figure 4-44.

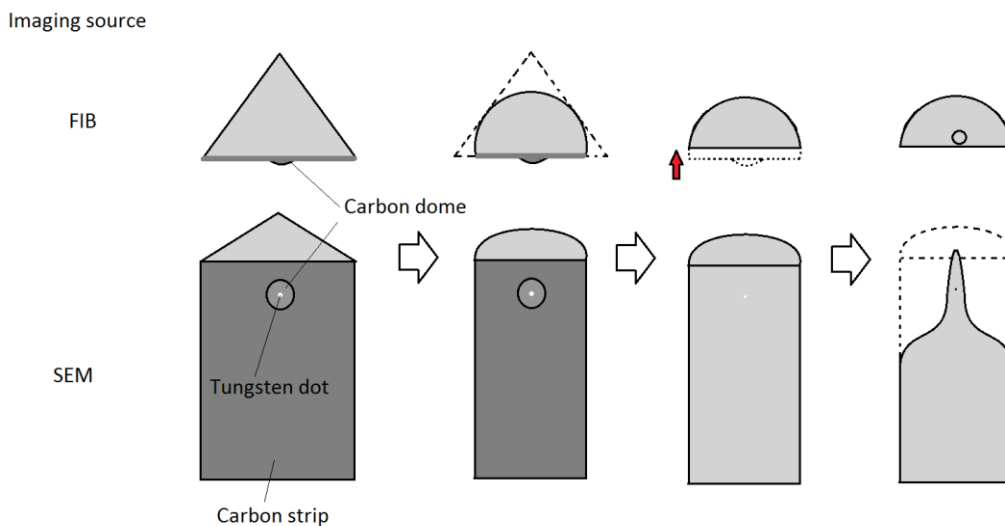


Figure 4-44. A schematic illustrating the sharpening method for dislocations. First, the edges of the wedge were removed by annular milling. Second, defect-marking components and the majority of the dislocation pit were removed by milling a rectangular pattern parallel to the marker surface (shown by red arrow). Third, the wedge was sharpened into an APT specimen by applying a series of annular milling patterns at various beam currents. Note that the distances between the dislocation and the edges were kept the same.

First, the edges of the wedge were removed by annular milling at an ion beam current of 3nA. Note that the centre of the annular pattern was placed about 200nm behind the marker – i.e., the tungsten dot encapsulated in the carbon dome – to account for the depth of the dislocation pit.

Second, the defect-marker components were removed, along with the majority of the dislocation pit. The reason for this was to minimise the amount of tungsten left on the marker surface while allowing it to be observed in the SEM, as shown in Figure 4-45.

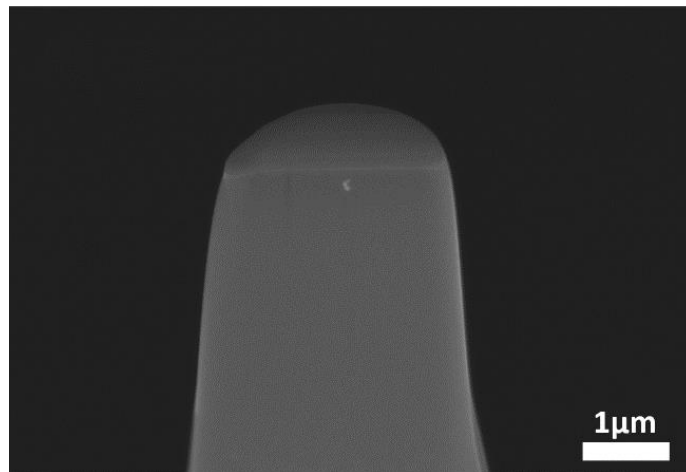


Figure 4-45. SEM image of the wedge after the removal of the defect-marking components, as well as most of the dislocation pit.

Third, the wedge was sharpened by applying a series of annular milling patterns. Similar to the previous method, the milling beam current was systematically decreased from 3nA to 40pA as the inner diameter of the annular milling pattern was decreased. In addition, the dislocation pit must be kept at the centre of the original surface, in order to maximise the chances of the dislocation intersecting with the APT specimen. This was achieved by monitoring the two distances between the dislocation and the edges after each annular milling step, using the SEM, and ensuring that they were equal. If they were not, the annular milling pattern was shifted accordingly. Figure 4-46 (a)–(b) shows the wedge at two different stages of the sharpening process, with the two distances being constantly measured using the measuring tool available in the instrumental software

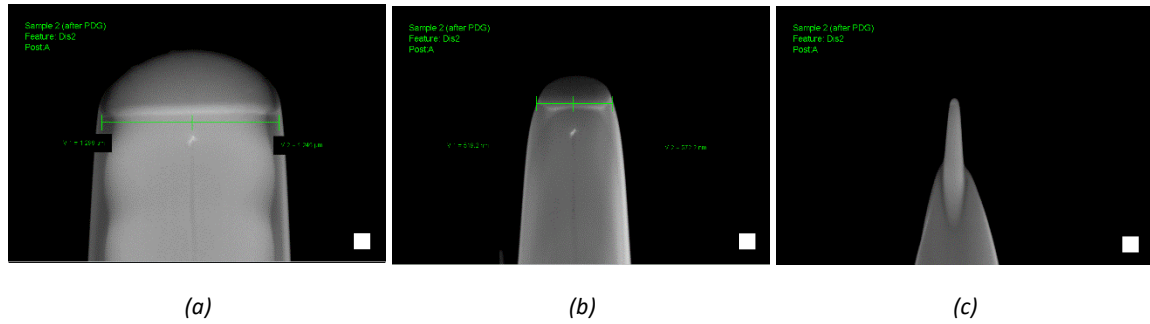


Figure 4-46. The SEM images in (a) and (b) show the specimen during the annular milling process. Note that the distances of the marker from the edges of the original sample surface are kept the same by correcting the position of the annular pattern in the FIB. (c) shows the final atom probe specimen. The scale bars are 200nm.

4.5.1.3 Assessing APT specimen fabrication methods

The APT specimen fabrication methods developed in Section 4.5.1.2 were used to fabricate several APT specimens. They were then observed in the TEM to confirm the presence, or absence, of the defects.

4.5.1.3.1 Grain boundaries

Figure 4-47 shows a typical example of an APT specimen containing a grain boundary. The specimen was fabricated from a gold-contaminated mc-Si sample. In the TEM, a grain boundary is identified by the differences in the diffraction contrast between the two adjacent grains. In this case, the grain boundary is running parallel to the imaging plane, with the nearer grain (Grain 1) appearing to be much darker than the further grain (Grain 2). In most cases, the selected grain boundary does not run along the centre of the specimen, due to the slight deviation of the tungsten dot-marker from the actual position of the grain boundary. Nonetheless, the distance between the tip and the grain boundary can be reduced in the low-ion beam cleaning stage.

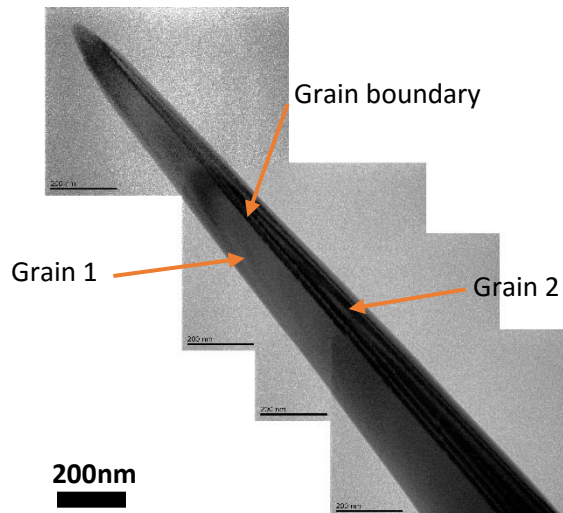


Figure 4-47. BF image of a grain boundary in a gold-contaminated mc-Si sample.

Figure 4-48 shows an APT specimen fabricated from a non-linear grain boundary containing only segments of the grain boundary. This implies that the fabrication method is limited to straight grain boundaries. In many cases, one or more dislocations were found to be lying in the plane of the grain boundary within the APT specimen.

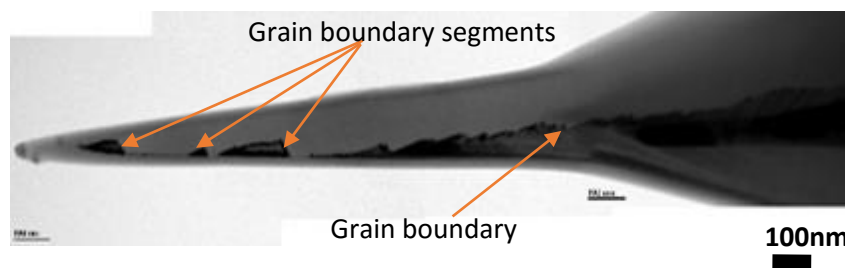


Figure 4-48. BF image showing an APT specimen containing segments of a grain boundary.

4.5.1.3.2 Dislocation

Only one APT specimen was made of a completely isolated dislocation, as a result of the difficulty of the method and the fact that it was developed at a much later stage of the work. Four attempts were made at making APT specimens from isolated dislocations marked by etched pits, during which the fabrication method underwent a number of modifications. Figure 4-49 shows the dislocation running normal to the length of the specimen. The dislocation appears as a dark dot, with the

characteristic bright region on one side and the dark region on the other side. The limitation of this method is that the length of the dislocation that can be analysed in the APT is restricted by the diameter of the APT specimen where the defect and the specimen intersect each other.

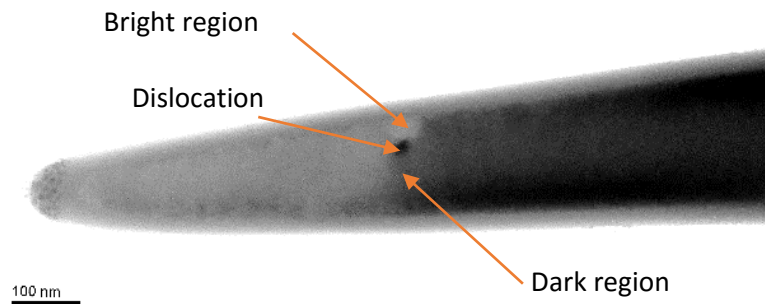


Figure 4-49. BF image of an APT specimen containing a dislocation.

Unfortunately, the geometry of the APT specimens made it difficult to obtain high-quality TEM images of the defects, and it was found to be impossible to characterise the defects using g.b analysis, which is a technique used to characterise extended defects in TEM.

4.5.2 APT specimen holders

The use of an APT specimen holder is essential when specimens are fabricated using the lift-out technique. Three holders were used at various stages, as described in this chapter, to facilitate TEM imaging and the APT specimen fabrication methods developed as described in Section 4.5.1.

In the early stage (as described Section 4.3) silicon coupons containing an array of 36 highly-doped flat-top posts were employed. This type of holder can hold up to 36 specimens, thus allowing multiple specimens to be analysed successively in the APT. However, their geometries prevent TEM analysis of the attached specimens. TEM is a necessary part of the characterisation procedure for verifying the presence of defects inside APT specimens. Hence, alternative holders were developed.

4.5.2.1 Tungsten post

4.5.2.1.1 Fabrication method

A 2–3cm long and 5mm thick tungsten wire was made into a sharp needle using the set-up shown in Figure 4-50. The wire was mounted onto a copper tube such that the wire was parallel to the length of the tube. The tube was then held by a pair of metal tweezers, which were attached to an A.C. generator. The other end of the generator was connected to a gold wire that was partly submerged in an electrolyte (0.5wt% potassium hydroxide solution). A switch was also introduced into the circuit to control the etch rate. The tungsten was sharpened by moving it in and out of the electrolyte until the lower part of the wire fell off, leaving a sharp needle. The potential used to sharpen the wire was 5V.

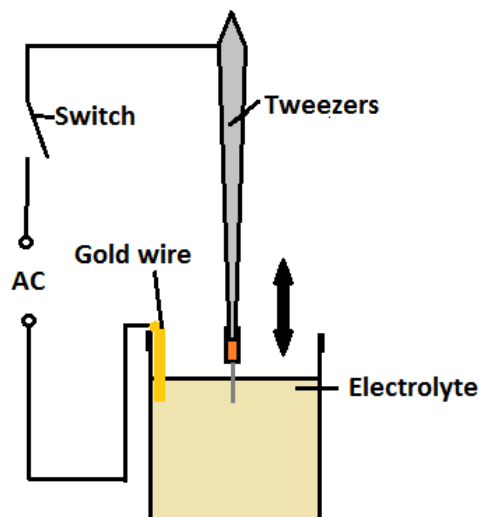


Figure 4-50. A schematic of the electrochemical polishing set-up for making atom probe posts from a tungsten wire

A 2 μ m wide platform was created at the tip of the tungsten needle in the Nivision. This was done by first measuring the diameter to determine the amount of material that needed to be removed from the tip, and, second, removing the tip by milling a rectangular pattern normal to the needle axis. The milling beam current was 700pA. The process is shown in Figure 4-51 (a)–(b).

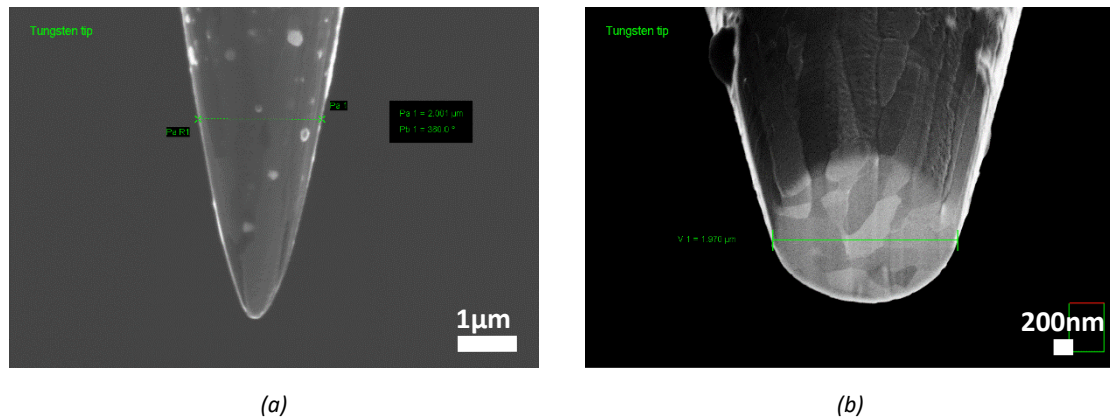


Figure 4-51. SEM images showing (a) diameter measurement of the tungsten needle to determine the amount of the tip to be removed by the FIB; and (b) the platform created on the needle after FIB milling.

4.5.2.1.2 Partial milling during wedge attachment

Partial milling was occasionally observed when attempting to mount wedge segments to tungsten platforms by depositing tungsten strips on both inclined surfaces of the wedge segment, as shown in Figure 4-52. The strip was applied using the FIB, applying the parameters described in Section 2.7.3.

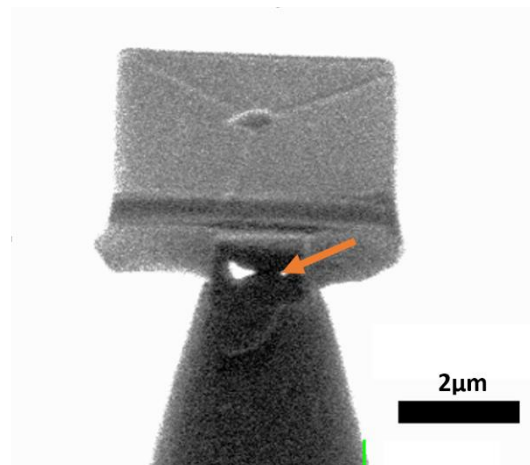


Figure 4-52. An FIB image showing the milling effect at the base of the wedge, marked by the orange arrow, when depositing tungsten using standard deposition conditions.

Partial milling is caused by the deposition rate of the precursor gas molecules being less than the sputtering rate of the focused ion beam. Since the tip of the tungsten post tends to deviate from its central axis, inconsistency in the deposition behaviour of tungsten is likely, due to the variation in the distance between the gas nozzle and the tungsten platform. The solution was to lower the beam

current in order to reduce the sputtering rate of the ion beam. In order to determine the optimum ion beam current for the tungsten strips, wedge segments were attached to tungsten posts by depositing tungsten strips at three different beam currents: 40pA, 10pA and 1pA. The results show that 1pA was the only beam current that did not induce partial milling. Hence, this current was used to mount wedge segments to tungsten posts as described in Section 4.5.1.1. However, the deposition rate was very slow: a deposition time of 10min was needed to reinforce the wedge–tungsten post attachment.

4.5.2.1.3 Tungsten post configuration

Figure 4-53 (a)–(b) shows the two configurations that were employed. Configuration 1 was used to create a platform on the tungsten needle by FIB milling normal to the needle axis. Configuration 2 was used for APT specimen fabrication.

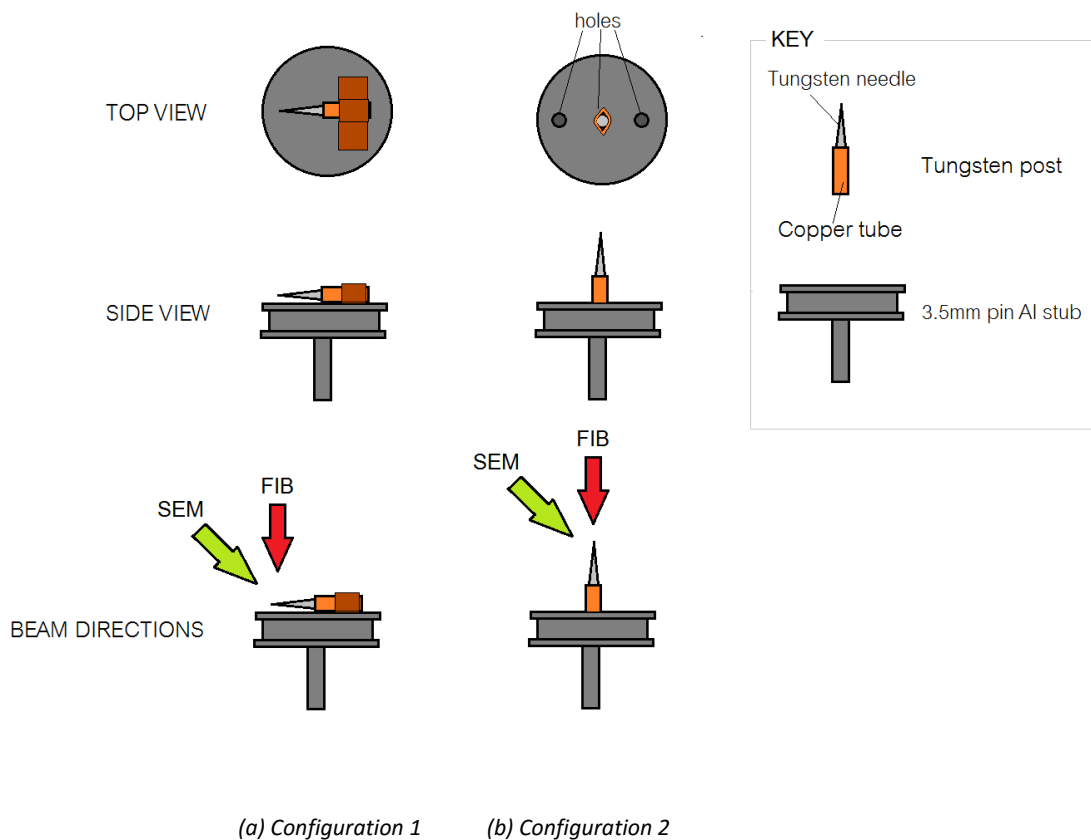


Figure 4-53. Schematic of two tungsten holder configurations for different Nvision processes: (a) is the configuration used to create a platform on the needle tip; and (b) is the configuration for APT specimen fabrication.

For TEM imaging, the specimen was attached to a specially designed TEM holder. The holder restricts the height of the tungsten post to 5 mm above the copper tube, with ± 2 mm tolerance.

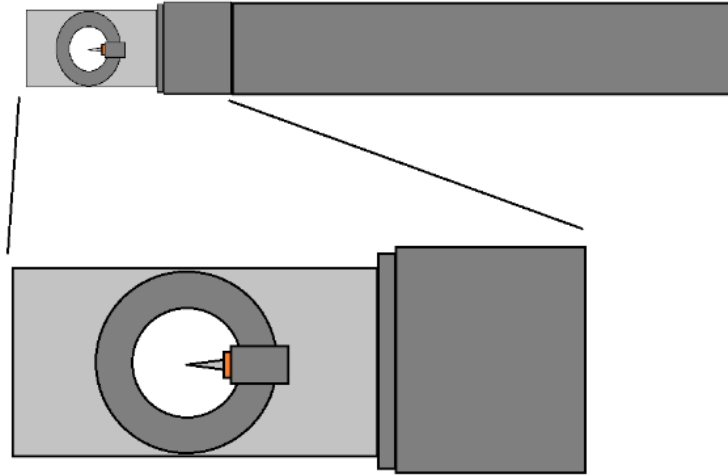


Figure 4-54. A schematic of the TEM holder for tungsten posts.

4.5.2.2 The lift-out grid

Two configurations were developed in order to overcome the limitations of the specimen stage brought about by the APT fabrication methods developed as described in Section 4.5.1.2. These configurations are summarised in Figure 4-55. Configuration 1 was used at the wedge attachment stage (Section 4.5.1.2.3) to allow the wedge to be attached to the copper post. The grid holder was provided by Dr. Peter Felfer, of the Australian Centre for Microscopy and Microanalysis, at the University of Sydney, Australia. Once the attachment had been reinforced and the wedge preparation (Section 4.5.1.2.4) had been performed, the whole configuration was taken out of the Nvision. The grid holder was removed from the copper base and then inserted into the Nvision single-hole holder, thus forming configuration 2. This was then inserted back into the Nvision and the specimen sharpening process was then performed (Section 4.5.1.2.5).

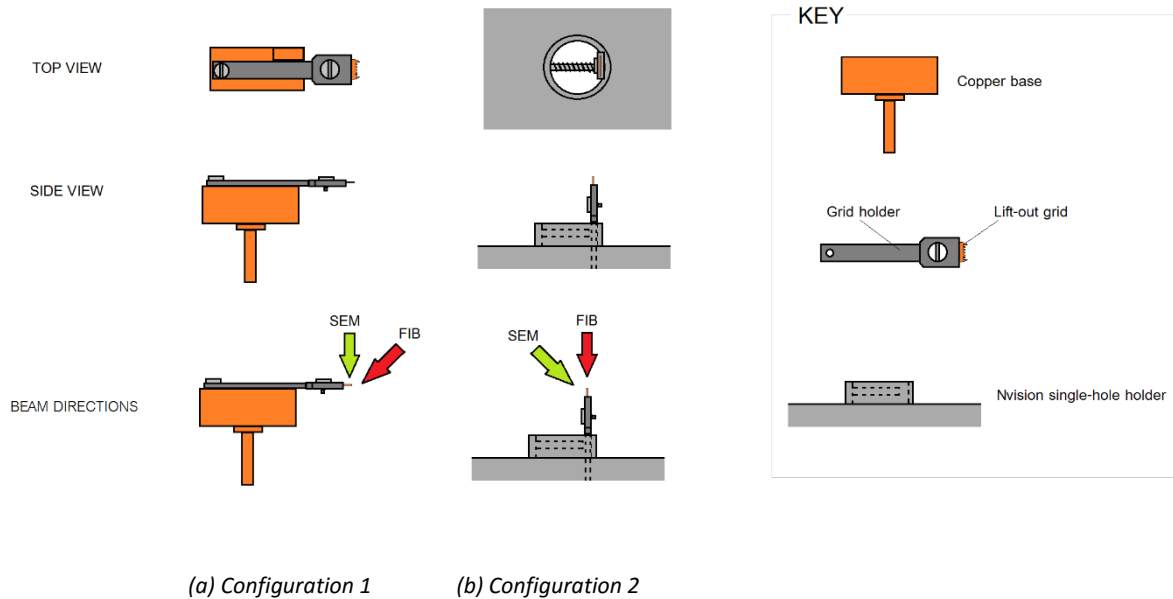


Figure 4-55. Schematic of two lift-out grid configurations for different Nvision processes: (a) is the configuration for wedge attachment; and (b) is the configuration for APT specimen fabrication.

4.5.3 Summary of the APT specimen fabrication methods

This section summarises the atom probe specimen fabrication procedures for grain boundaries and isolated dislocations.

1. The selected defect is marked using the marking techniques developed as described in Section 4.4.
2. A cantilever is fabricated, with the wedge having a length of $30\mu\text{m}$ and a width of $4\mu\text{m}$.
3. The wedge is lifted-out of the bulk sample.
4. The bottom of the wedge is attached to the tip of a copper post.
5. Material is removed from the top portion of the wedge such that the marker is sufficiently close to the end of the wedge.
6. The wedge is prepared for the specimen sharpening step using the methods described in Section 4.5.1.2.5.
7. The wedge is sharpened into an APT specimen using the method developed in Section 4.5.1.3.1 for grain boundaries and Section 4.5.1.3.2 for dislocations.

4.5.4 References

- ¹ Miller, M. K., Russell, K. F., Thompson, K., Alvis, R., & Larson, D. J. (2007). Review of atom probe FIB-based specimen preparation methods. *Microscopy and Microanalysis*, 13(06), 428-436.
- ² Miller, M. K., Russell, K. F., & Thompson, G. B. (2005). Strategies for fabricating atom probe specimens with a dual beam FIB. *Ultramicroscopy*, 102(4), 287-298.
- ³ Saxey, D. W., Cairney, J. M., McGrouther, D., Honma, T., & Ringer, S. P. (2007). Atom probe specimen fabrication methods using a dual FIB/SEM. *Ultramicroscopy*, 107(9), 756-760.
- ⁴ Felfer, P., Ringer, S. P., & Cairney, J. M. (2011). Shaping the lens of the atom probe: Fabrication of site specific, oriented specimens and application to grain boundary analysis. *Ultramicroscopy*, 111(6), 435-439.
- ⁵ Jenkins, D. W. K., Allen, G. C., Prewett, P. D., & Heard, P. J. (1991). Focused ion-beam assisted deposition of tungsten and carbon. *Journal of Physics: Condensed Matter*, 3(S), S199.
- ⁶ Thompson, K., Lawrence, D., Larson, D. J., Olson, J. D., Kelly, T. F., & Gorman, B. (2007). In situ site-specific specimen preparation for atom probe tomography. *Ultramicroscopy*, 107(2), 131-139.
- ⁷ Schönecker, A., Geerligs, L. J., & Müller, A. (2003). Casting technologies for solar silicon wafers: block casting and ribbon-growth-on-substrate. *Solid State Phenomena*, 95, 149-158.

5 Optimisation of LEAP parameters

Table of Contents

5.1	Introduction	- 154 -
5.2	Objective	- 154 -
5.2.1	The $\text{Si}^+/\text{Si}^{2+}$ ratio	- 155 -
5.2.2	The $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio.....	- 156 -
5.2.3	The signal-to-noise ratio	- 157 -
5.3	Materials	- 159 -
5.4	Instrumentation	- 159 -
5.5	Methodology.....	- 159 -
5.6	Optimisation of LEAP parameters.....	- 160 -
5.6.1	Errors.....	- 160 -
5.6.2	Results.....	- 160 -
5.6.3	Discussion.....	- 169 -
5.6.4	Conclusion.....	- 172 -
5.7	Determining Fe detection efficiency.....	- 173 -
5.7.1	The fabrication method used to make the Fe calibration specimens	- 173 -
5.7.2	Calculating the iron detection efficiency	- 175 -
5.8	Summary	- 177 -
5.9	References	- 178 -

5.1 Introduction

Fe is considered to be one of the most important metal impurities in mc-Si solar cell^{1,2,3} materials because it is inevitably incorporated into commercial mc-Si ingots from various sources: namely Si feedstocks, crucibles and their wall linings.⁴ In many cases, Fe is the highest concentration metallic impurity present in solar grade Si, after casting: ranging from 6×10^{14} to 1.5×10^{16} atom/cm³[5]). Unfortunately, Fe concentrations of this level cannot easily be detected by the LEAP, due to the background noise limitations of the instrument. Still, the segregation of Fe to extended defects in mc-Si is well-known^{6,7,8} and is considered to be a major problem in the solar cell industry. This is because Fe-decorated defects are effective recombination sites for minority carriers, resulting in a reduction in the light-to-electricity conversion efficiency of mc-Si solar cells. Although the Fe concentration at the defects has yet to be experimentally determined, this part of my project was based on the assumption that the concentration is sufficiently high to be detectable by the LEAP. However, the LEAP parameters need to be optimised in order to maximise the Fe detection sensitivity. Therefore, this chapter outlines the experimental work carried out to optimise the LEAP parameters to maximise the Fe detection sensitivity of the instrument. The optimum parameters were then used to analyse Fe-contaminated calibration specimens, to determine the detection sensitivity in respect of Fe. The fabrication process in respect of the calibration specimens is described in Section 5.7.1.

5.2 Objective

The objective was to maximise the detectability of the very small concentrations of Fe that are expected at or close to the dislocations. There are three factors that limit the Fe detection efficiency in a LEAP: a) the relative proportions of the $^{56}\text{Fe}^+$ and $^{56}\text{Fe}^{2+}$ ions produced (this is because the $^{56}\text{Fe}^{2+}$ peak overlaps the $^{28}\text{Si}^+$ peak and thus cannot be distinguished); b) the proportion of Si_2^+ ions produced (because the 2^{28}Si^+ peak overlaps the intended Fe^+ peak at 56amu); and c) the noise in the spectrum as a whole (since “real” ion counts need to be detectable above the noise counts).

5.2.1 The $\text{Si}^+/\text{Si}^{2+}$ ratio

A major factor that limits the lowest concentration of Fe ions that can be detected in Si samples is the overlapping of $^{56}\text{Fe}^{2+}$ ions with $^{28}\text{Si}^+$ ions at a mass-to-charge ratio of 28 amu in the mass spectrum (Figure 5-1). This can lead to problems in making an accurate determination of the amount of Fe, and will lead to an apparent reduction in the overall concentration of Fe present. This is because those ^{56}Fe ions emitted in the doubly-charged state will be included in the $^{28}\text{Si}^+$ ion count. This effect makes a negligible difference to the overall measured concentration of Si (the majority element present) but may lead to a substantial underestimation of the concentration of Fe. Although it is theoretically possible to determine the Fe concentration from mass peaks associated with other Fe isotopes (i.e., ^{54}Fe and ^{57}Fe) that do not overlap with the Si peaks, *these isotopes only make up*, respectively, 5.8% and 2.2% of the total field-evaporated Fe ions and, hence, cannot be observed above the background noise in the mass spectrum.

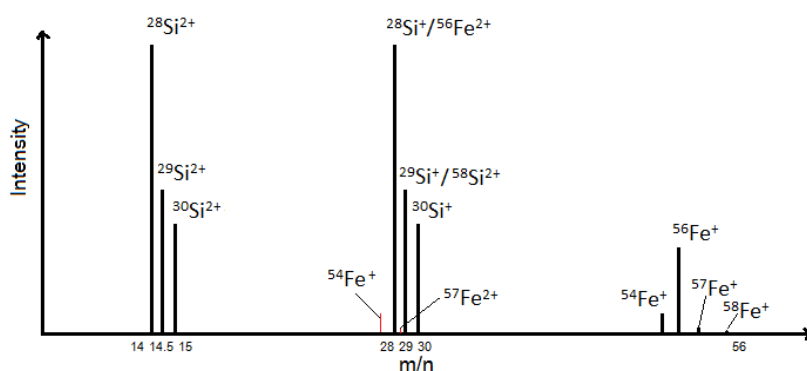


Figure 5-1. A schematic of a mass spectrum showing the positions of mass peaks associated with singly and doubly-charged Si and Fe. The mass peaks highlighted in red are Fe^{2+} peaks that do not overlap with Si peaks.

The problem with the overlapping of $^{56}\text{Fe}^{2+}$ with $^{28}\text{Si}^+$ can be minimised by maximising the yield of emitted Fe ions in the singly-charged state. This can be done by reference to the Kingham diagram, which shows the relative abundance of different charge states of an element as a function of electric field strength, for the two elements.⁹ The Kingham diagram in Figure 5-2 shows similarities in the relative abundance of singly and doubly-charged ions for Si and Fe as a function of field strength. It can therefore be assumed that experimental parameters that lead to an increase in the

concentration of Si^+ ions will also lead to a higher concentration of Fe^+ ions. Thus, experiments were carried out on pure Si specimens to determine the parameters for maximising the $\text{Si}^+/\text{Si}^{2+}$ ratio, and to measure what values of this ratio could be achieved. The same parameters were then applied to an Fe-doped calibration specimen and to mc-Si specimens which were known to contain Fe impurities.

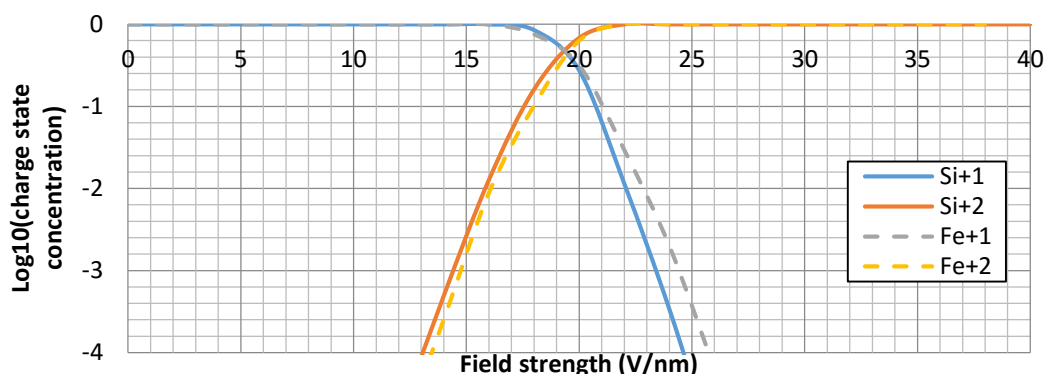


Figure 5-2. The relative abundance of singly and doubly-charged states of Si and Fe as a function of field strength⁹.

5.2.2 The $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio

The second important factor that limits the detection sensitivity in respect of Fe is the formation of Si_2^+ clusters, because one of its possible isotope peaks (i.e., $^{28}\text{Si}^+$) overlaps the Fe_{56}^+ peak. Even a small number of $^{28}\text{Si}_2^+$ ions can overwhelm the small Fe signal and, in turn, lead to inaccuracy when determining the Fe concentration. Therefore, the parameter $\text{Si}_2^+/\text{Si}_{\text{total}}$, where Si_{total} is the sum of Si^+ and Si^{2+} , was employed in order to observe changes in the concentration of Si_2^+ clusters. Note that because of the three stable isotopes of Si, there are five mass peaks associated with Si_2^+ : 56amu, 57amu, 58amu, 59amu and 60amu. Since the height of the last two peaks was always below the background noise, they were not included in the total number of Si_2^+ . Pre-sharpened Si specimens are ideal for determining the effect of the LEAP parameters on the $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio, since they do not contain Fe—which means that if a peak is observed to be at 56 amu it can with confidence be assigned to Si_2^+ .

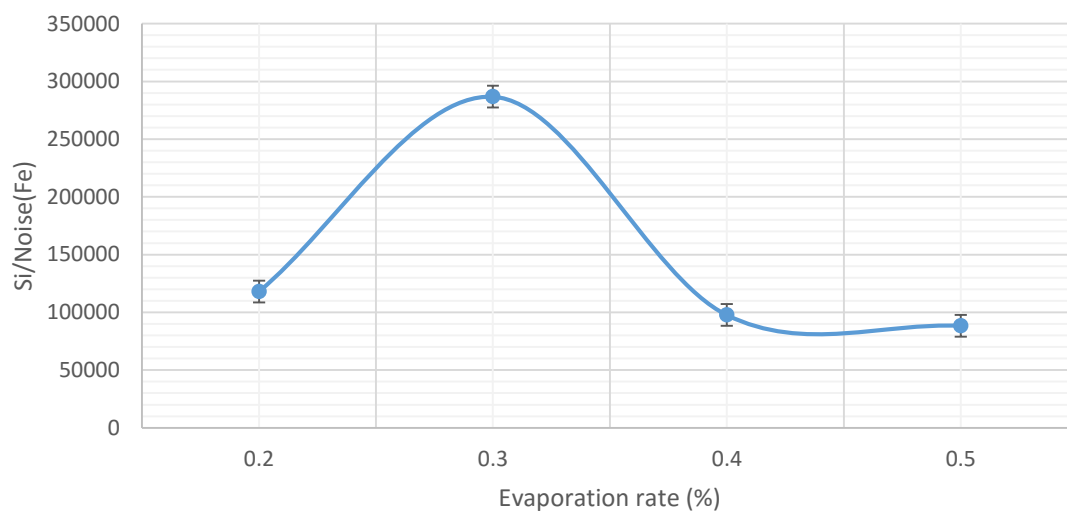
5.2.3 The signal-to-noise ratio

The background noise limits the detection sensitivity in respect of Fe, as well as other elements/compounds, in APT specimens. In cases where the concentration of a chemical species in an APT specimen is very low, its corresponding peaks can simply be masked by the background noise and thus will not appear in the three-dimensional reconstruction of the specimen. Therefore, it is important to maximise the signal-to-noise ratio, in order to maximise the detection efficiency of dilute chemical species.

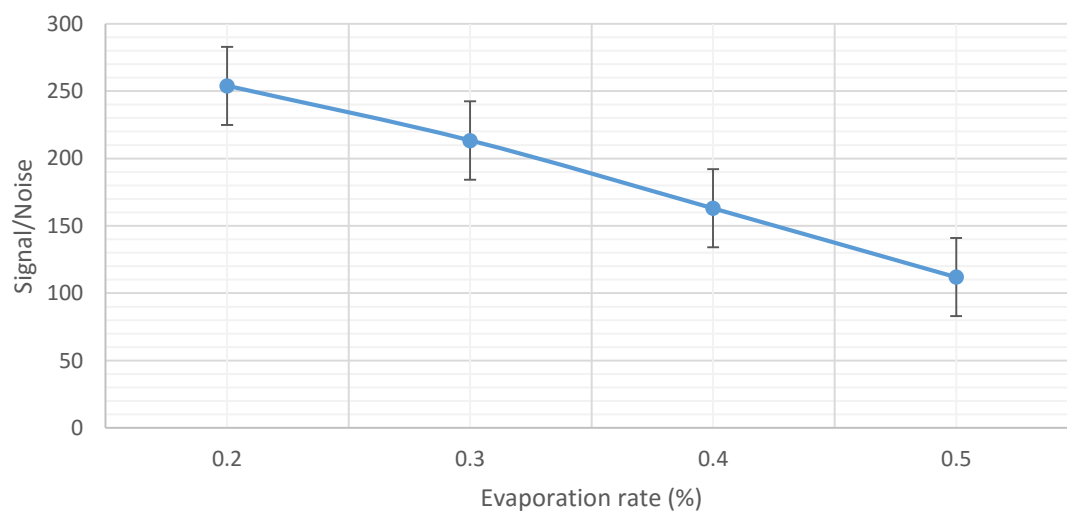
Initially, the signal-to-noise ratio was defined as the ratio between the total number of Si ions – i.e., Si_{total} – and the background noise at 56amu, with a width range of 0.4amu. This particular range was chosen because it was the approximate width of the Fe peak found in the spectrum of the Fe calibration specimen described in Section 5.7. However, such a definition made the ratio sensitive to small changes in the background noise at 56amu, since the value is often very small (10–20) compared to the total number of Si atoms detected. In most cases, this resulted in unexplainable relationships between the signal-to-noise ratio and the LEAP parameters, as demonstrated in Figure 5-3(a) where the evaporation rate varied from 0.2% to 0.5%.

In order to overcome this problem, an alternative definition of the signal-to-noise ratio was proposed: the signal is the total number of ions in identifiable peaks, including those normally excluded from the specimen reconstruction, e.g. H_x^+ peaks. The background noise, on the other hand, is assigned to the ions in the rest of the spectrum. When this definition of the signal-to-noise ratio is applied to the same datasets as those used to create Figure 5-3(a), a downward trend can clearly be observed, see Figure 5-3(b). The reason for this trend is explained in Section 5.6.2.4. Therefore, it can be concluded that this definition of the signal-to-noise ratio provides a better understanding of the effect of LEAP parameters on the background noise than the previous definition. For this reason, it was used, as described in Section 5.6, to optimise the LEAP parameters. It is important to note that this definition of the signal-to-noise ratio relates to all the noise in the

entire mass spectrum. When determining the actual detection sensitivity in respect of Fe in a sample, however, the important mass range is at 56amu, which is the position of the main Fe peak (Fe_{56}^+). Hence, an alternative definition, described in Section 2.9.9, was used to determine the Fe detection sensitivity.



(a)



(b)

Figure 5-3. The signal-to-noise ratio as a function of evaporation rate, with the former being defined as: (a) the ratio between the total number of Si ions and the background noise at 56; and (b) the ratio between the total number of ions in identifiable peaks and those in the rest of the mass spectrum, which are considered as noise.

5.3 Materials

The APT specimens employed in this chapter were from a coupon containing an array of pre-sharpened sc-Si tips and an Fe calibration APT specimen. The former was used as-received to optimise the evaporation parameters for APT. Once optimised, these parameters were applied to the Fe calibration specimens to determine the Fe detection efficiency. The calibration specimens were fabricated from a Cz-Si wafer, which was RCA-cleaned and ion implanted with Fe at one of its surfaces. APT specimens were fabricated from the wafer using the method developed as described in Chapter 4.

5.4 Instrumentation

The instruments used for the work described in this chapter were the NVision FIB and LEAP 3000X HR. The former was used to fabricate the Fe calibration specimens. The latter was used to analyse both pre-sharpened and Fe calibration specimens, to maximise the Fe detection sensitivity and to determine the Fe detection efficiency, respectively.

5.5 Methodology

A matrix of pre-sharpened Si posts was subjected to analyses using a variety of parameters. In the first set of specimens, the specimen temperature was varied from 40K to 60K, in 5K increments. Other parameters were kept the same—i.e., 0.5nJ beam energy, evaporation rate 0.3% and repetition rate 160 kHz. In the second set of specimens, the beam energy was varied from 0.1nJ to 0.9nJ, in 0.2nJ increments. These analyses were performed at an evaporation rate of 0.3%, a repetition rate of 160 kHz and a temperature of 55K. In the third set of specimens, the repetition rate was varied from 80 kHz to 250 kHz. The other parameters were kept the same—i.e., 0.5nJ beam energy, 0.3% evaporation rate and 55K temperature. In the last set of specimens, the evaporation rate was varied from 0.2% to 0.5%, in 0.1% increments. The beam energy, repetition rate and the temperature were kept the same at 0.5nJ, 160 kHz and 55K, respectively. Each dataset contained about 1.2 million ions. The Fe detection efficiency for the chosen parameters was then evaluated

using two Fe calibration specimens. The pressure inside the LEAP's analysis chamber was kept below 5×10^{-11} mbar for all the APT analyses.

5.6 Optimisation of LEAP parameters

5.6.1 Errors

All error bars in all the graphs are given by the standard deviation of four APT analyses performed on pre-sharpened specimens at the same evaporation parameters: i.e., 0.3% evaporation rate, 0.5nJ beam energy, 160 kHz repetition rate and 55K temperature.

5.6.2 Results

5.6.2.1 Laser beam energy

Figure 5-4 shows that $\text{Si}^+/\text{Si}^{2+}$ ratio increases with laser beam energy, from about 0.002 (or 0.2% relative Si^+ concentration) at 0.1nJ to about 11 (91% relative Si^+ concentration) at 0.9nJ. The crossover point where the ratio is more than one occurs between 0.3nJ and 0.5nJ. In other words, Si^+ becomes the dominant charge state when the beam energy is 0.5nJ or higher.

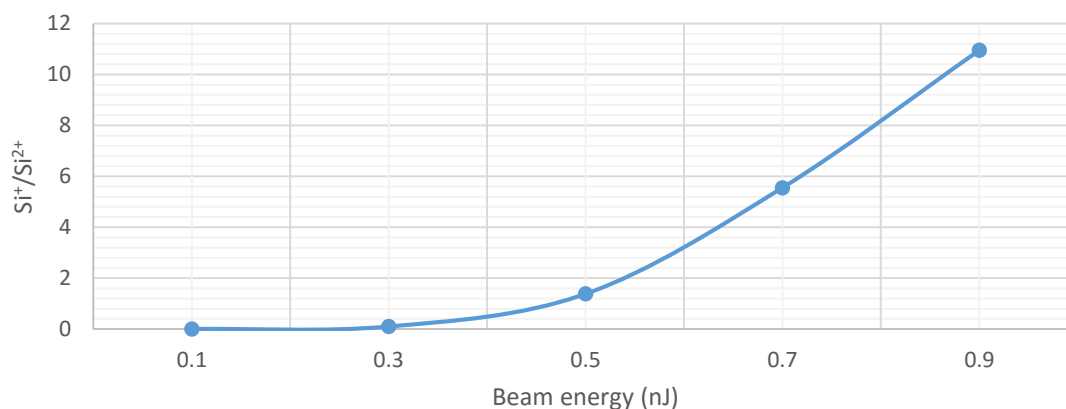


Figure 5-4. $\text{Si}^{2+}/\text{Si}^+$ ratio as a function of beam energy. APT analyses were performed at 0.3% evaporation rate, 160kHz pulse repetition rate and 55K specimen temperature. The line is a guide for the eye only.

Figure 5-5 shows mass spectra obtained from the experiments at different beam energies. All the spectra contain single element ions: namely Si, O and H, as well as molecular ions, namely SiO , H_2O and SiH_xO —with the latter appearing to be more prominent at higher beam energy. In addition,

mass peaks associated with Si_2^+ and Si_2O^+ peaks were found at 0.7nJ beam energy and became more prominent at 0.9nJ. The laser beam energies normally used in the APT group to analyse semiconductor materials rarely exceed 0.5nJ. Another noticeable feature is the change in the relative height of Si^+ and Si^{2+} mass peaks, which can be explained by a reduction in the DC field required to field-evaporate surface atoms at higher laser beam energies. According to the Kingham diagram (Figure 5-2), lower field leads to a larger proportion of Si ions being field-evaporated as Si^+ .

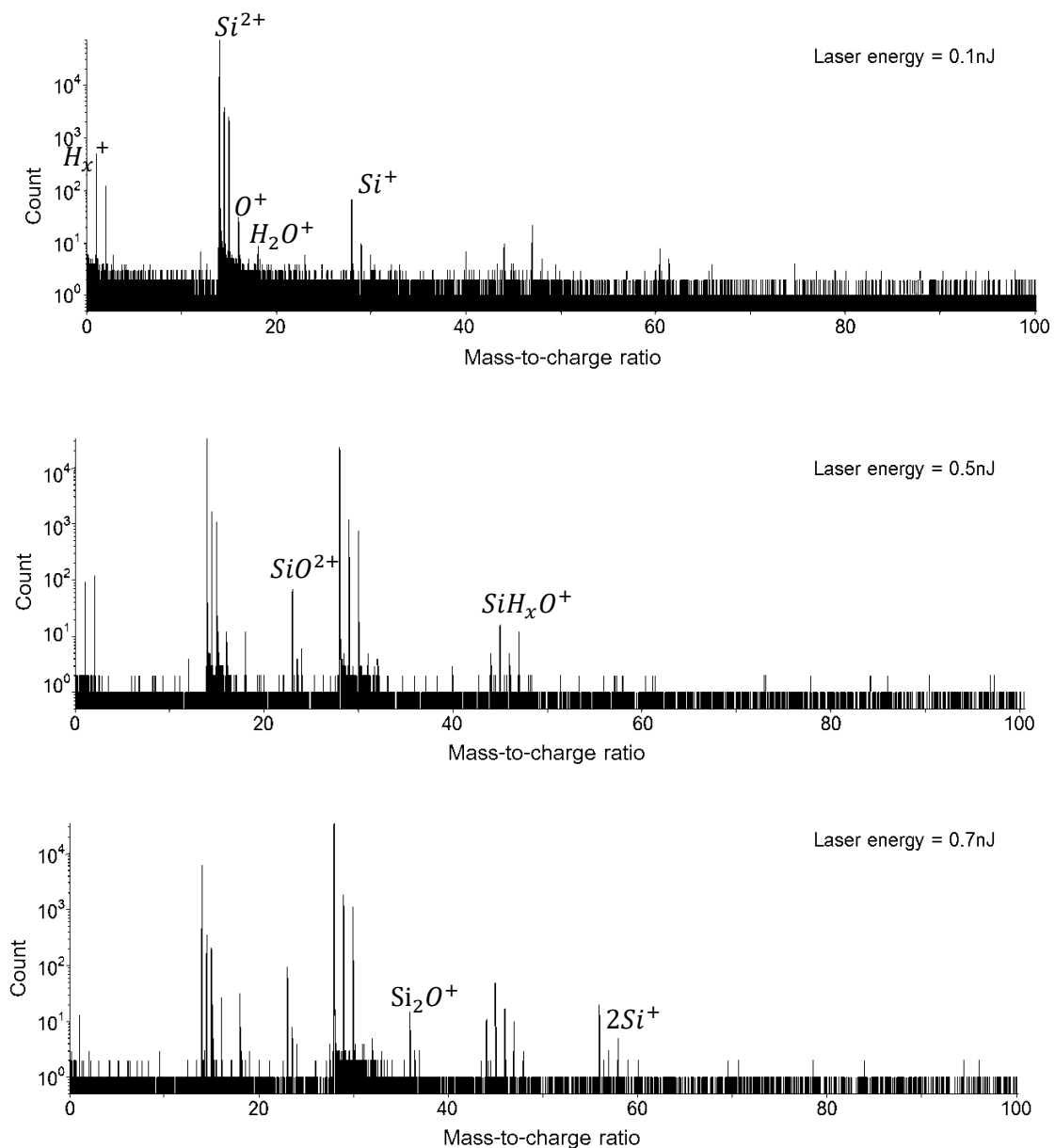


Figure 5-5. Mass spectra of pre-sharpened Si at three different beam energies. APT analyses were performed at 0.3% evaporation rate, 160kHz pulse repetition rate and 55K specimen temperature.

Figure 5-6 shows that the concentration of Si_2^+ remains at about $4\text{--}5 \times 10^{-5}$ at laser beam energies of between 0.1nJ and 0.5nJ. A sudden increase in Si_2^+ is then observed when the laser beam energy is higher than 0.5nJ. This behaviour is consistent with the mass spectra in Figure 5-5, where the Si_2^+ peak is only seen at the highest laser beam energy. The $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio between 0.1nJ and 0.5nJ is eight times lower than that at 0.9nJ.

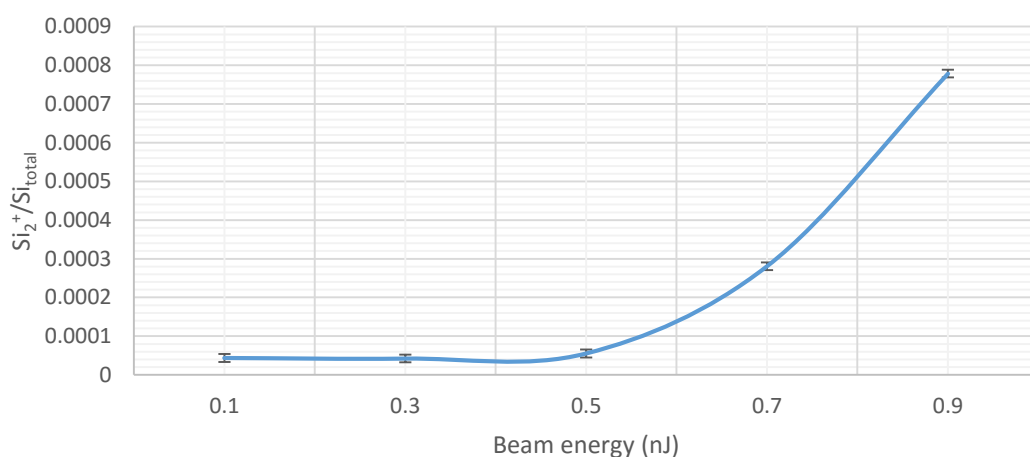


Figure 5-6. $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio as a function of laser beam energy. APT analyses were performed at 0.3% evaporation rate, 160kHz pulse repetition rate and 55K specimen temperature. The line is a guide for the eye only.

A reduction in the background noise with higher beam energy is shown in Figure 5-7, which indicates that the signal-to-noise ratio at 0.9nJ is almost four times that at 0.1nJ.

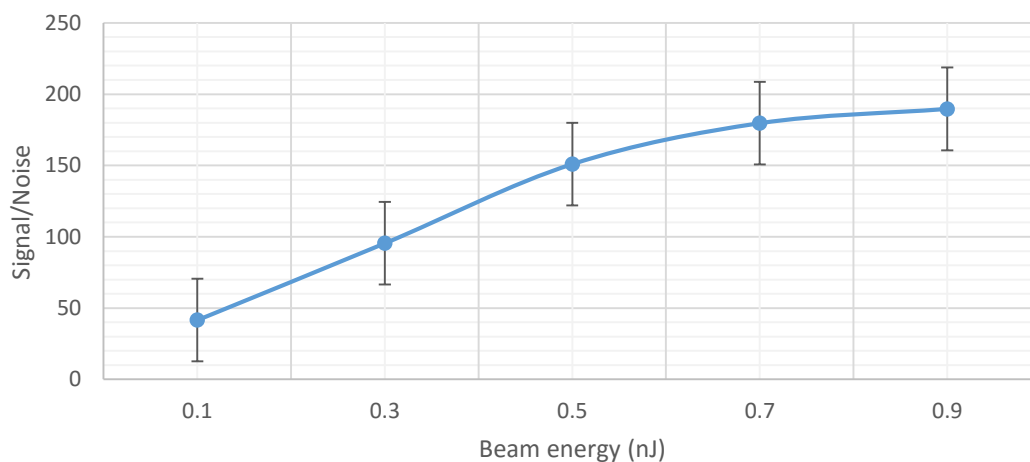


Figure 5-7. Signal-to-noise ratio as a function of beam energy. APT analyses were performed at 0.3% evaporation rate, 160kHz pulse repetition rate and 55K specimen temperature. The line is a guide for the eye only.

5.6.2.2 Temperature

Figure 5-8 shows an increase in the $\text{Si}^+/\text{Si}^{2+}$ ratio with increasing temperature. The ratio increases from about 0.9 at 40K to about 1.5 at 60K.

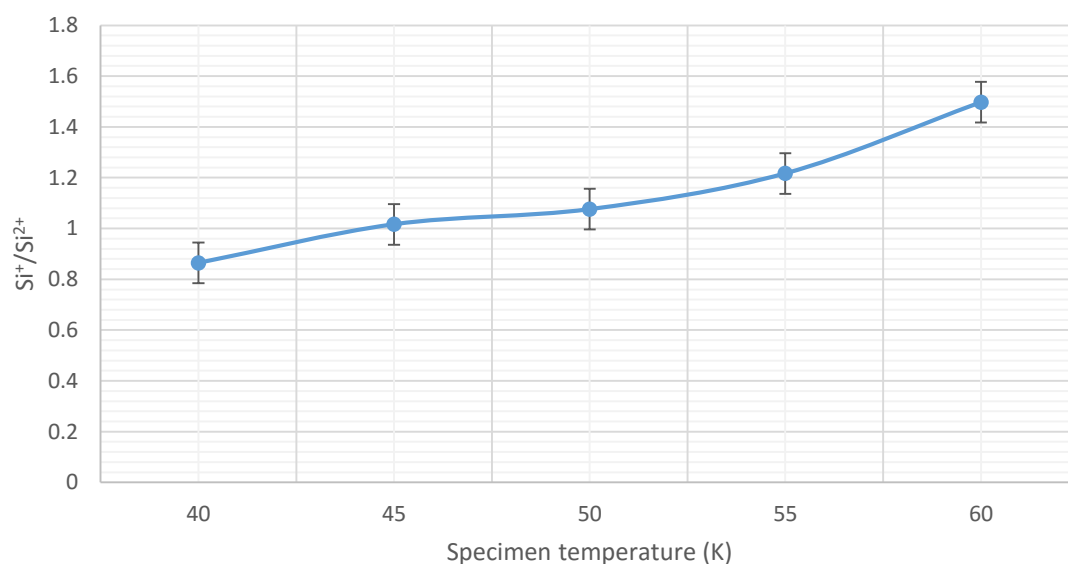


Figure 5-8. $\text{Si}^{2+}/\text{Si}^+$ ratio as a function of temperature. APT analyses were performed at 0.5nJ laser beam energy, 0.3% evaporation rate and 160kHz pulse repetition rate. The line is a guide for the eye only.

Figure 5-9 shows an increase in mass peaks associated with molecular clusters – i.e., SiO_x , H_2O and SiH_xO – at higher specimen temperature—with the exception of those associated with Si_2^+ peaks.

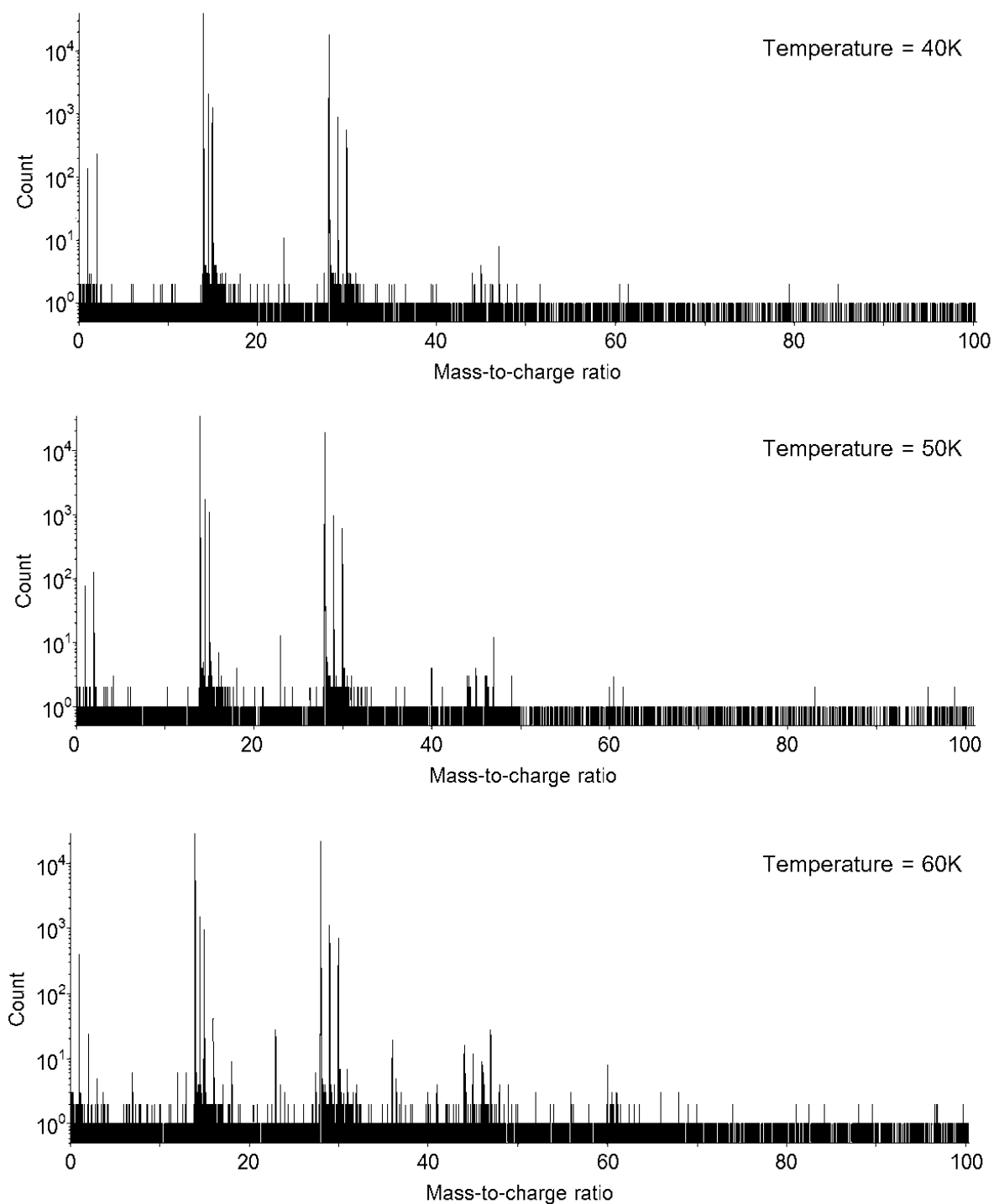


Figure 5-9. Mass spectra of pre-sharpened Si at three different temperatures. APT analyses were performed at 0.5nJ laser beam energy, 0.3% evaporation rate and 160kHz pulse repetition rate.

Figure 5-10 shows no significant change in the concentration of Si_2^+ clusters with the specimen temperature. The average $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio is at about 3×10^{-5} .

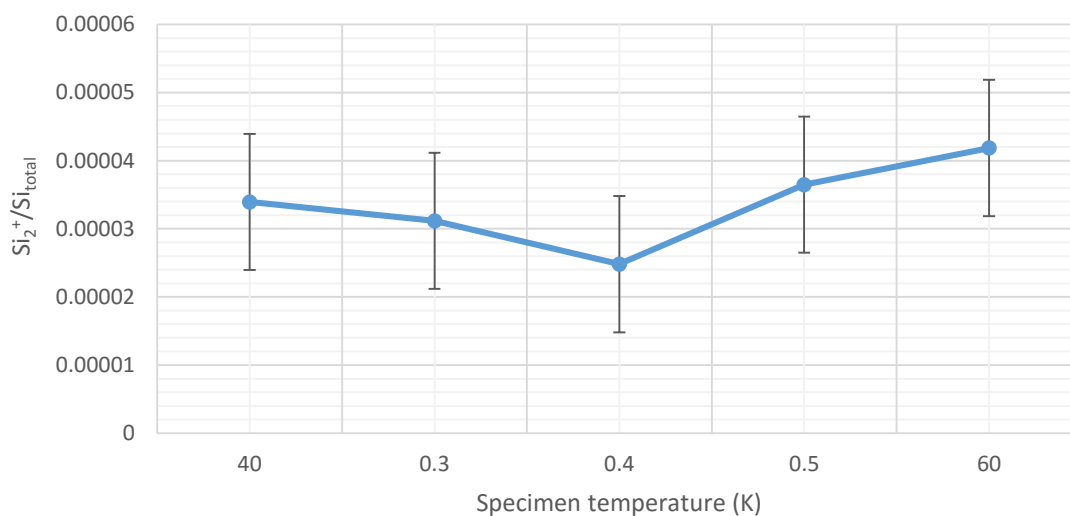


Figure 5-10. $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio as a function of specimen temperature. APT analyses were performed at 0.5nJ laser beam energy, 0.3% evaporation rate and 160kHz pulse repetition rate. The line is a guide for the eye only.

The effect of temperature on the signal-to-noise ratio is shown in Figure 5-11. It was found that the ratio remained at about 170 across all the temperatures.

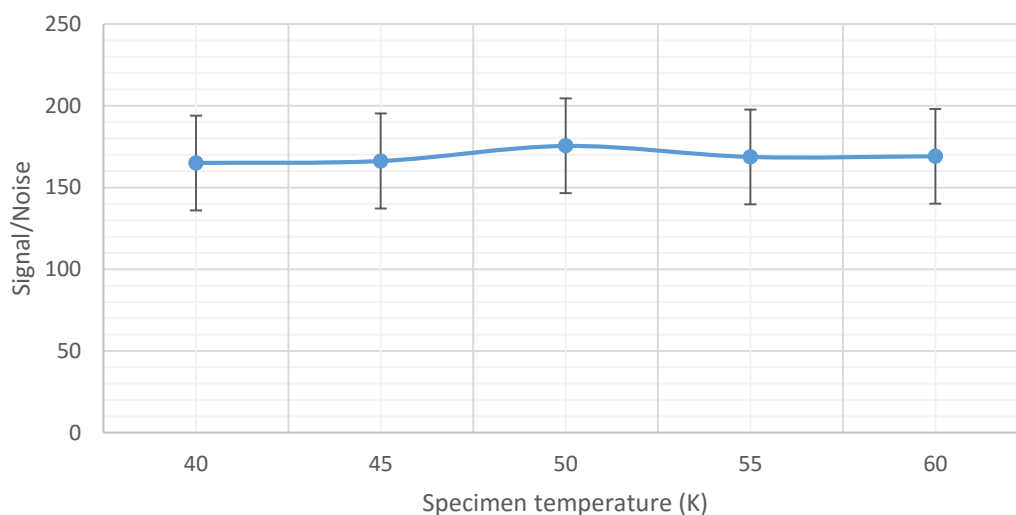


Figure 5-11. Signal-to-noise ratio as a function of temperature. APT analyses were performed at 0.5nJ laser beam energy, 0.3% evaporation rate and 160kHz pulse repetition rate. The line is a guide for the eye only.

5.6.2.3 Repetition rate

Figure 5-12 shows that repetition rate has a negligible effect on the $\text{Si}^+/\text{Si}^{2+}$ ratio: the variation in the ratio is about 0.1 over the whole range used. The average $\text{Si}^+/\text{Si}^{2+}$ ratio is about 1.4, which means that 58% of Si ions are singly-charged. The repetition rate normally used in the group is between 200kHz and 250kHz.

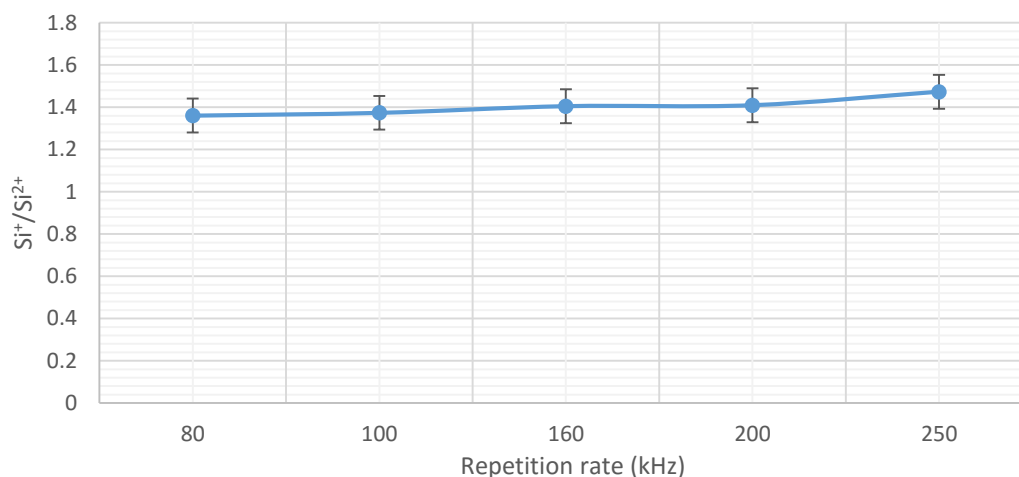


Figure 5-12. $\text{Si}^+/\text{Si}^{2+}$ ratio as a function of repetition rate. APT analyses were performed at 0.5nJ laser beam energy, 0.3% evaporation rate and 55K specimen temperature. The line is a guide for the eye only.

The repetition rate does not appear to have a profound effect on the concentration of Si_2^+ clusters, as shown in Figure 5-13.

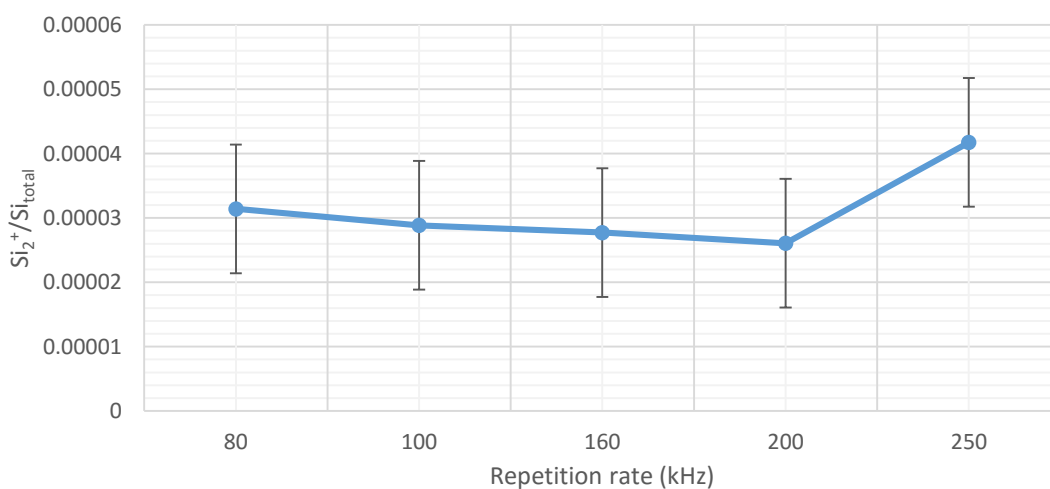


Figure 5-13. $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio as a function of repetition rate. APT analyses were performed at 0.5nJ laser beam energy, 0.3% evaporation rate and 55K specimen temperature. The line is a guide for the eye only.

Figure 5-14 shows that the signal-to-noise ratio increases with a higher repetition rate: the signal-to-noise ratio at 250kHz is about two times greater than that at 80kHz.

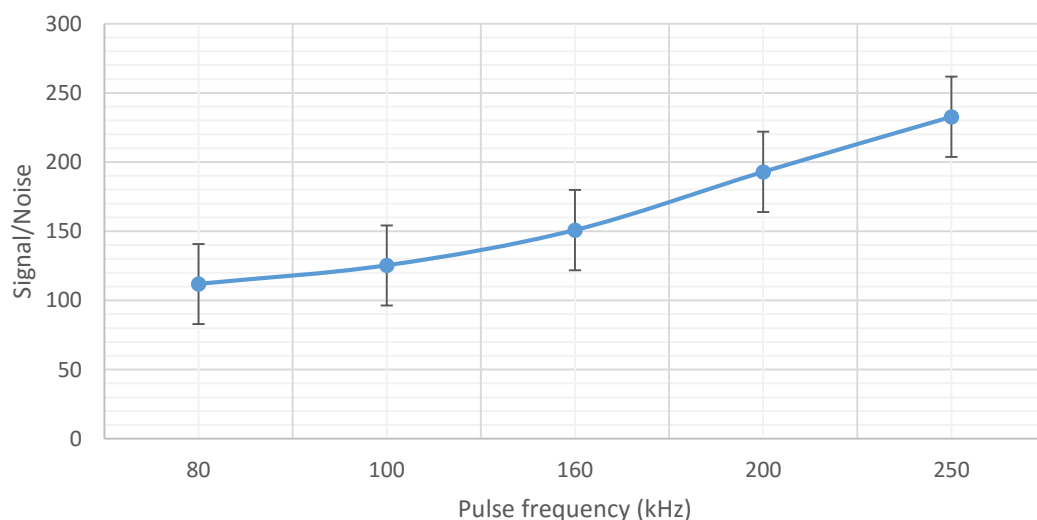


Figure 5-14. Signal-to-noise ratio as a function of repetition rate. APT analyses were performed at 0.5nJ laser beam energy, 0.3% evaporation rate and 55K specimen temperature. The line is a guide for the eye only.

The effect of the repetition rate on the detectable mass range is shown in Figure 5-15. The mass range at 80 kHz and 100 kHz remains at 400amu; it then steadily declines at higher repetition rates, as the sampling windows (ToF) between laser pulses become smaller.

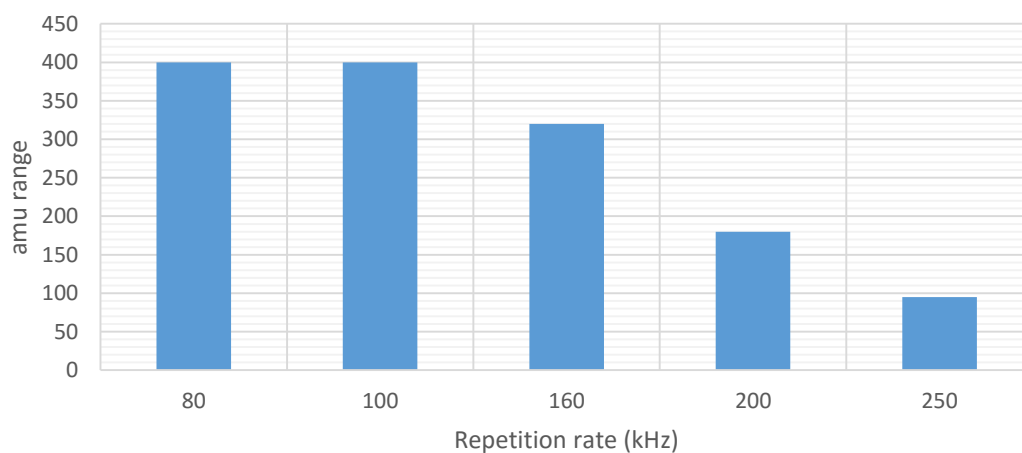


Figure 5-15. Amu range as a function of repetition rate. APT analyses were performed at 0.5nJ laser beam energy, 0.3% evaporation rate and 55K specimen temperature. The line is guide for the eye only.

5.6.2.4 Evaporation rate

Similar to the repetition rate, Figure 5-16 shows that the $\text{Si}^+/\text{Si}^{2+}$ ratio does not change with the evaporation rate. The average $\text{Si}^+/\text{Si}^{2+}$ ratio is about 1.3, which is equivalent to a relative concentration of Si^+ ions of about 57%.

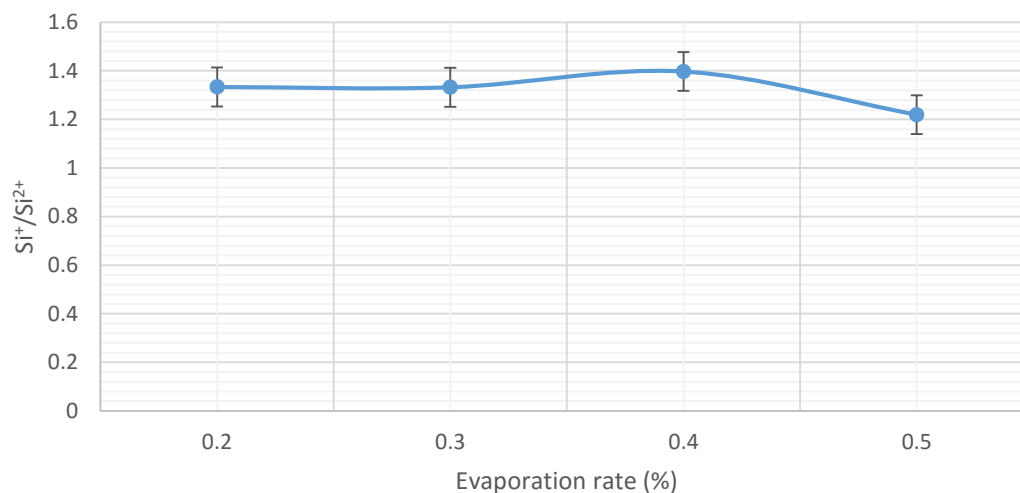


Figure 5-16. $\text{Si}^{2+}/\text{Si}^+$ ratio as a function of evaporation rate. APT analyses were performed at 0.5nJ laser beam energy, 160kHz repetition rate and 55K specimen temperature. The line is a guide for the eye only.

Figure 5-17 shows that the evaporation rate does not have an observable effect on the concentration of Si_2^+ clusters. The average $\text{Si}_2^+/\text{Si}_{\text{total}}$ for all the evaporation rates is 4×10^{-5} .

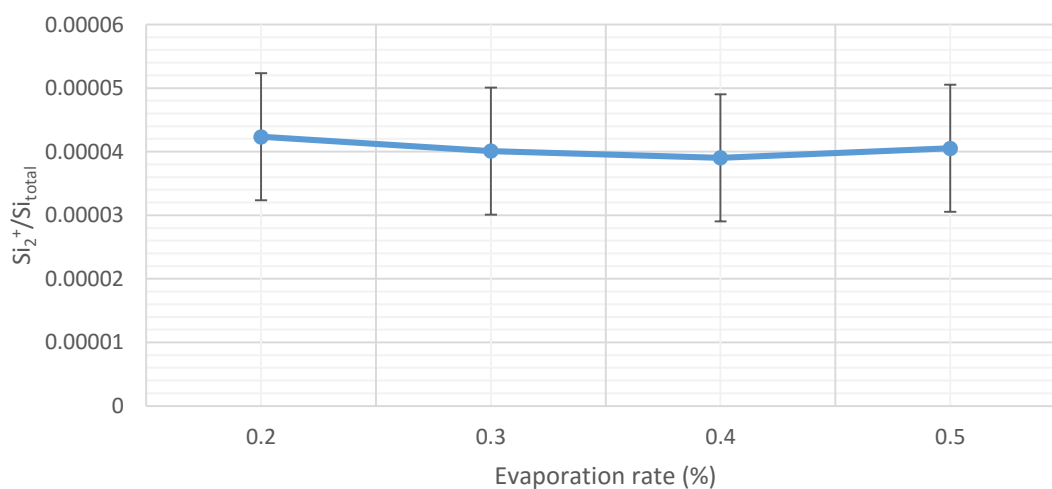


Figure 5-17. $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio as a function of evaporation rate. APT analyses were performed at 0.5nJ laser beam energy, 160kHz repetition rate and 55K specimen temperature. The line is a guide for the eye only.

Figure 5-18 shows that the signal-to-noise ratio decreases with an increasing evaporation rate, with the ratio at the highest evaporation rate (0.5%) being less than half that at the lowest evaporation rate (0.2%).

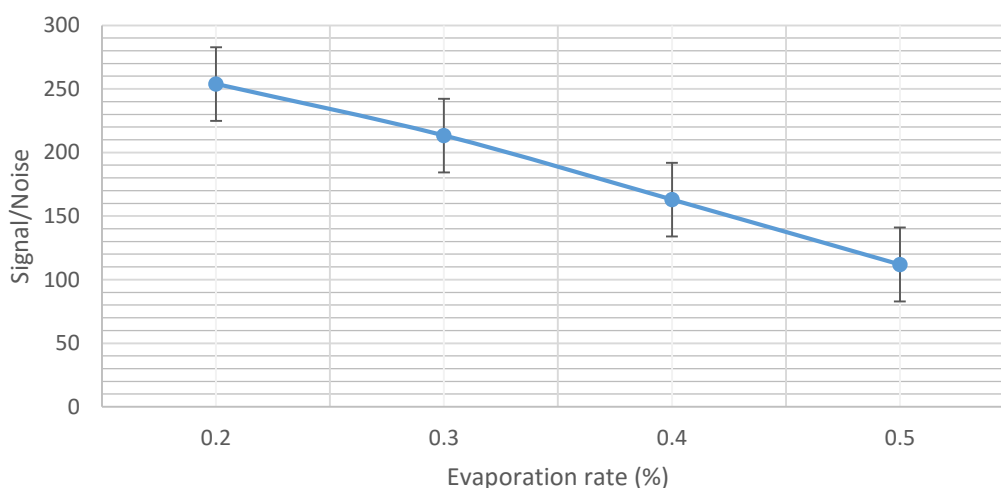


Figure 5-18. Signal-to-noise ratio as a function of evaporation rate. APT analyses were performed at 0.5nJ laser beam energy, 160kHz repetition rate and 55K specimen temperature. The line is a guide for the eye only.

5.6.3 Discussion

5.6.3.1 $\text{Si}^+/\text{Si}^{2+}$ ratio

The $\text{Si}^+/\text{Si}^{2+}$ ratio is affected by the specimen temperature, and particularly by the laser beam energy. This can be explained by the fact that an increase in either of the parameters leads to an increase in the specimen temperature, which allows the surface atoms to field evaporate at a lower DC field. According to the Kingham diagram of Si, a reduction in the electric field strength leads to an increase in the relative concentration of Si^+ ions. Shariq et al.¹⁰ have estimated that an increase in laser beam energy can lead to a much larger temperature rise within the specimen, in comparison to the investigated specimen temperature range. Hence, the impact on $\text{Si}^+/\text{Si}^{2+}$ ratio is more significant.

5.6.3.2 *The signal-to-noise ratio*

The background noise in a mass spectrum of a specimen analysed by laser pulses can originate from: (a) field-evaporation of residual gas within the analysis chamber¹¹; (b) a dark current in the microchannel plates;¹² and (c) unsynchronised field-evaporation of surface atoms by DC field-evaporation.^{13,14} The latter can be used to explain the influence of the laser beam energy and the evaporation rate on the signal-to-noise ratio. At low laser beam energy, field-evaporation of the specimen atoms occurs mainly by DC field-evaporation, and hence the background noise is high. However, as the laser beam energy increases, a larger portion of ions is being evaporated by laser-assisted field excitation, thus resulting in lower background noise.

The opposite is true for the evaporation rate: when the evaporation rate is increased, without changes to other parameters, the DC voltage is elevated. This means an increase in ions being evaporated by DC field-evaporation, and hence higher background noise.

The electric field strength for a particular condition can be estimated using the relative abundance of Si^+ and Si^{2+} ions via the Kingham diagram. The differences in the electric field strength at lowest and highest specimen temperatures was less than 0.5V/nm, which is much lower than in the case of the laser beam energy, where the difference between the two values is about 5.5V/nm. Therefore, the reason as to why the signal-to-noise ratio does not vary with the specimen temperature is because the temperature range employed in the experiments does not induce sufficient changes in the electric field strength to effect the background noise.

The positive dependence of the signal-to-noise ratio on the repetition rate is probably due to the fact that the DC field-evaporation of ions, ionisation of residual gas molecules and noise generated in the channel plate, will all lead to a constant rate of ion counts not associated with the intended laser-assisted field-evaporation process—these are the noise counts. Therefore, increasing the repetition rate of the laser-assisted process will increase the ratio of intended counts to the noise counts.

5.6.3.3 *Cluster and complex formation*

Cluster formation often occurs during APT analysis of semiconductor materials, and is known to increase at higher specimen temperatures and laser beam energies.^{15,16} There are three possible reasons for this: the first reason is that higher temperature allows surface migration to occur more easily, thus allowing chemical species to diffuse to high electric field regions and evaporate as clusters. The second reason is that the electric field can penetrate deeper into the specimen surface at higher temperature, thus exposing sub-surface atoms to a sufficiently high electric field to evaporate together with surface atoms, as clusters. The last reason is that complex ions have the tendency to field dissociate in to individual ions during the flight at lower beam energies. This is due to higher electric field induced by higher DC voltage.

Hydrogen was found in the form of single ions (H^+) as well as clusters containing up to three ions ($2H^+$ and $3H^+$). Hydrogen gas is very common even in ultra-high vacuum systems because it is extremely light and thus cannot be readily removed by the vacuum pump. The gas can adhere to the surface of the specimen and can then be field-evaporated by the laser beam. In most cases, mass peaks associated with H and its clusters are ignored since it is not expected to be in the specimen.

The most common Si complexes in all the mass spectra are SiO and $SiOH_x$. The formation of SiO can be explained by the fact that the specimens were not kept in a high vacuum environment before use, and hence they became oxidised. The Si and O can then field evaporate together, in the form of SiO complexes. SiO can also form complexes with H and its clusters ($2H^+$ and $3H^+$) in the analysis chamber, to form $SiOH_x$. Fortunately, the mass peaks associated with these complexes do not overlap with Fe peaks, and hence do not affect the Fe detection efficiency.

Si_2^+ cluster were observed in the spectra of the specimens evaporated at laser beam energies higher than 0.5nJ. This cluster poses a major problem when attempting to optimise the Fe detection sensitivity because one of the mass peaks associated with the cluster (i.e., $2Si_{28}^+$) overlaps with the Fe_{56}^+ peak, which could potentially lead to artificial Fe concentration.

5.6.4 Conclusion

In conclusion, the $\text{Si}^+/\text{Si}^{2+}$ ratio increases with higher temperature, and most prominently with greater beam energy, while other parameters appear to have little effect. The laser beam energy is the only parameter that affects the $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio, with higher energy resulting in a larger $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio. The signal-to-noise ratio increases with a higher laser beam energy and repetition rate, while it decreases with a higher evaporation rate. The temperature appears to have a negligible effect on the ratio.

A beam energy of 0.5nJ was chosen for subsequent work since higher beam energies will lead to the formation of Si_2^+ clusters while lower beam energies will produce higher background noise and a larger proportion of Si^{2+} ions. The temperature should ideally be as high as possible. However, 55K was chosen instead of 60K due to the long waiting time for the pressure inside the analysis chamber to reach an acceptable level ($<5 \times 10^{-11}$ torr) at higher temperatures. The repetition rate should be as high as possible in order to maximise the signal-to-noise ratio. However, it is also important to consider the mass detection range. A 160 kHz repetition rate was chosen because it has a reasonable ion mass detection range of 0–320amu at 1.2million ions, and a moderate signal-to-noise ratio. The evaporation rate should be kept as low as possible in order to minimise the background noise. However, a modest evaporation rate of 0.3% was chosen due to unacceptably low ion acquisition rates at lower evaporation rates.

It is important to note that the relative concentration of Si being emitted as Si^+ *when the chosen LEAP parameters are applied* is approximately 50%. Although all of the Si ions should ideally be singly-charged, any further increase in the proportion of Si^+ is limited by the formation of Si_2^+ clusters at laser beam energies higher than 0.5nJ. Since the mass peak associated with the cluster overlaps with the $^{56}\text{Fe}^+$ peak, the formation of this cluster must be avoided—otherwise this will lead to artificial Fe concentration in the specimen. The Fe detection sensitivities of five different pre-sharpened specimens analysed using the optimum LEAP parameters were calculated using the

Equation 2-8, with N_{noise} ions being the noise counts between 55.8amu and 56.2amu. The average Fe detection sensitivity was determined to be about 53ppm or 2.65×10^{19} atom/cm³, which is still significantly higher than the concentration of Fe expected in a mc-Si sample (about 10^{14} to 10^{16} atom/cm³ [17]). Still, one would expect the Fe concentration to be considerably higher at the defects.

The optimisation experiments were not performed on the Fe calibration specimens because the same specimen geometry is non-reproducible, since the specimens have to be fabricated manually in the Nvision. In contrast, the pre-sharpened specimens were prepared on a single coupon at the same time, by deep reactive ion etching (the Bosch process). Therefore, one would expect the specimens to have the same geometry. This was confirmed when the specimens were observed in the Nvision before they were inserted into the LEAP. Using specimens with the same geometry should allow general trends regarding the LEAP parameters to be observed.

5.7 Determining Fe detection efficiency

The optimum LEAP parameters established in the previous section were used to analyse Fe calibration specimens to determine the actual Fe detection efficiency that could be obtained.

5.7.1 The fabrication method used to make the Fe calibration specimens

Iron calibration specimens were fabricated using the method described in Section 2.7.4.2. For the first specimens, a carbon strip, 15µm long and 4µm wide, was deposited over the sample surface prior to specimen fabrication, to protect the Fe-implanted region from FIB irradiation in subsequent fabrication stages. The protective layer was later removed in the low-energy ion beam cleaning stage. However, it was not possible to correlate the experimental Fe concentration depth profile with the calculated implanted profile because a portion of the specimen surface was also removed in the cleaning stage, resulting in an incomplete Fe concentration profile towards the surface of the specimen.

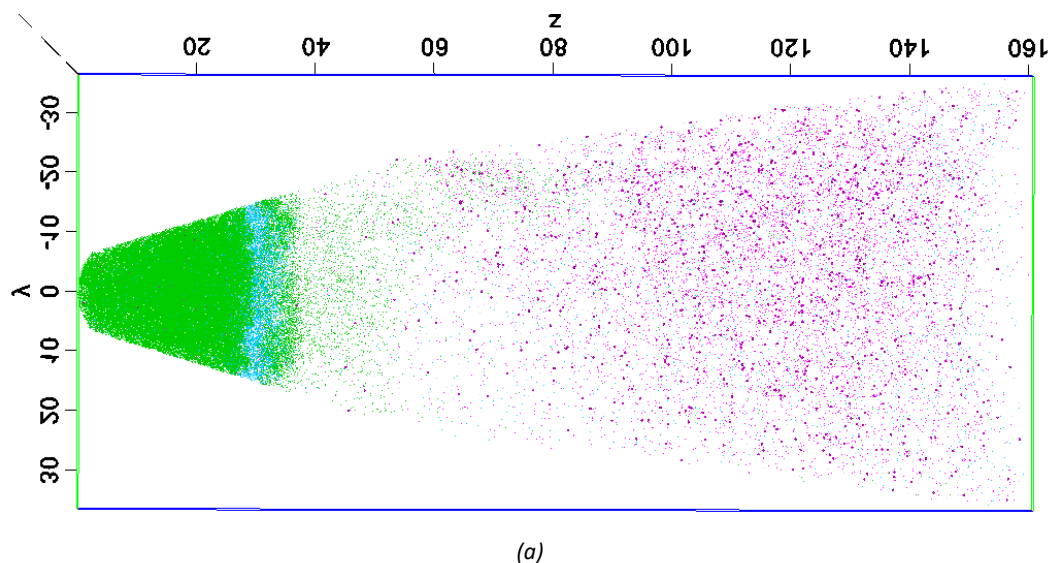
This problem was overcome for later specimens by applying a thin layer of material to the specimen surface to mark the location of the surface in the subsequent APT analysis. Carbon and tungsten were chosen because they were available in the Nvision. APT specimens were fabricated with either carbon or tungsten at the tip, by applying a thicker rectangular layer of the corresponding materials. The length and the width of the layers were kept constant at 15 μ m and 4 μ m, respectively. The deposition time for carbon and tungsten were, respectively, 120sec and 300sec, producing rectangular layers with a thickness of about 165nm. The thickness was reduced to about 50nm and 70nm in the low-energy ion beam cleaning stage.

Four specimens were made for each type of surface-marker. They were analysed in APT using 0.5nJ beam energy, 160 kHz repetition rate and 55K specimen temperature. The evaporation rate was initially 0.3% but was later reduced to 0.1% because early specimens fractured before the Si peaks could be observed in the mass spectra. However, the specimens still failed, despite a very low evaporation rate being employed. The most likely cause for these failures was the weak interface between the specimen surface and the marker layer, which could be due to: (a) damage to the specimen surface caused by gallium implantation; (b) native oxide at the surface of the Si; and (c) instability of the markers, since they contain volatile organic components of the precursor gases. Hence, an alternative material was needed for the surface-marker.

Nickel was deposited onto the Fe-implanted surface of a sc-Si sample using a thermal evaporator at the Begbroke Science Park, Oxford. Note that the sample was not RCA-cleaned prior to the deposition, as this would remove part of the Fe-rich regions that had been oxidised, which would have resulted in an incomplete Fe concentration profile. The thickness of the nickel layer was 80nm. A protective layer was applied over the nickel layer in order to ensure that the surface-marker remained on APT specimens after the fabrication process. Carbon was used for this application because it has a faster deposition rate than tungsten. The protective layer and about 40nm of the nickel layer were removed in the low-energy ion beam cleaning stage.

5.7.2 Calculating the iron detection efficiency

An iron calibration specimen was analysed in the LEAP using the parameters chosen in Section 5.6: i.e., 0.5nJ beam energy, 160 kHz repetition rate, 55K specimen temperature and 0.3% evaporation rate. A three-dimensional reconstruction of the specimen, and its corresponding concentration profile, is shown in Figure 5-19 (a)–(b). The calculated profile was determined by Dr. Nianhua Peng at the University of Surrey, Guildford, UK. The experimental Fe concentration profile was created, with all the complexes being decomposed into their solute atoms: e.g. SiO into Si and O. Note that Ga and H were also excluded from the calculation because the former was introduced during the APT specimen fabrication process, while the latter is the residual gas in the analysis. In other words, both solute atoms are not originally present in the specimen. Unfortunately, the specimen failed before the entire Fe concentration profile could be obtained. However, the Ni and the silicon oxide layers made it possible to align the calculated Fe concentration profile with the experimental profile.



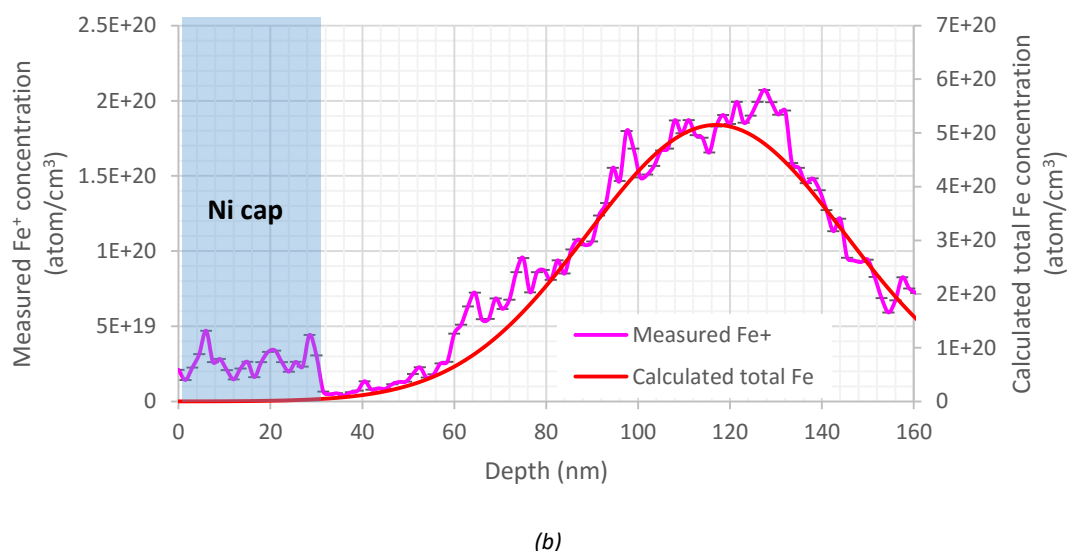


Figure 5-19. (a) A three-dimensional reconstruction of the Fe calibration specimens and (b) the depth concentration profiles of experimental (pink) and calculated Fe (red). The y-axis of the left-hand side shows the experimental Fe profile while the one on the right-hand side shows the calculated Fe concentration profile. The blue region marks the position of the Ni cap.

The iron detection efficiency (%) was determined by:

Equation 5-1
$$Fe_{efficiency} = \frac{Fe_{+peak\ measured}}{Fe_{peak\ calculated}} * 100$$

Where $Fe_{+peak\ measured}$ and $Fe_{peak\ calculated}$ are, respectively, the peak Fe^{+} concentration of the experimental data and the peak value of the total Fe concentration (calculated using TRIM software from the ion implantation parameters). Using the equation, the Fe detection efficiency was determined to be about 35%. Alternatively, the iron detection efficiency can be determined by taking the ratio between the concentrations of the measured Fe^{+} ions and the calculated total Fe concentration when the two curves are scaled to overlap each other as shown in figure 1-19. This approach gives an iron detection efficiency of about 36%, which is similar to the value calculated previously. It is important to note that the calculated iron detection efficiency also take in to account the detection efficiency of the instrument. In other words, out of the total number of Fe detected by the instrument, which has the detection efficiency of about 37%, 35% (or 36%) of these ions can be observed at 56amu as Fe_{56}^{+} .

The iron detection sensitivity of the Fe calibration specimen was calculated using Equation 2-8, with N_{noise} being the noise counts between 54.8 and 55.2amu. The sensitivity was determined to be about 54ppm or 2.70×10^{18} atom/cm³, which is consistent with the average Fe detection sensitivity of pre-sharpened s-Si specimens (53ppm or 2.65×10^{18} atom/cm³).

5.8 Summary

The optimisation of the LEAP parameters to maximise the Fe detection sensitivity was carried out by analysing a matrix of pre-sharpened sc-Si specimens using different parameters. Three variables were used to assist with the selection of the LEAP parameters: $\text{Si}^+/\text{Si}^{2+}$ ratio, $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio and the signal-to-noise ratio. The results show that the first variable increases with higher laser beam energy and with the specimen temperature. The $\text{Si}_2^+/\text{Si}_{\text{total}}$ ratio only increases with higher laser beam energy. The signal-to-noise ratio increases with higher laser beam energy and repetition rate while it decreases with a higher evaporation rate. The optimum parameters were determined to be 0.5nJ laser beam energy, 55K specimen temperature, a 160kHz repetition rate and a 0.3% evaporation rate. Iron calibration specimens were fabricated using the APT specimen fabrication method described in Section 2.7.4.2 to determine the Fe detection sensitivity using the optimised parameters. However, it was necessary to apply a layer of materials over the surface of the specimen in order to mark the location of the surface, as well as to prevent the removal of the Fe-rich region near the specimen surface. Three materials were assessed for the surface-marker: W, C and Ni. The latter was chosen because it was the only material that did not cause the specimen to fracture near, or at the interface between, the marker and the specimen. The Fe detection efficiency using these parameters was determined, using an Fe calibration specimen, to be about 35%. The efficiency is much higher than the expected ratio of detectable Fe^+ (16%) compared to undetectable Fe^{2+} . The iron detection sensitivity of the Fe calibration specimen is about 54ppm or 2.70×10^{18} atom/cm³, which is consistent with the average Fe detection sensitivity of pre-sharpened s-Si specimens (53ppm or 2.65×10^{18} atom/cm³). Although the maximum sensitivity is about two orders of

magnitude higher than the average concentrations found in mc-Si, it is possible that Fe will be detected at or near the extended defects because the Fe concentrations at these locations are expected to be much higher than the average in the bulk.

5.9 References

- ¹ Istratov, A. A., Buonassisi, T., Pickett, M. D., Heuer, M., & Weber, E. R. (2006). Control of metal impurities in “dirty” multicrystalline silicon for solar cells. *Materials Science and Engineering: B*, 134(2), 282-286.
- ² Coletti, G., Kvande, R., Mihailetschi, V. D., Geerligs, L. J., Arnberg, L., & Øvrelid, E. J. (2008). Effect of iron in silicon feedstock on p-and n-type multicrystalline silicon solar cells. *Journal of applied physics*, 104(10), 104913.
- ³ Yoshida, Y., Suzuki, K., Kobayashi, Y., Nagatomo, T., Akiyama, Y., Yukihiro, K., ... & Langouche, G. (2013). 57Fe charge states in MC-Si solar cells under light illumination after GeV-implantation of 57Mn. In *ICAME 2011* (pp. 133-137). Springer Netherlands.
- ⁴ Riepe, S., Reis, I. E., Kwapil, W., Falkenberg, M. A., Schön, J., Behnken, H., ... & Koch, W. (2011). Research on efficiency limiting defects and defect engineering in silicon solar cells-results of the German research cluster SolarFocus. *physica status solidi (c)*, 8(3), 733-738.
- ⁵ Istratov, A. A., Buonassisi, T., McDonald, R. J., Smith, A. R., Schindler, R., Rand, J. A., ... & Weber, E. R. (2003). Metal content of multicrystalline silicon for solar cells and its impact on minority carrier diffusion length. *Journal of applied physics*, 94(10), 6552-6559.
- ⁶ Istratov, A. A., Hieslmair, H., & Weber, E. R. (2000). Iron contamination in silicon technology. *Applied Physics A*, 70(5), 489-534.
- ⁷ Buonassisi, T., Istratov, A. A., Pickett, M. D., Heuer, M., Kalejs, J. P., Hahn, G., ... & Weber, E. R. (2006). Chemical natures and distributions of metal impurities in multicrystalline silicon materials. *Progress in Photovoltaics: Research and Applications*, 14(6), 513-531.
- ⁸ Liu, A., Walter, D., Phang, S. P., & Macdonald, D. (2012). Investigating internal gettering of iron at grain boundaries in multicrystalline silicon via photoluminescence imaging. *Photovoltaics, IEEE Journal of*, 2(4), 479-484.
- ⁹ Kingham, D. R. (1982). The post-ionization of field evaporated ions: A theoretical explanation of multiple charge states. *Surface Science*, 116(2), 273-301.
- ¹⁰ Shariq, A., Mutas, S., Wedderhoff, K., Klein, C., Hortenbach, H., Teichert, S., ... & Gerstl, S. S. A. (2009). Investigations of field-evaporated end forms in voltage-and laser-pulsed atom probe tomography. *Ultramicroscopy*, 109(5), 472-479.
- ¹¹ Miller, M. K., Kelly, T. F., Rajan, K., & Ringer, S. P. (2012). The future of atom probe tomography. *Materials Today*, 15(4), 158-165.
- ¹² Miller, M. K., & Forbes, R. G. (2014). *Atom-Probe Tomography: The Local Electrode Atom Probe*. NY: Springer. 274-275
- ¹³ Thompson, G., Fraser, H., & Miller, M. (2003). Atom Probe Tomography Characterization of Multilayer Films. *Microscopy and Microanalysis*, 9(S02), 574-575.

¹⁴ Li, F., Ohkubo, T., Chen, Y. M., Kodzuka, M., & Hono, K. (2011). Quantitative atom probe analyses of rare-earth-doped ceria by femtosecond pulsed laser. *Ultramicroscopy*, 111(6), 589-594.

¹⁵ Müller, M., Gault, B., Smith, G. D. W., & Grovenor, C. R. M. (2011, November). Accuracy of pulsed laser atom probe tomography for compound semiconductor analysis. In *Journal of Physics: Conference Series* (Vol. 326, No. 1, p. 012031). IOP Publishing.

¹⁶ Müller, M., Smith, G. D. W., Gault, B., & Grovenor, C. M. (2012). Compositional nonuniformities in pulsed laser atom probe tomography analysis of compound semiconductors. *Journal of Applied Physics*, 111(6), 064908.

¹⁷ Istratov, A. A., Buonassisi, T., McDonald, R. J., Smith, A. R., Schindler, R., Rand, J. A., ... & Weber, E. R. (2003). Metal content of multicrystalline silicon for solar cells and its impact on minority carrier diffusion length. *Journal of applied physics*, 94(10), 6552-6559.

6 Defect characterisation in multicrystalline silicon samples

Table of Contents

6.1	Introduction	- 181 -
6.2	Materials	- 181 -
6.3	Methodology	- 181 -
6.3.1	Chemical composition analysis in the LEAP atom probe	- 181 -
6.4	Results	- 188 -
6.4.1	Gold contaminated grain boundary	- 188 -
6.4.2	As-grown grain boundary	- 197 -
6.4.3	Post-phosphorus diffusion gettering grain boundary	- 204 -
6.4.4	Dislocation in post-phosphorus diffusion gettering sample	- 211 -
6.5	Discussion	- 215 -
6.5.1	Gold	- 216 -
6.5.2	Iron	- 217 -
6.5.3	Copper	- 219 -
6.5.4	Nickel	- 219 -
6.5.5	Oxygen	- 221 -
6.5.6	Carbon	- 222 -
6.5.7	Chemical compositions at the grain boundary before and after PDG	- 222 -
6.6	Conclusion	- 223 -
6.7	References	- 223 -

6.1 Introduction

The experiments described in Chapter 3 to Chapter 5 have led to the development of APT specimen fabrication methods and the optimisation of the LEAP parameters to allow the characterisation by APT of individual defects found in mc-Si solar cells whilst maximising the iron detection sensitivity. This chapter describes the experimental work on the characterisation of four defects taken from p-type mc-Si samples subjected to various processing conditions. One of the defects was an isolated dislocation while the others were grain boundaries which also contained dislocations. The characterisation of most of these defects was carried out using three methods: Electron Beam Induced Current (EBIC), Transmission Electron Microscopy (TEM) and APT.

6.2 Materials

The materials used in this work were 5mm by 5mm square mc-Si samples taken from the top section of a directionally solidified ingot. One of the samples was used as-received while others were subjected to two different processes; gold-contamination and phosphorous diffusion gettering (PDG). The sample preparation procedures are described in Section 2.2.

6.3 Methodology

This section describes the methods used to determine chemical composition of various features of interest, namely in the bulk, a dislocation, a grain boundary and a solute cluster.

6.3.1 Chemical composition analysis in the LEAP atom probe

This section describes various methods used to determine the concentration of solute atoms in the bulk of APT specimens, at defects (grain boundaries and dislocations) and in clusters present in the material. They were performed using the IVAS software associated with the instrument. The concentration of a selected solute was calculated by taking in to account solute detected in molecular ions. For example, when determining the concentration of Ni, NiC is decomposed into Ni and C. The method described in Section 2.9.8 was used to determine solute concentrations in term of atom/cm³.

6.3.1.1 Bulk materials

In order to determine the concentration of solute atoms in the bulk of an APT specimen, the defect region of the specimen must first be 'removed' from the three-dimensional reconstruction of the specimen. This was achieved by encapsulating the entire defect in either a cylindrical object (for dislocations) or rectangular object (for grain boundaries). The method is illustrated in Figure 6-1(a)-(b) on a grain boundary and a dislocation, respectively. The bulk composition was determined by excluding the volume inside the object and using all the other detected runs to create a reference dataset for the interior of a single grain.

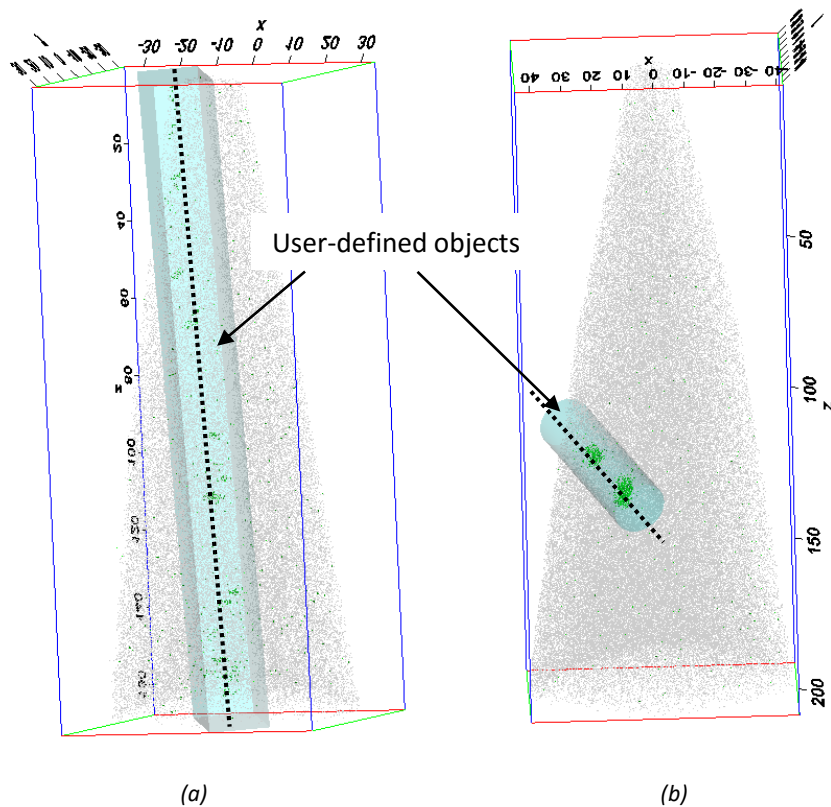


Figure 6-1. Atom maps illustrate the (software) defect encapsulation method for (a) grain boundaries and (b) dislocations, respectively. The black dotted lines indicate the approximate location of the defects. The chemical species displayed in both atom maps are Ni (green) and Si (grey). Note that only 0.9% of the total number of Si atoms are displayed to allow the distribution of Ni atoms to be observed.

6.3.1.2 Grain boundaries

The concentration of a solute atom at the grain boundary was determined by, first, positioning a rectangular object across the defect, as shown in Figure 6-2(a). A concentration profile was then determined across the grain boundary, as illustrated in Figure 6-2(b). For calculation purposes, the y-axis of the figure has been converted from at% to the number of solute atoms by multiplying the former by the total number of atom counts in the sampling bin. The width of the sampling bin and the distance between the sampling planes were one nanometre. Region A in the figure corresponds to solute counts at the grain boundary, N_{gb} , and was determined by the subtracting the total solute counts, i.e., the entire concentration profile, by the background count, i.e., Region B. The background count was determined by taking an average of two sampling ranges on either side of the solute peak concentration (Region C and D). The obtained value was then multiplied by the entire length of the concentration profile to estimate the total background counts. The sum of the two sampling ranges was kept the same at ten nanometers. Furthermore, the relative length of C and D can vary depending on the position of the grain boundary. For example, if the grain boundary is closer to the right then, then C becomes larger than D.

Once N_{gb} had been determined, the concentration of the solute atom at the grain boundary, C_{gb} (atom/cm³), was estimated by:

Equation 6-1
$$C_{gb} = \frac{N_{gb}}{V_{gb}} \times 10^{21}$$

where V_{gb} is the volume of the grain boundary in nm³. Since grain boundary is an interface between two grains, the thickness of the defect was assumed to be one nanometer. By doing so, V_{gb} is equal to the area of the rectangular object that intersects with the grain boundary, A_{gb} , in nm². Therefore, Equation 6-1 can be written as:

Equation 6-2
$$C_{gb} = \frac{N_{gb}}{A_{gb}} \times 10^{21}$$

It should be noted that the assumption of a 1nm grain boundary thickness is somewhat arbitrary. It is used because it is difficult to know over what thickness region impurities at a grain boundary are located and in general they will not be further away from the boundary than 0.5nm. A less ambiguous measure of defect decoration is the number of impurity atoms per unit area (cm^2) and this may be obtained from C_{gb} simply by dividing by 10^7 . In the remainder of the thesis the concentration per unit volume is used because it allows a more direct comparison with bulk concentrations but it should be remembered that this value assumes an arbitrary grain boundary thickness of 1nm.

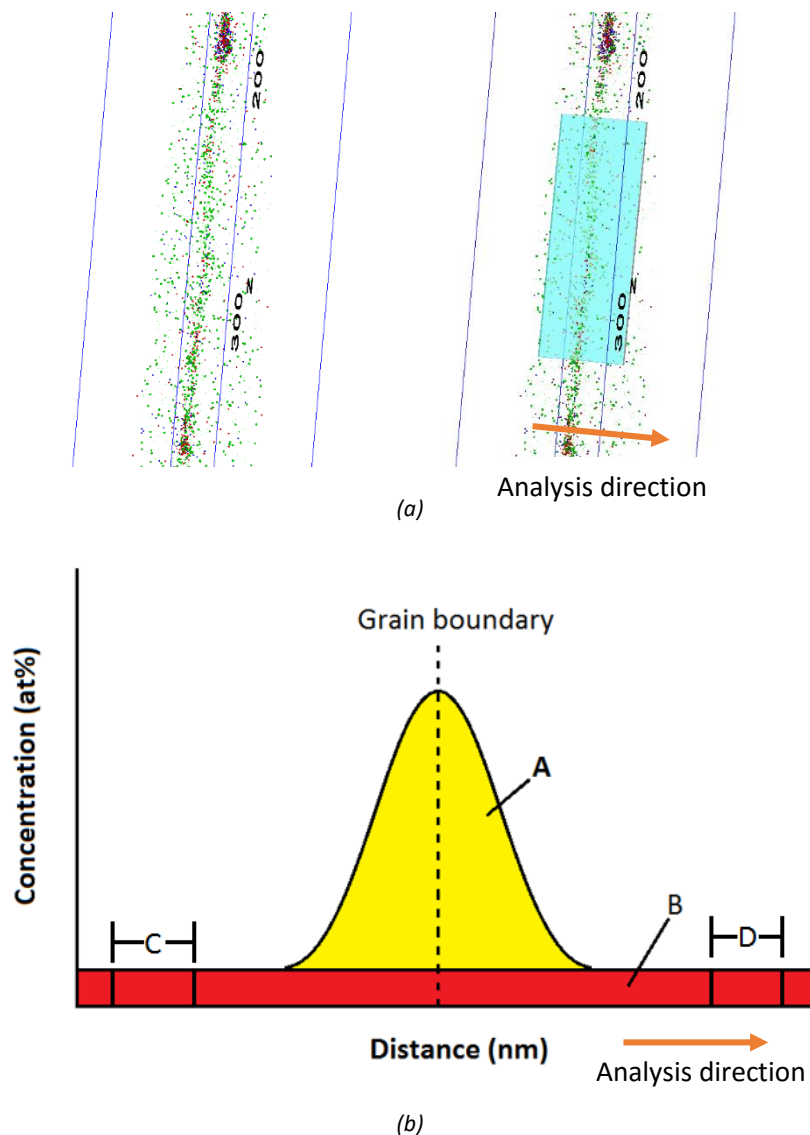


Figure 6-2 (a) Atom maps of the gold-contaminated specimen illustrating the position of the rectangular object relative to the grain boundary; (b) a typical concentration profile determined along the length of the object, in which regions A (yellow) and B (red) corresponds to the concentration of solute atoms segregating to the grain boundary and the background counts, respectively. Region C and D are the two sampling ranges used to estimate the total background counts.

6.3.1.3 Dislocations

Similar to the method used for grain boundaries, the concentration of chemical species at dislocation lines was determined using a cylindrical object. However, each defect was fully encapsulated within the cylinder, and it is important to limit the number of chemical species that lie outside the defect but still within the cylindrical object, particularly silicon, as this will affect the calculation of the defect concentration. This was achieved by creating a two-dimensional contour plot at one end of the cylinder. The plot shows the distribution of selected chemical species on a plane normal to the analysis axis, which in this case is along the length of the cylinder. It is colour coded ranging from red being regions with highest concentration to blue being those of lowest concentration. The shape of cylinder was then adjusted to include the region with high concentration of the selected species. The process is illustrated in Figure 6-3 (a)-(b). The chemical composition was obtained by determining the bulk composition in the cylinder. It should be noted that this will always underestimate the peak concentration at the core of the dislocation and is only indicative of the amount of decoration present. The number of impurity atoms per unit length of a dislocation can be calculated by dividing the total number of impurity atom counts in a cylinder by its length however this data is not included here.

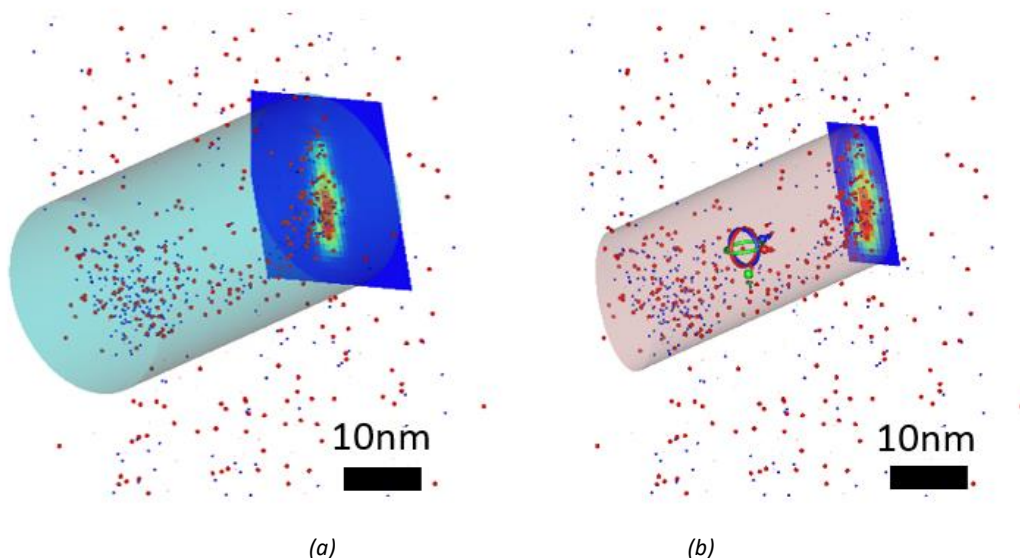


Figure 6-3 (a)-(b). Three-dimensional reconstructions illustrate changes in the cylinder's dimensions (a) before and (b) after they are optimised with the aid of a two-dimensional contour plot. The red and the blue dots are NiC and SiN, respectively.

6.3.1.4 Clusters

Initially, the concentration of solute atoms in a cluster was determined by encapsulating it in an iso-concentration surface, which is a surface that passes through all the points in the reconstruction space where the concentration of selected chemical species/solute atoms is at a predetermined value. The bulk composition in the encapsulated volume was then determined. However, it became apparent that clusters did not have well-defined interfaces with the silicon matrix due to smearing effects caused by the difference in the evaporation field between clusters and the matrix^{1,2,3}, which meant that the calculated chemical composition varied depending on the value assigned to the iso-concentration surface of the cluster.

An alternative approach was to determine the concentration of the cluster by its peak concentration. The peak concentration lies at the centre of the clusters and thus, is expected to be independent of the concentration value of the iso-surface. The method used to obtain the peak concentration was the proximity histogram⁴, or proxigram. Similar to the previous method, the cluster was encapsulated in an iso-concentration surface. The concentration value for the iso-concentration surface was chosen such that only the clusters in the defect were encapsulated. This process will inevitably include artefacts since there will be some regions where a small number of selected solute atoms are sufficiently close together to be considered as a very small cluster. Fortunately, these clusters are extremely small and often contain fewer than 10 of the selected solute atoms. Consequently, a cluster selection criterion was applied in order to distinguish between random from non-random distributions of solute atoms; a cluster needs to contain ten or more solute atoms in order to be defined as a cluster. A similar criterion was also employed in [5] and [6]. Once artificial clusters have been omitted, the peak concentration of each 'real' cluster was determined by generating a one-dimensional concentration profile with respect to that surface, from which the peak concentration was obtained.

This method is demonstrated on a grain boundary containing nickel clusters. Figure 6-4 (a) shows the atom map of the specimen with the clusters being detected by drawing 1.09at% iso-concentration

surfaces. The number of Ni atoms in each cluster was determined, after which those containing less than ten Ni atoms are treated as artefacts. After having applied the cluster selection criterion, a concentration profile of each cluster was created using proxigram, as illustrated in Figure 6-4 (b). Note that the positive and the negative values on the x-axis of the profile indicate the distance in and out of the cluster surface, respectively. The peak Ni concentration in the case is $18.18 \pm 6.71 \text{ at\%}$. This value can also be expressed in the form of atom/cm^3 using the method described in Section 2.9.8. It is important to note that the reliability of this method can be limited by (a) smoothing/delocalisation of the iso-concentration surfaces; (b) the value of the iso-concentration surfaces; and (c) the width of the sampling bins.

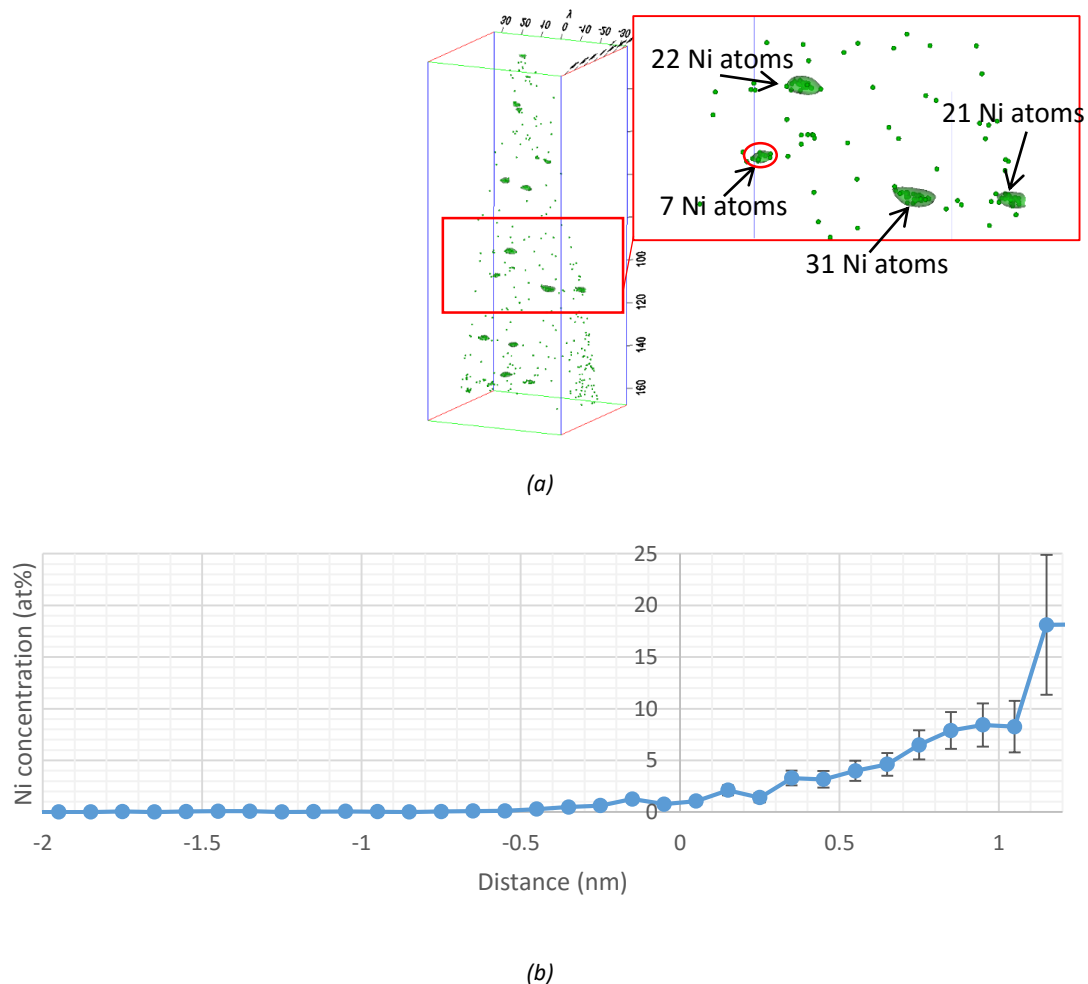


Figure 6-4. (a) An example of cluster analysis by proxigram. Shown here are detected nickel clusters (green) segregating at a grain boundary encapsulated by a 1.09at% iso-concentration surface. Note that only 0.04 atomic% of the total silicon atoms (grey dots) are displayed to allow nickel to be observed. The inset shows four Ni clusters including the number of Ni atoms in each cluster. The Ni cluster in the red circle contains less than ten Ni atoms and thus is considered an artefact. These clusters were taken from a section of the specimen reconstruction marked by the red rectangle. (b) A concentration profile of one of the Ni clusters in (a) showing only Ni profile.

6.3.1.5 *Determining the statistical significance of solute concentrations*

The manual noise cancellation method described in Section 2.9.10 was employed to accurately quantify the number of the selected solute atoms and, in turn, their concentration. However, there were occasions when the number of solute atoms in the mass peak range was slightly higher than that in the noise range, due to statistical variations, resulting in an artificial concentration of the solute atom being calculated. Consequently, a simple method was devised to determine whether the concentration of a solute atom was an actual signal or background noise. This involved comparing the apparent detected concentration of the solute atom with its detection sensitivity. The latter can be calculated using Equation 2-8, with N_{noise} being the background noise counts in the range positioned to the left of each solute mass peak in the mass spectrum. If the two values were comparable or lower, then the concentration of solute atom could be regarded as background noise. By contrast, if the concentration of the solute atom was considerably higher than the detection sensitivity then it could be considered as a real signal.

6.4 Results

6.4.1 Gold contaminated grain boundary

In the early stages of this project, it was difficult to obtain any APT specimens in which defects could be observed. This could have been due either to the specimen fabrication technique not working to produce specimens containing defects or to the fact that the defects were “clean” rendering them invisible in the atom probe. Thus, the purpose of the gold-contaminated mc-Si sample was to produce intentionally decorated defects, which would certainly be visible in the atom probe, so indicating whether the APT fabrication method was working effectively. The electrical activity of such gold decorated defects would not be typical of mc-Si and so was not measured prior to APT specimen fabrication.

6.4.1.1 Transmission Electron Microscope analysis

Figure 6-5 (a) shows a grain boundary running along the centre of the specimen, with the grain to the right of the boundary appearing much darker than that to the left due to diffraction contrast. The grain boundary plane is normal to the imaging plane. Dark lines running at regular intervals along the grain boundary were observed when the specimen was rotated by 15° about the specimen axis, see Figure 6-5 (b). These lines were found to disappear and reappear during the rotation. This behaviour strongly indicates that these lines are in fact dislocations and they are only visible when the diffracting conditions in one or both grains are suitable to satisfy the g.b criterion⁷. Prior to APT analysis, the height of the specimen was reduced by 100nm in the low-energy ion beam cleaning stage in order to eliminate Ga implanted regions at the surface.

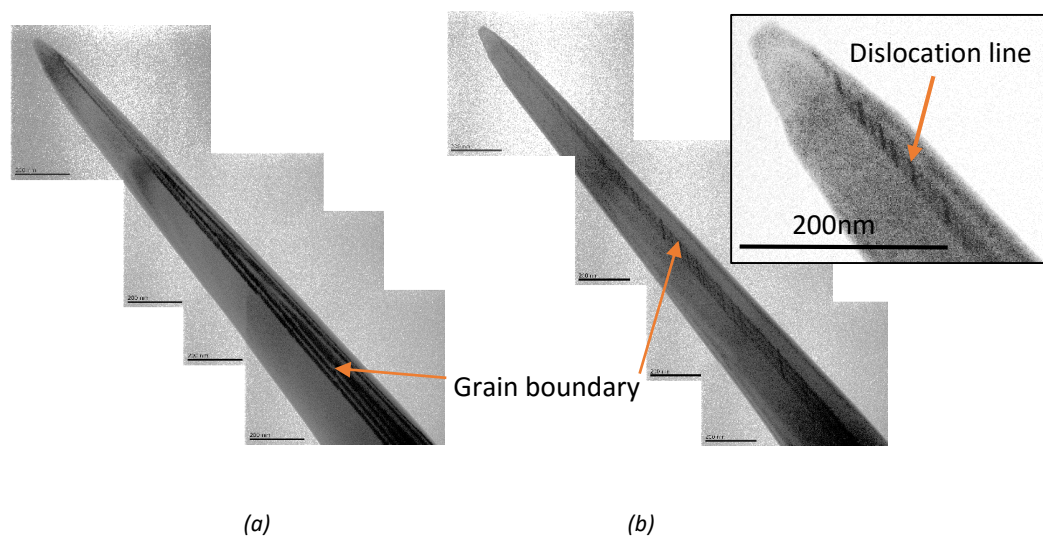
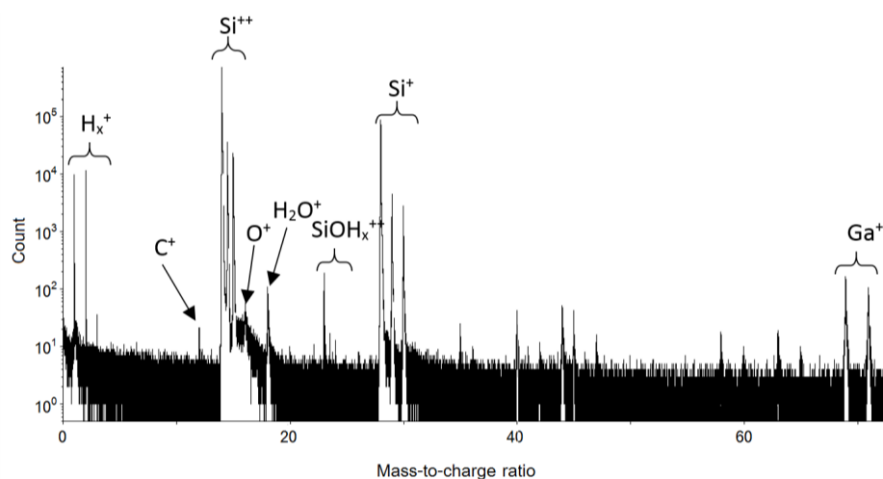


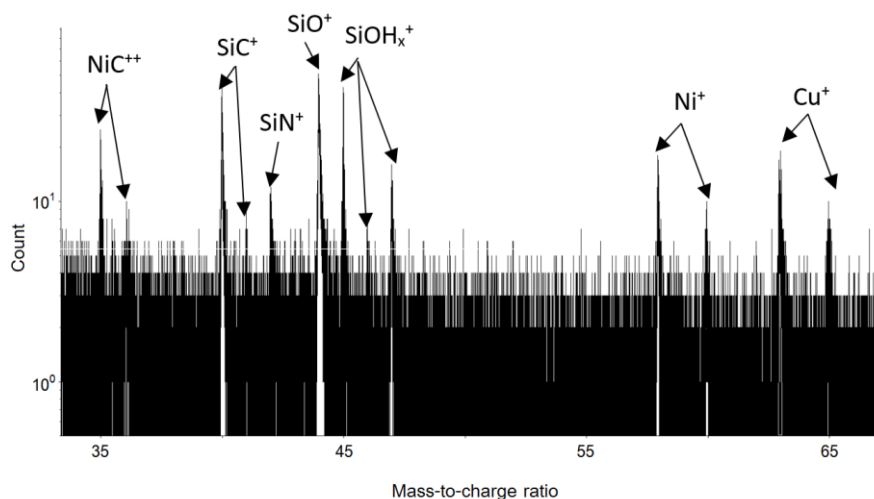
Figure 6-5. BF images of the APT specimen containing a grain boundary at (a) 0° tilt and (b) 15° tilt. Inset (b): a high magnification BF image of the top section of the specimen in (b).

6.4.1.2 Atom Probe Tomography analysis

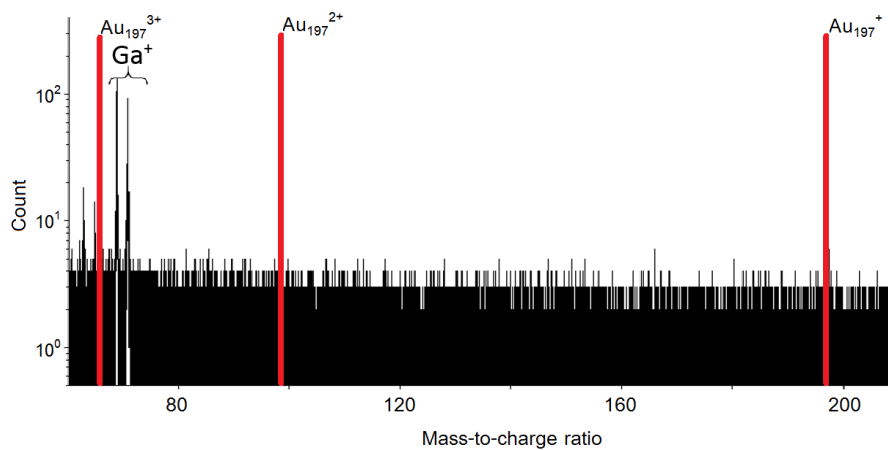
APT analysis of the gold-contaminated specimen produced a dataset containing about 25 million ions. A mass spectrum of the specimen, Figure 6-6, also contains mass peaks associated with Cu and Ni. Figure 6-6 (c) shows the absence of Au peaks in the mass spectrum.



(a)



(b)



(c)

Figure 6-6. Mass spectrums of the gold-contaminated APT specimen containing a grain boundary with mass peaks assigned to chemical species: (a) and (b) show sections of the mass spectrum with amu ranging from 0amu to ~70amu and ~35amu to ~65amu, respectively. (c) shows a section of the mass spectrum (70amu to 200amu) where mass peaks associated with gold are expected. The positions of the mass peaks associated with Au are marked by red lines in the spectrum.

Although Cu peaks were observed in the mass spectrum, Cu was found to segregate to the laser-irradiated side of the specimen, as shown in Figure 6-7. This is likely due to the surface migration of Cu atoms during the analysis. The only notable feature that can be observed in the atom map is the accumulation of Cu at the specimen height of 200-300nm from the tip. Otherwise, no further analysis could be made on this solute.

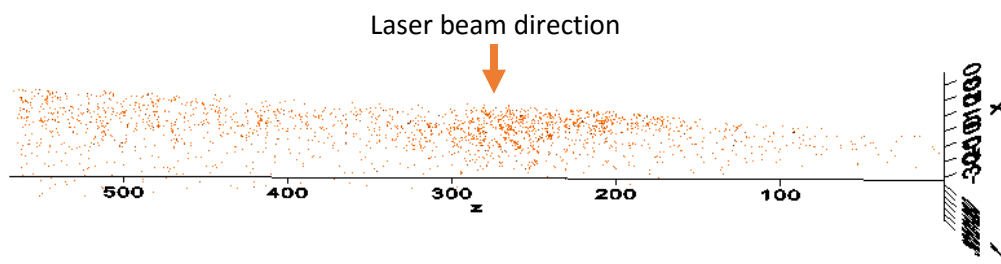


Figure 6-7. A three-dimensional reconstruction shows segregation of Cu to laser-irradiated side of the APT specimen. Still, it can be seen that the Cu concentration is high where the specimen's height is between 200nm and 300nm.

Figure 6-8 (a) and (b) show atom maps for Ni, N and C taken with the grain boundary plane normal and parallel to the imaging plane, respectively. These images indicate that the grain boundary and associated dislocations (see below) are visible in the APT reconstruction even without gold decoration. Two characteristic distributions of chemical species were observed at the grain boundary; (a) the enrichment of C and Ni at the grain boundary with the former detected in the form of SiC; and (b) the segregation of Ni, C, N, and O at three particular regions along the grain boundary. All of these solute atoms with the exception of Ni were only found as complex ions, namely SiN, SiC and SiO. Nickel was found as individual atoms as well as NiC. The TEM image in Figure 6-5 (b) suggests that these regions are dislocations that are present at the grain boundary.

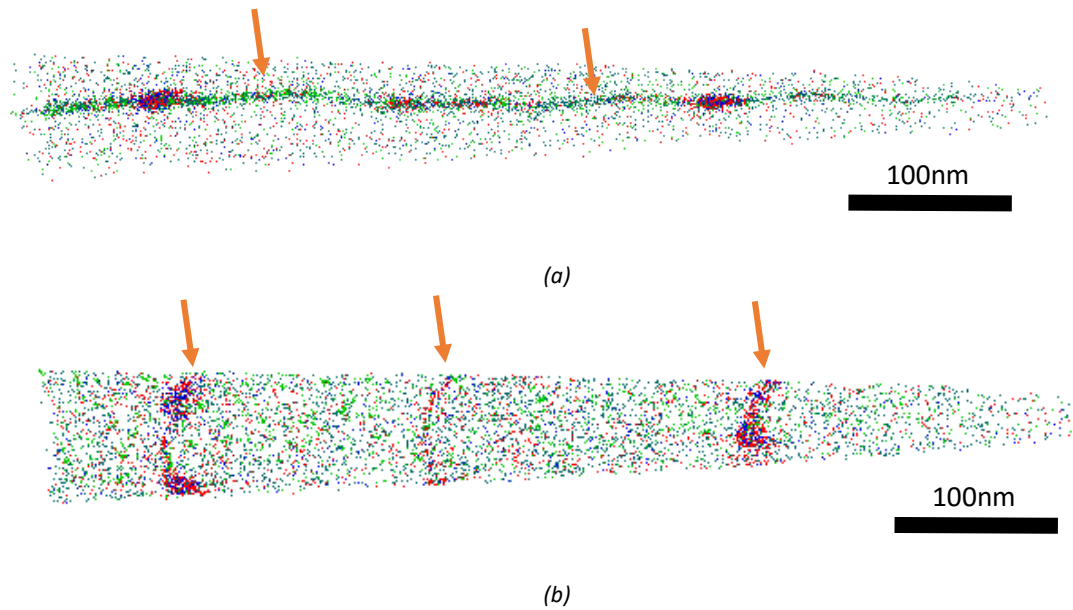


Figure 6-8. Atom maps of the APT specimen containing a grain boundary taken from the gold-contaminated mc-Si sample. The reconstructions were taken at two different angles with the grain boundary plane in (a) and (b) being normal and parallel to the imaging plane, respectively. In addition, (a) shows a uniform distribution of Ni (light green) and SiC (dark green) throughout the grain boundary. The reconstruction in (b) shows segregation of NiC (red) and SiN (blue) to linear features at three distinct locations (marked by orange arrows) on the grain boundary plane.

6.4.1.2.1 Bulk composition

The bulk composition of the gold-contaminated mc-Si specimen is shown in Table 6-1. The dataset contains about 11 million ions. The concentrations of C and Ni were found to be comparable to their detection sensitivities of $3.16 \times 10^{18} \text{ atom/cm}^3$ and $2.13 \times 10^{18} \text{ atom/cm}^3$, respectively. Hence, they were treated as background noise.

Ion type	Concentration ($\times 10^{19} \text{ atom/cm}^3$)
C	n/a
Ni	n/a
Cu	0.37 ± 0.01
O	4.73 ± 0.05

Table 6-1. Bulk composition of the gold-contaminated specimen containing a grain boundary. The concentrations were obtained with the complex ions being decomposed into their associated solute atoms.

6.4.1.2.2 The grain boundary

Two rectangular objects 35nm long by 35nm wide by 90nm high were positioned across different sections of the grain boundary labelled GB(A) and GB(B). The cross-sectional areas of the objects intersecting the grain boundary were the same at 1225nm². Concentration profiles were then determined across these sections of the grain boundary. The profiles of GB(A) and GB(B) are shown in Figure 6-9 (b) and (c), respectively. The average concentrations of C and Ni are $5.22 \pm 0.12 \times 10^{21}$ atom/cm³ and $6.55 \pm 0.12 \times 10^{21}$ atom/cm³, respectively.

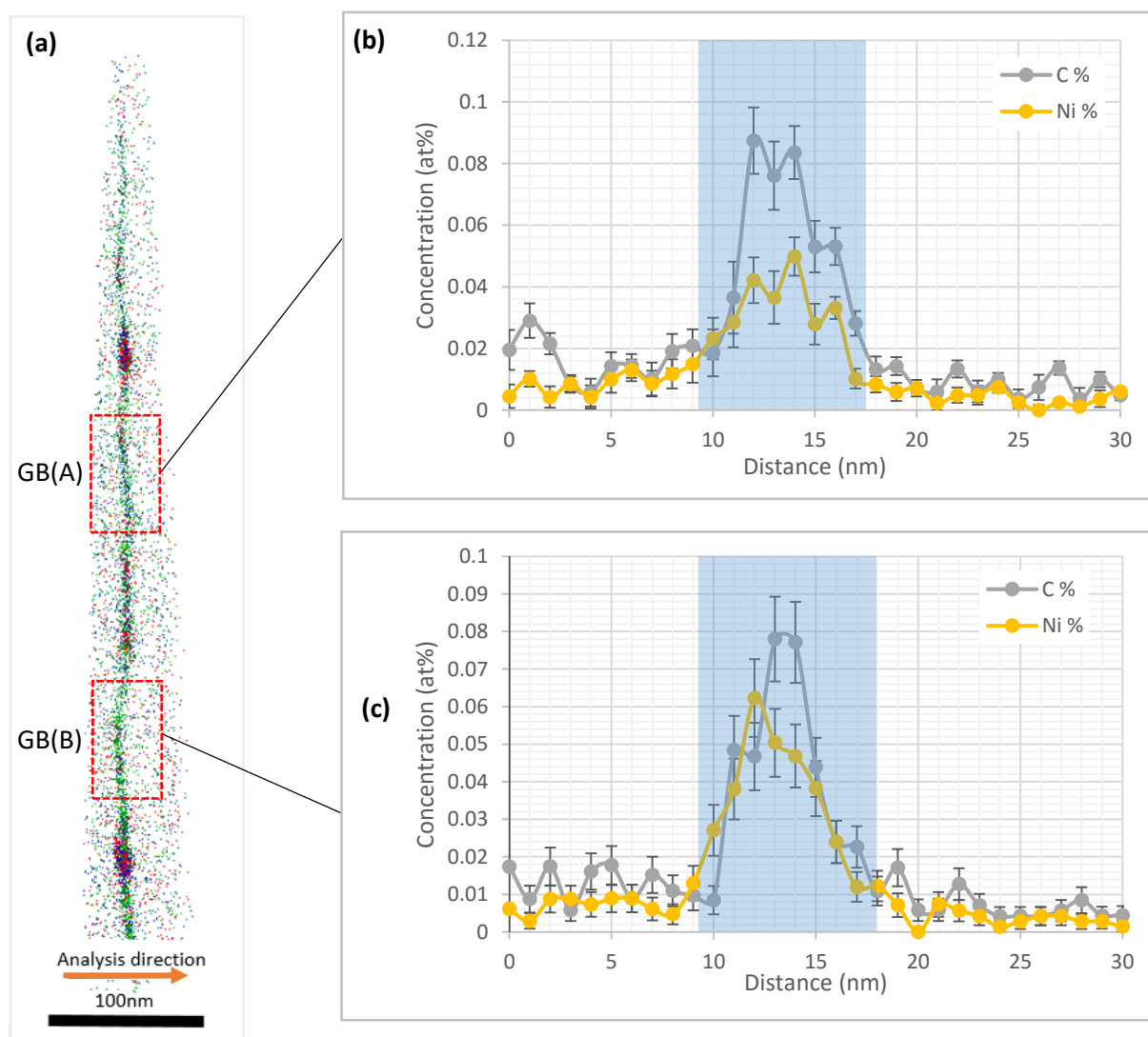


Figure 6-9. (a) An atom map of the APT specimen containing a grain boundary taken from the gold-contaminated mc-Si sample. Chemical composition is identified at two positions along the grain boundary. They are referred to as GB(A) and GB(B). The chemical species displayed in the reconstruction are Ni (light green), SiC (dark green), NiC (red) and SiN (blue). The graphs in (b) and (c) are concentration profiles of C and Ni taken across GB(A) and GB(B), respectively. All the profiles were determined with the complex ions being decomposed into their associated solute atoms. The analysis direction of both profiles is from left to right, as indicated by the orange arrow in (a). The transparent blue rectangles mark the position of the grain boundary. The dotted line in the latter is a guide for the eye only.

6.4.1.2.3 Dislocations

Three dislocations labelled in Figure 6-10(a) as **D1**, **D2** and **D3** were isolated from the rest of the specimen using the method described in Section 6.3.1.3. The chemical species that segregated to the dislocations were C, SiC, Ni, NiC, SiN, O and SiO. The atom maps of the dislocations containing these chemical species are displayed in Figure 6-10 (b)-(d). Clusters were found on **D1** and **D3**, as indicated by the orange arrows. These clusters will be referred to as **C1**, **C2** and **C3**.

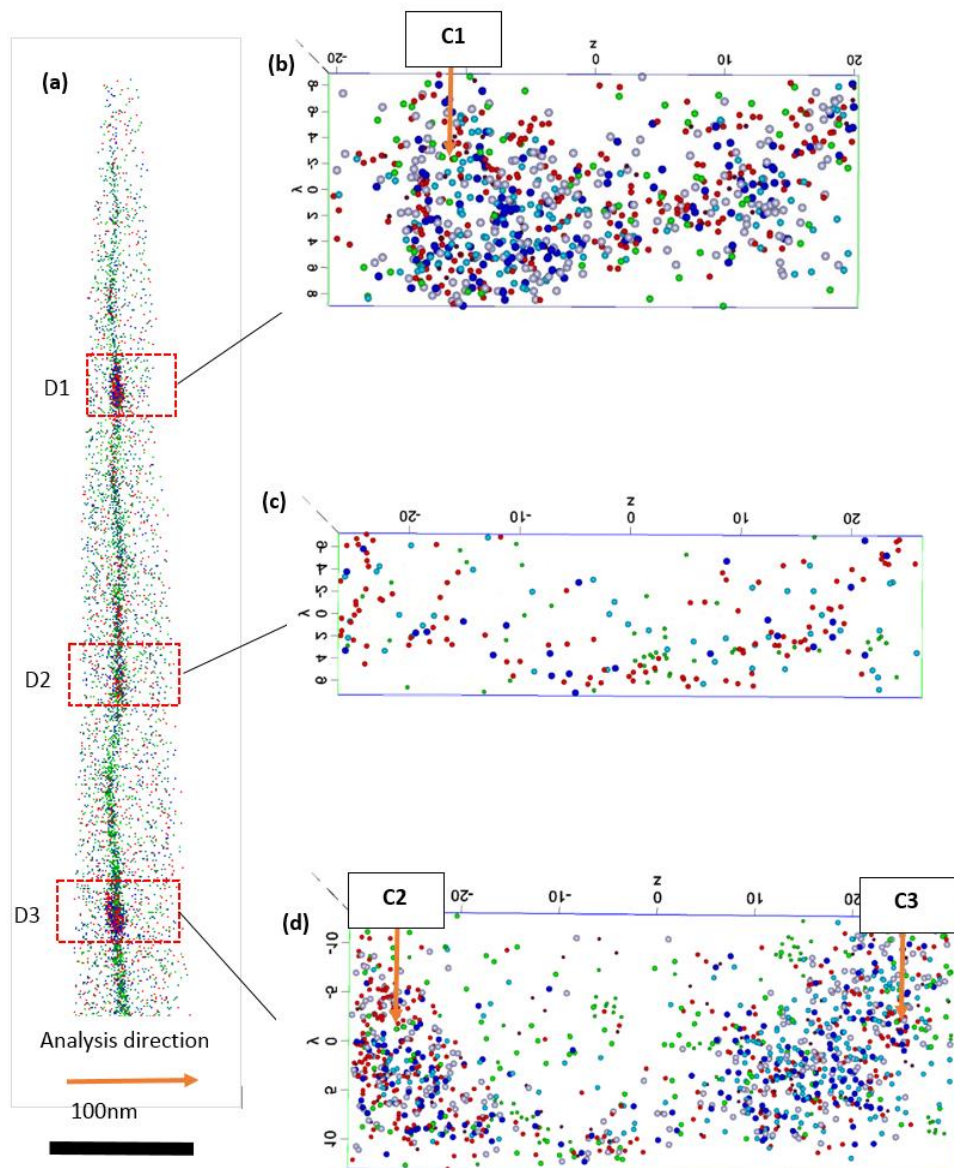
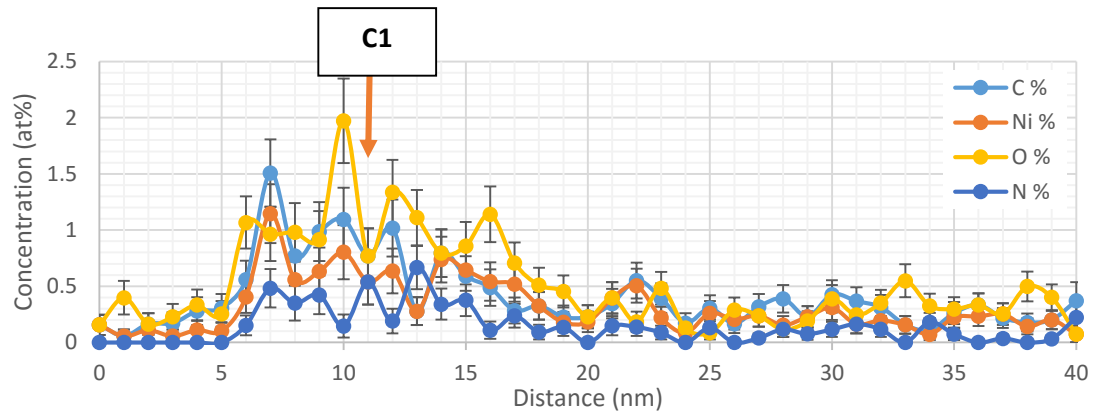
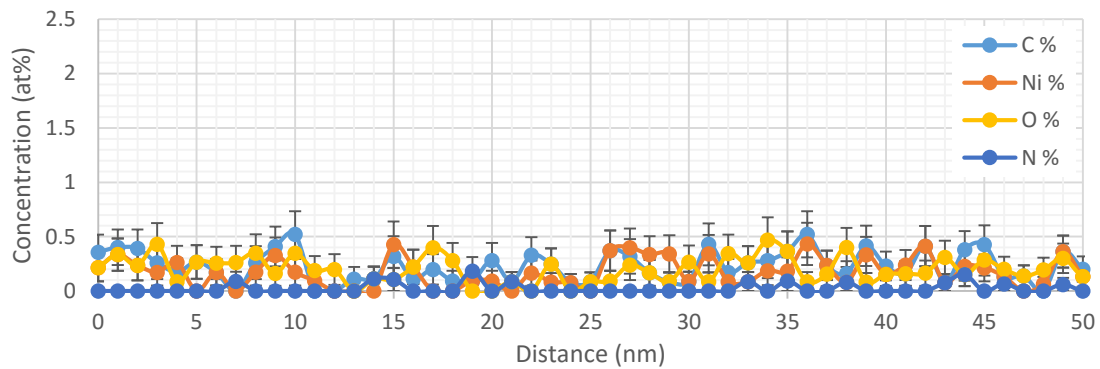


Figure 6-10. (a) An atom map of the APT specimen containing a grain boundary taken from the gold-contaminated mc-Si sample. The chemical species displayed (a) are Ni (light green), SiC (dark green), NiC (red) and SiN (blue). (b)-(d) show solute distribution along the length of D1, D2 and D3, respectively. The atom maps are rotated through 90° relative to (a). The chemical species displayed in (b)-(c) are C (dark purple), SiC (dark green), Ni (light green), NiC (red), SiN (navy blue), O (light blue) and SiO (grey). Orange arrows mark clusters formed on D1 and D3.

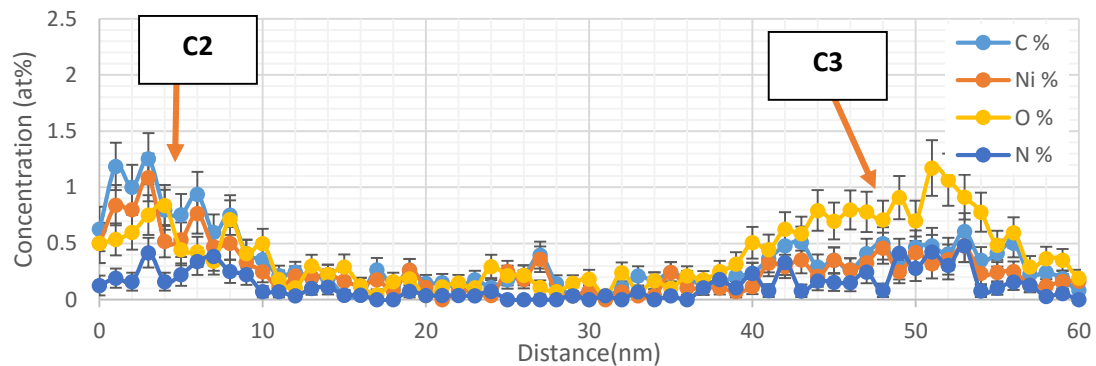
The concentration profiles along the length of **D1** and **D3** (Figure 6-11 (a) and (c)) show that the clusters contain C, Ni, O and N. Similar concentrations of O and N were observed in all the clusters. However, the concentrations of Ni and C are similar in **C1** and **C2** while being significantly lower in **C3**. Figure 6-11(b) shows that there is no significant variation in the concentration of solute atoms along the length of **D2**.



(a)



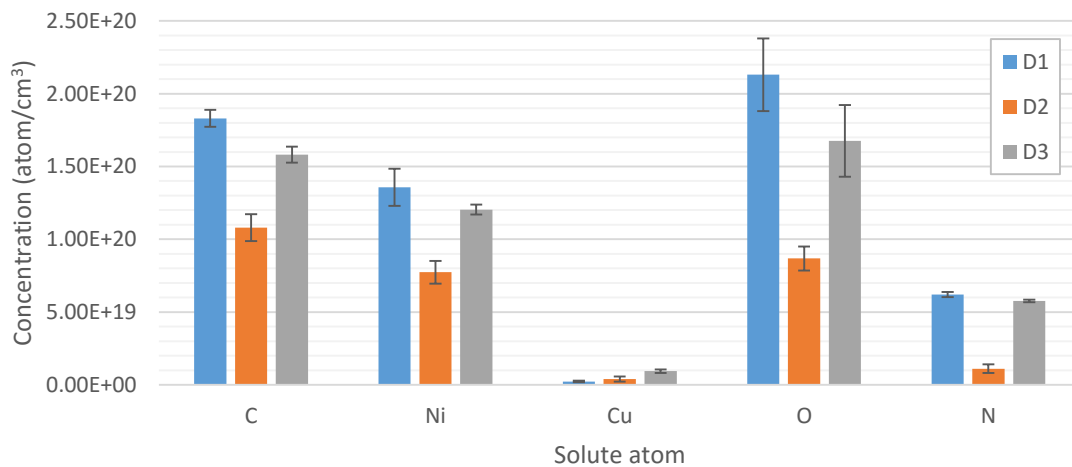
(b)



(c)

Figure 6-11. Concentration profiles along the length of three dislocations: (a) D1, (b) D2 and (c) D3.

Figure 6-12 shows the chemical composition at **D1**, **D2** and **D3** determined from datasets containing 83000 ions, 64000 ions, and 166000 ions, respectively. The concentration of solute atoms with the exception of Cu was found to be significantly higher at **D1** and **D3** than in **D2**. This can be explained by the fact that the impurities segregated to the grain boundary are able to rapidly diffuse along it to the dislocations. Hence, if the dislocations were positioned close together with a larger gap around them in the grain boundary plane, then D1 and D3 would be decorated with those impurities coming from some distance along the plane, whereas D2 would tend to have those just coming from a limited region of the plane between D1 and D3. Unfortunately, it is difficult to find the exact analysed volume of the specimen. This is due partly to the imperfection of the three-dimensional reconstruction and partly to the fact that the height of the specimen was reduced in the low-energy ion beam cleaning stage after the TEM images in Figure 6-5 were taken.



(a)

Ion type	Concentration ($\times 10^{19}$ atom/cm ³)		
	D1	D2	D3
C	18.3±1.85	10.81±0.92	15.82±0.69
Ni	13.57±0.89	7.74±0.78	12.04±0.60
Cu	0.23±0.16	0.40±0.18	0.94±0.17
O	21.30±1.11	8.68±0.83	16.75±0.71
N	6.21±0.60	1.11±0.30	5.77±0.42

(b)

Figure 6-12. (a) A bar chart showing relative concentrations of four chemical species, namely C, Ni, O and N, at three dislocations: **D1**, **D2** and **D3**. The complex ions were decomposed into their associated solute atoms. (b) A table containing the chemical compositions of **D1**, **D2** and **D3**.

6.4.2 As-grown grain boundary

6.4.2.1 *Electron Beam Induced Current analysis*

Figure 6-13 shows the EBIC map of an as-grown mc-Si sample. The red rectangle marks a grain boundary chosen for APT analysis. The recombination strength of the selected grain boundary is about 58% and is intermediate amongst those observed.

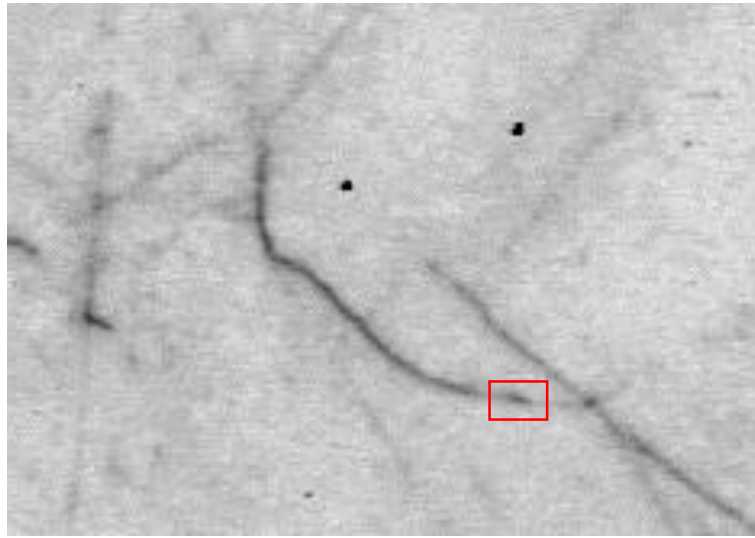


Figure 6-13. EBIC map of the as-grown mc-Si sample. The red rectangle marks the selected grain boundary. The image was taken at 1000x magnification with a beam size of 110nm and accelerating voltage of 20kV.

6.4.2.2 Transmission Electron Microscope analysis

After the fabrication of the APT specimen from the grain boundary, it was subjected to TEM imaging. Figure 6-14 shows the grain boundary with its plane normal to the imaging plane. Similar to other specimens, the adjacent grains have different contrast due to the difference in their crystallographic orientation. Small clusters were also observed along the grain boundary (see inset of Figure 6-14). The grain boundary intersects with the specimen surface at about 500nm below the tip. The excess height was removed from the specimen in a low-energy ion beam cleaning stage.

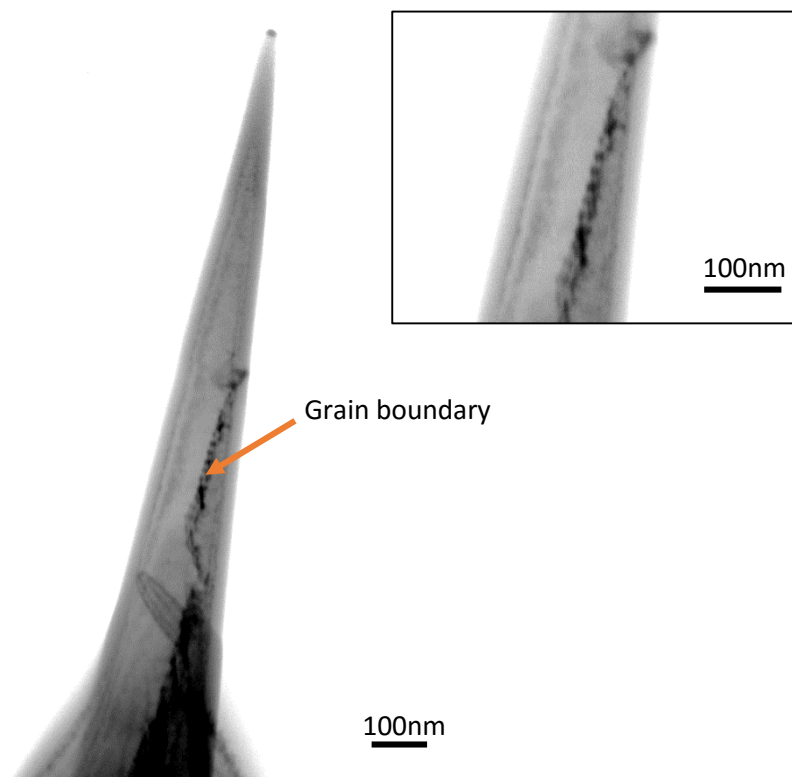
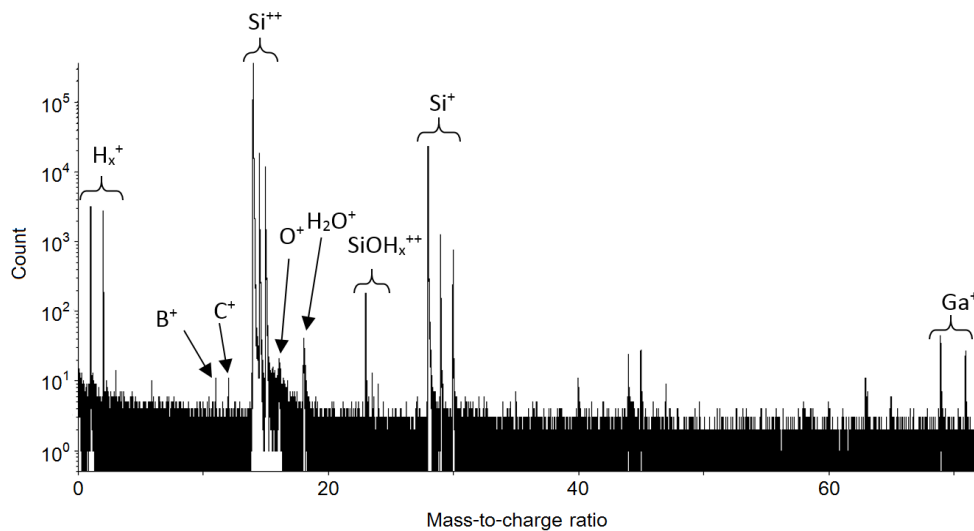


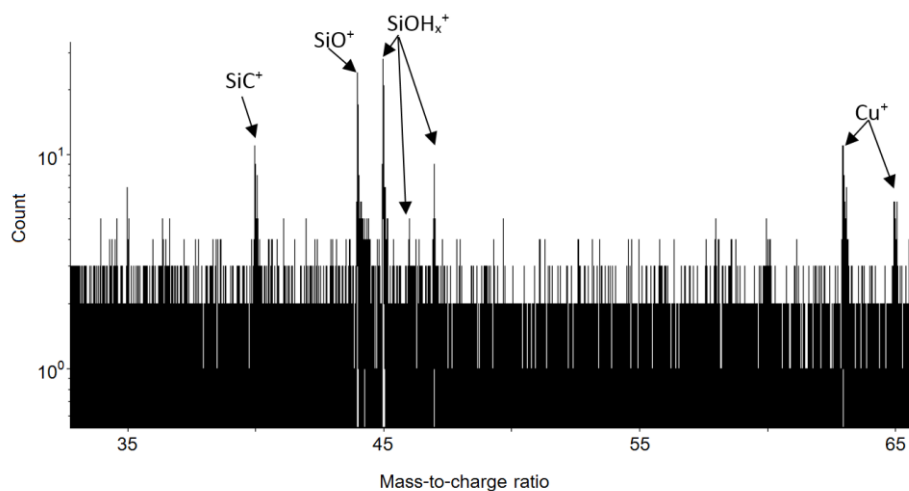
Figure 6-14. A BF image of the APT specimen containing a grain boundary taken from the as-grown mc-Si sample. Inset: a high magnification BF image of the grain boundary.

6.4.2.3 Atom Probe Tomography analysis

Analysis of this specimen in the LEAP produced a dataset containing about 8.4 million ions. The dataset was then used to construct the mass spectrum in Figure 6-15. The spectrum contains similar chemical species to those in the gold-contaminated specimen, with the differences being the absence of Ni peaks and the presence of a B peak at 11amu. Boron is a common dopant in p-type silicon and is therefore expected to be in the specimen.



(a)



(b)

Figure 6-15. The mass spectrum of the as-grown APT specimen containing a grain boundary with mass peaks assigned to chemical species: (a) and (b) show sections of the mass spectrum with amu ranging from 0amu to ~70amu and ~35amu to ~65amu, respectively. (a) shows the whole spectrum while (b) shows a part of the spectrum ranging from 32amu to 68amu.

Visual inspection of the specimen reconstruction (Figure 6-16(a)) reveals the enrichment of Cu at the grain boundary. The solute atoms also form clusters, as indicated by the black arrows in Figure 6-16(b).

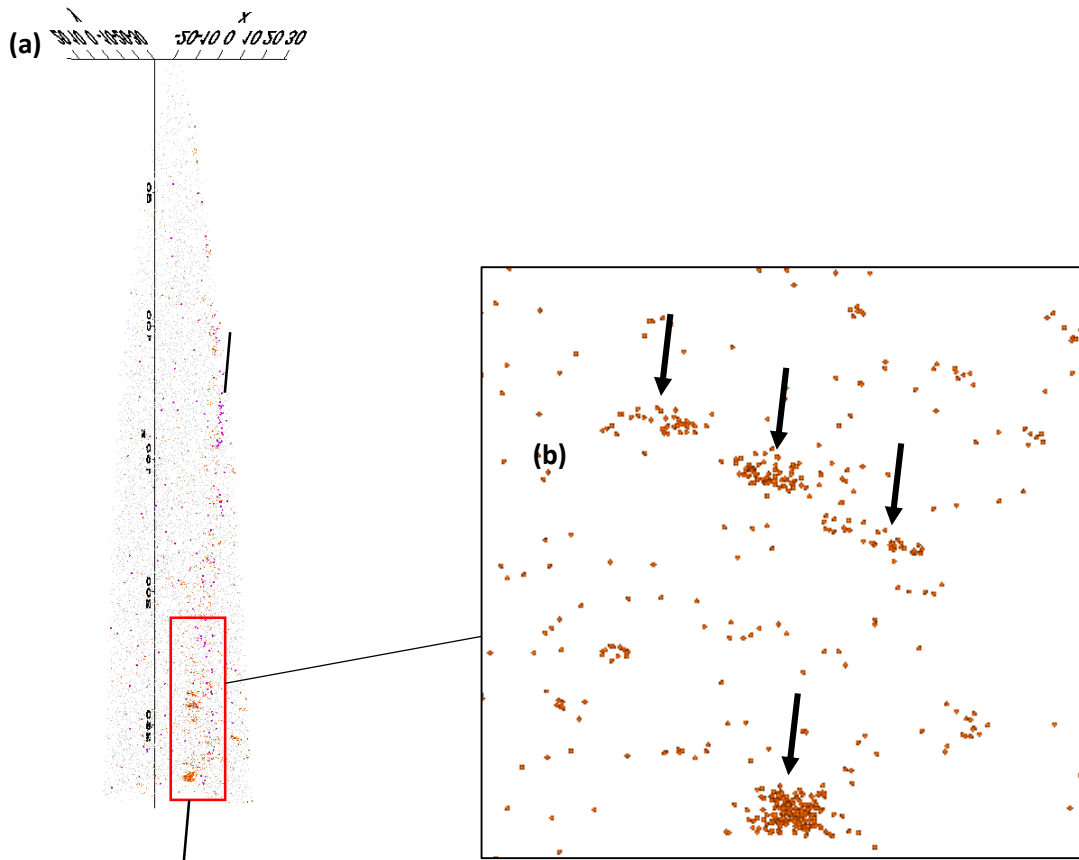


Figure 6-16. (a) An atom map of a grain boundary taken from an as-grown mc-Si sample. The displayed chemical species are Si (grey) and Cu (orange). Only 0.01% of Si are displayed to allow others important features to be observed while outlining the shape of the specimen. (b) An atom map shows signs of Cu clusters at the bottom section of the grain boundary, as indicated by black arrows.

6.4.2.3.1 Bulk composition

The bulk composition of the specimen was determined from a dataset of six million ions. The result in Table 6-2 shows low concentrations of all the solute atoms. The solute atoms made up 0.001at% of the bulk. The concentrations of Cu, B and Ni were found to be comparable to their detection sensitivities of $2.79 \times 10^{18} \text{ atom/cm}^3$, $8.54 \times 10^{17} \text{ atom/cm}^3$ and $3.93 \times 10^{17} \text{ atom/cm}^3$, respectively. Hence, they are considered to be background noise. As mentioned in the APT analysis of the gold-contaminated specimen (Section 6.4.1.2.1), oxygen and carbon are expected to be much lower than the detected values.

<i>Ion type</i>	<i>Concentration ($\times 10^{19} \text{ atom/cm}^3$)</i>
<i>Cu</i>	n/a
<i>O</i>	6.41 $\pm$ 0.08
<i>B</i>	n/a
<i>C</i>	0.31 $\pm$ 0.02
<i>Ni</i>	n/a

Table 6-2. Bulk composition of the as-grown specimen containing a grain boundary. The concentrations were obtained with the complex ions being decomposed into their associated solute atoms.

6.4.2.3.2 The grain boundary

A two-dimensional copper concentration plot taken across the grain boundary in Figure 6-17 (a) shows signs of copper clusters decorating the grain boundary, in agreement with the TEM image in Figure 6-14. However, the atom map taken with the grain boundary plane parallel to the imaging plane, Figure 6-17 (b), indicates that most clusters contain fewer than 10 Cu atoms. Since they do not meet the cluster selection criteria, it can be concluded that the distribution Cu at this section of the grain boundary is homogenous.

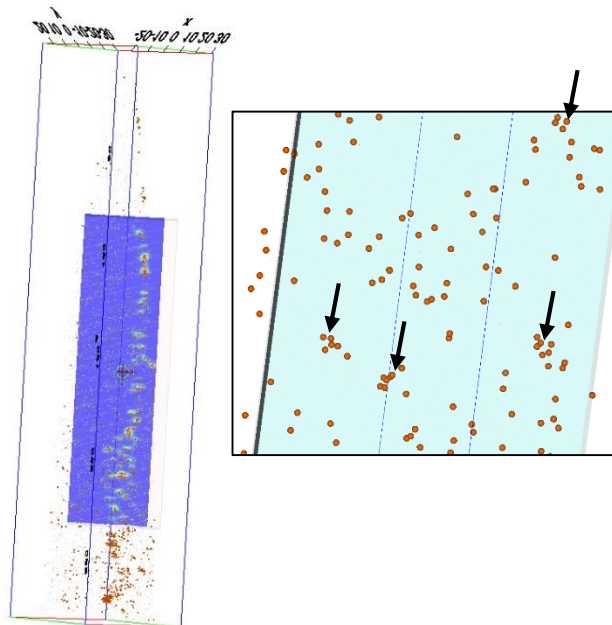


Figure 6-17. An atom map of the as-grown specimen with the grain boundary plane normal to the imaging surface with a two-dimensional concentration plot of Cu (orange) to the grain boundary. Only 0.03% of Si (grey) are displayed to allow others important features to be observed while outlining the shape of the specimen. Inset: an atom map shows the segregation of Cu atoms with the grain boundary plane parallel to the imaging plane. Potential copper clusters are marked by the black arrows.

A concentration profile was determined across a section of the grain boundary defined by the rectangular object positioned as shown Figure 6-18 (a). The dimensions of the object were 40nm long by 30nm wide by 50nm high, and the cross-sectional area of the object intersecting the grain boundary was 1200nm^2 . The concentration profile, Figure 6-18(b), shows that only Cu segregates to the grain boundary at the concentration of about $2.05 \pm 0.02 \times 10^{22} \text{ atom/cm}^3$.

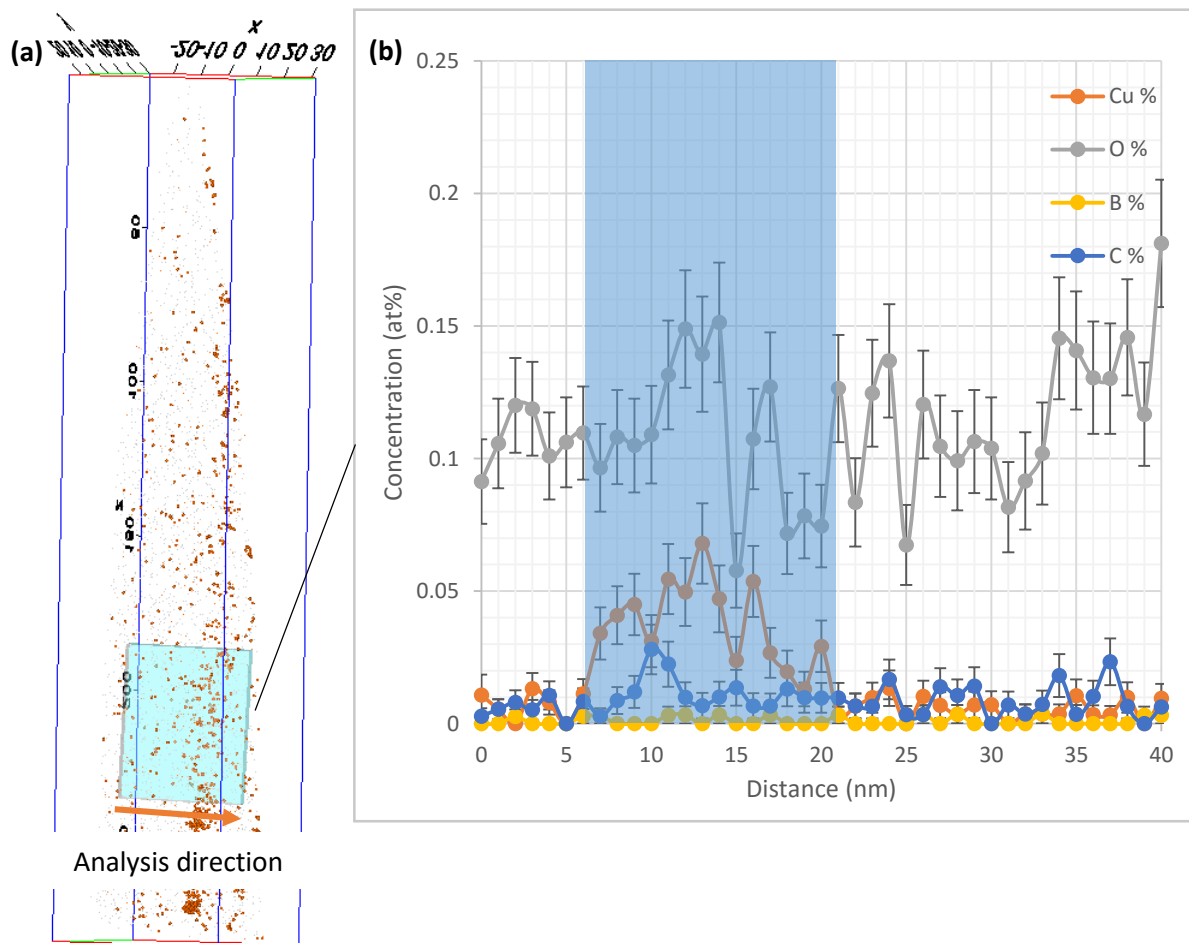


Figure 6-18. (a) An atom map shows the position of a cylindrical project intersecting the grain boundary taken from the as-grown mc-Si sample. The displayed solute atoms are Si(grey) and Cu(orange). Only 0.03% of Si are displayed to allow other important features to be observed while outlining the shape of the specimen. (b) shows the concentration profiles of Cu, O, B, C and Ni. The transparent blue rectangle marks the location of the grain boundary. The profiles were determined along the length of the cylindrical object in (a) with all the complex ions being decomposed into their associated solute atoms.

6.4.2.3.3 Copper clusters

Larger copper clusters observed in the lower section of the grain boundary were encapsulated in iso-concentration surfaces with the Cu concentration threshold set at 1.4at%, as shown in Figure 6-19. The cluster selection criteria, where a cluster must contain more than ten of the selected solute atom, was then applied to the remove artificial clusters, and only four out of 13 possible clusters meet the criteria. These clusters will be referred to as **Cu1-Cu4**. The size of these clusters ranges from 4nm to 9nm. A large variation in the peak Cu concentrations were observed between the clusters, as shown in Table 6-3. The average peak Cu concentration of in these clusters is 26.46at% or 1.32×10^{22} atom/cm³, which is about four orders of magnitude higher than the Cu concentration in the bulk.

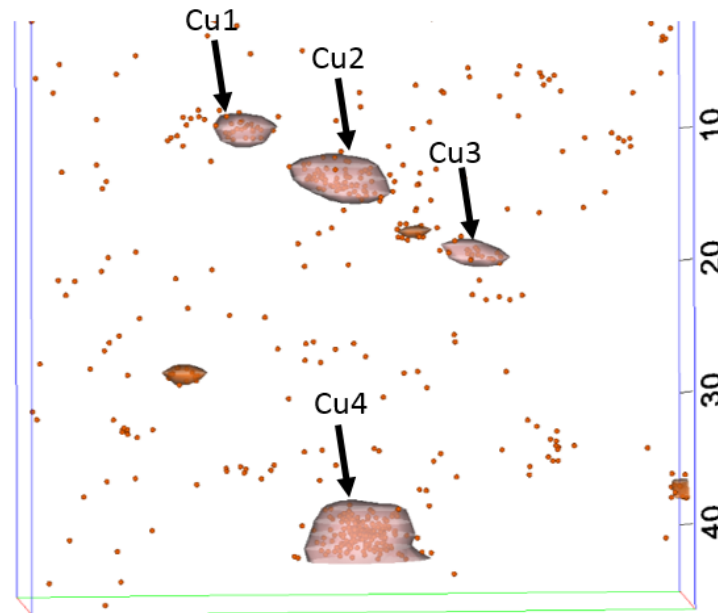


Figure 6-19. An atom map show Cu clusters encapsulated in iso-surface at concentration of 1.4%. The black arrows mark the clusters selected for chemical analysis. These clusters are labeled as Cu1, Cu2, Cu3 and Cu4.

Cluster	Concentration	
	%	$\times 10^{22}$ atom/cm ³
Cu1	22.22 $\pm$ 13.86	1.11 $\pm$ 0.69
Cu2	21.43 $\pm$ 10.97	1.07 $\pm$ 0.55
Cu3	33.33 $\pm$ 15.71	1.67 $\pm$ 0.79
Cu4	28.89 $\pm$ 17.07	1.44 $\pm$ 0.85

Table 6-3. A table shows peak Cu concentrations of the four Cu clusters in Figure 6-19.

6.4.3 Post-phosphorus diffusion gettering grain boundary

6.4.3.1 *Electron Beam Induced Current analysis*

Figure 6-20 is an EBIC map of the post-PDG sample with the red rectangle marking the grain boundary chosen for APT analysis. Since the defect was the same as that characterised in Section 6.4.2, it can be concluded that the recombination activity of the defect had been reduced by PDG from about 58% to about 22%.

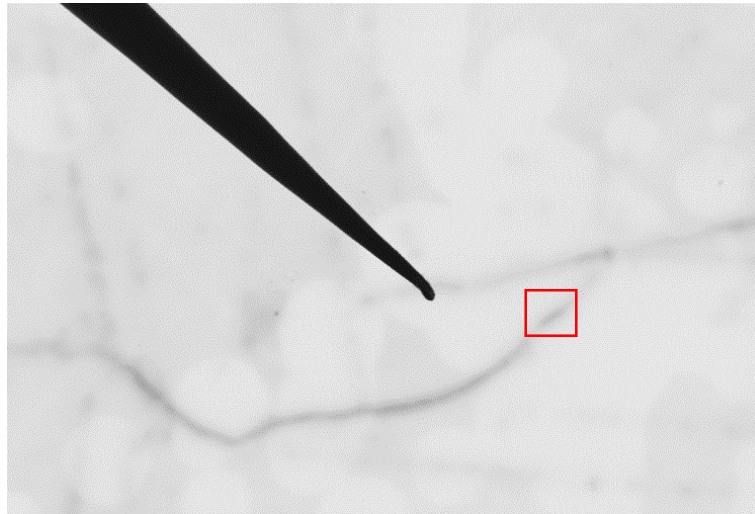


Figure 6-20. An EBIC image of the same selected grain boundary in the post-PDG mc-Si sample. The red rectangle marks the selected grain boundary. The image was taken at 1000x magnification with a beam size of 110nm and accelerating voltage of 20kV.

6.4.3.2 Transmission Electron Microscope analysis

After having fabricated an APT specimen from the grain boundary, the specimen was observed in the TEM. Figure 6-20 shows the grain boundary running the length of the specimen with the grains on either side of the boundary having different crystallographic contrasts. The grain boundary intersects with the specimen at the height of about 250nm below the tip. The excess height was removed from the specimen in the low energy ion beam cleaning stage.

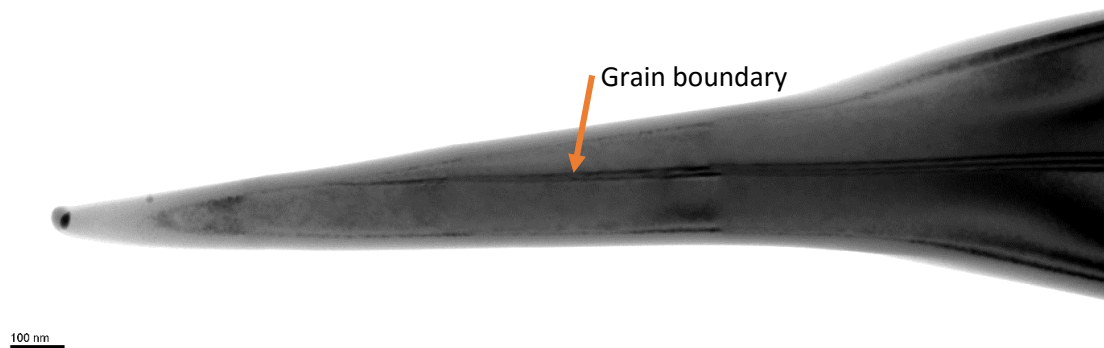
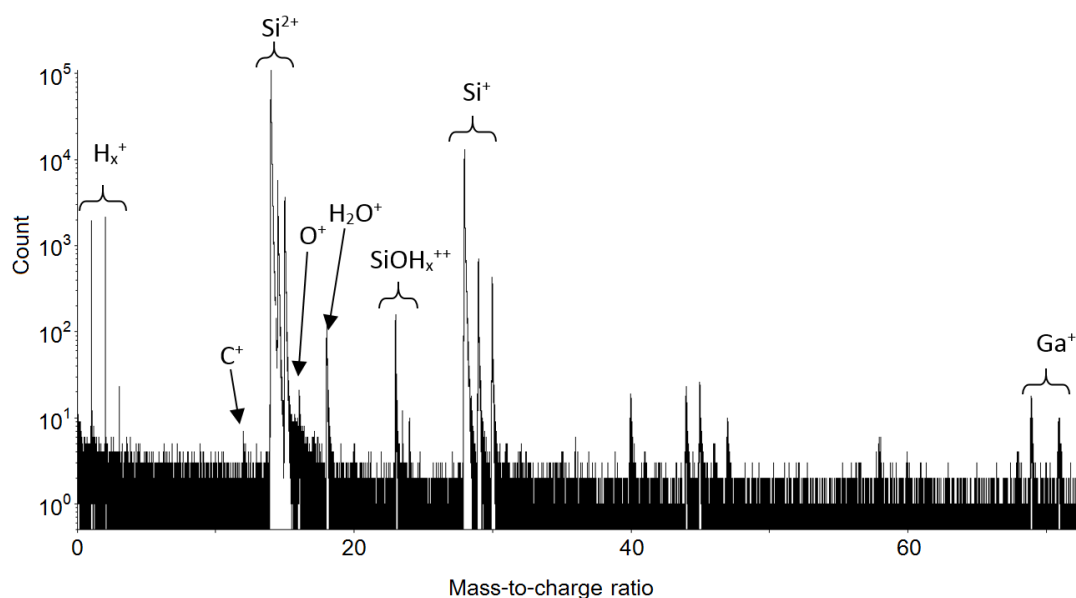


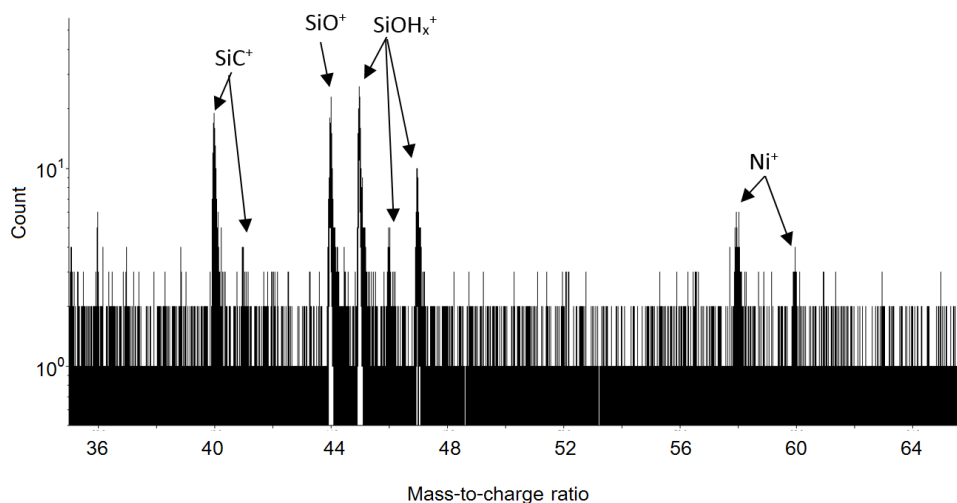
Figure 6-21. A BF image of an APT specimen containing a grain boundary taken from the post-PDG mc-Si sample.

6.4.3.3 Atom Probe Tomography analysis

APT analysis of the specimen generates a dataset with the sample size of about 6.5 million ions. Figure 6-22 shows similar complex ions to those in the as-grown specimen were observed with only differences being the absence of Cu and B peaks and the presence of Ni peaks.



(a)



(b)

Figure 6-22. The mass spectrum of the post-PDG APT specimen containing a grain boundary with mass peaks assigned to chemical species: (a) and (b) show sections of the mass spectrum with amu ranging from 0amu to ~70amu and ~35amu to ~65amu, respectively.

Visual analysis of the specimen reconstruction, Figure 6-23, reveals enrichments of C and Ni at the grain boundary. The former were found mostly as SiC while the latter forms small clusters.

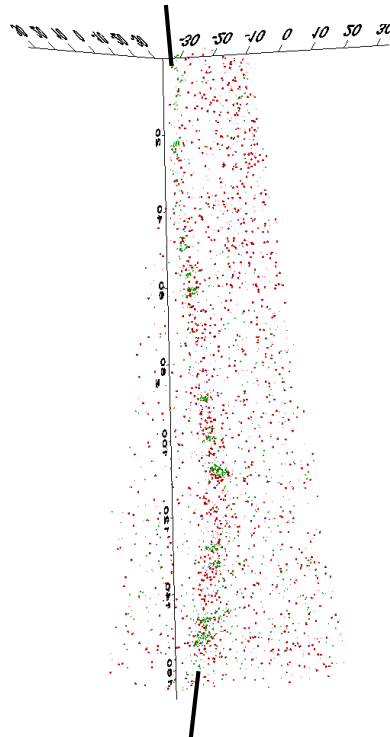


Figure 6-23. An atom map of the grain boundary taken from the PDG mc-Si sample. The displayed chemical species are Ni (green) and SiC (red). The position of the grain boundary is marked by the black lines on either side of the defect.

6.4.3.3.1 Bulk composition

Table 6-4 shows the bulk chemical composition of the specimen that was determined from a dataset containing four million ions. The solute atoms made up 0.003at% of the bulk. The nickel concentration was found to be comparable to its detection sensitivity of 2.07×10^{18} atom/cm³ and hence it was discarded as background noise. Similar to other specimens, the oxygen concentration was higher than the value expected in mc-Si.

<i>Ion type</i>	<i>Concentration ($\times 10^{19}$ atom/cm³)</i>
<i>O</i>	17.46 $\pm$ 0.17
<i>C</i>	1.01 $\pm$ 0.04
<i>Ni</i>	n/a

Table 6-4. The bulk composition of the post-PDG specimen containing a grain boundary. The concentrations were obtained with the complex ions being decomposed into their associated solute atoms.

6.4.3.3.2 The grain boundary

A concentration profile was determined across the grain boundary using a rectangular object, as shown in Figure 6-24 (a). The object was 25nm long by 25nm wide by 30nm high, and the cross-sectional area of the object intersecting the grain boundary was 625nm². It was positioned such that the Ni clusters were not included in the sampling volume. The concentration profiles, Figure 6-24 (b), shows enrichment of only C at the grain boundary with the concentration of $6.67 \pm 0.26 \times 10^{21} \text{ atom/cm}^3$.

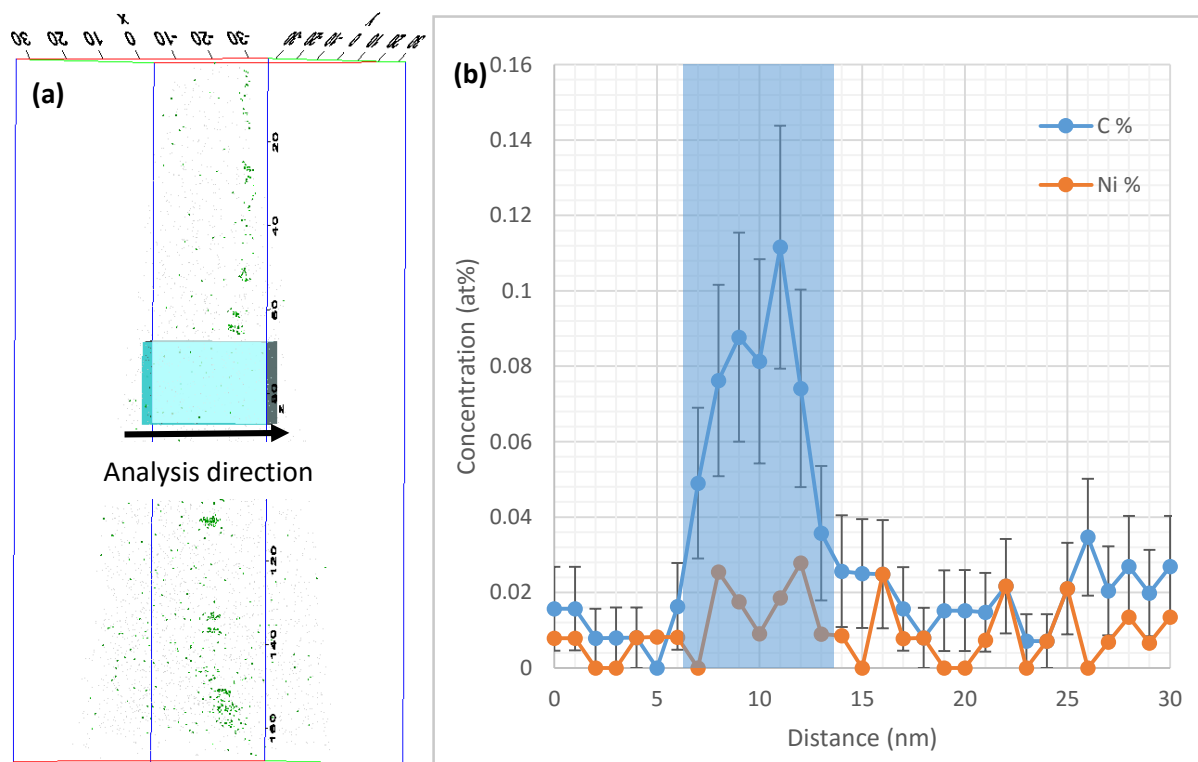


Figure 6-24. (a) An atom map shows the position of a cylindrical project intersecting the grain boundary taken from the post-PDG mc-Si sample. The displayed chemical species are Ni(green) and SiC(red). Only 0.01% of Si are displayed to allow others important features to be observed while outlining the shape of the specimen. (b) The concentration profiles of C and Ni. The transparent blue rectangle marks the location of the grain boundary. The profile was determined along the length of the rectangular object in (a) with all the complex ions being decomposed into their associated solute atoms.

6.4.3.3.3 Ni clusters

Ni clusters were encapsulated in iso-concentration surfaces with the threshold Ni concentration of 1.25at%. After the application of the cluster selection criteria, 8 out of 18 clusters were discarded as artificial. The remaining clusters are labelled as shown in Figure 6-25. The majority of the clusters have a platelet-like structure with a diameter between 4nm and 7nm and a thickness between 2nm to 4nm.

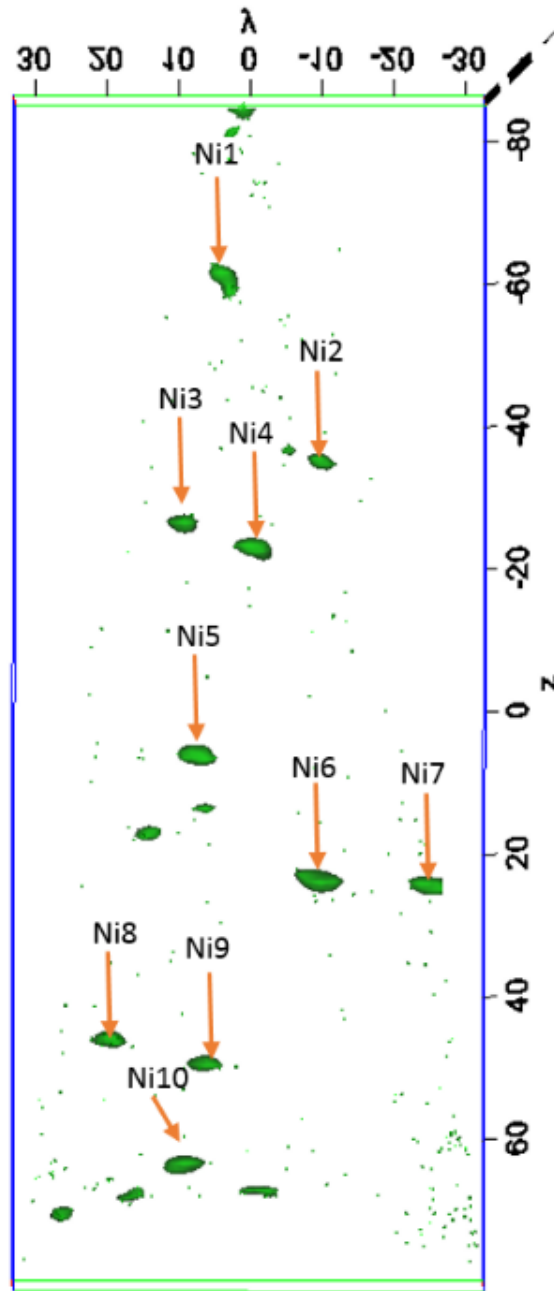


Figure 6-25. An atom map shows Ni clusters decorating the grain boundary of the post-PDG specimen. The clusters are encapsulated in iso-concentration surfaces with the concentration threshold of 1.25at%. Those with labels are clusters containing more than 10 Ni atoms.

The nickel peak concentrations of the clusters are shown in Table 6-5. The concentrations were found to vary between $5 \times 10^{21} \text{ atom/cm}^3$ and $1.7 \times 10^{22} \text{ atom/cm}^3$, with an average concentration of 22.89at% or $1.14 \times 10^{22} \text{ atom/cm}^3$.

<i>Cluster</i>	<i>Concentration</i>	
	at%	$\times 10^{21} \text{ atom/cm}^3$
<i>Ni1</i>	26.67±11.42	13.33±5.71
<i>Ni2</i>	11.76±5.53	5.88±2.76
<i>Ni3</i>	37.5±17.12	18.75±8.56
<i>Ni4</i>	11.54±7.41	5.74±3.69
<i>Ni5</i>	25.00±12.50	12.50±6.25
<i>Ni6</i>	18.18±6.71	9.09±3.36
<i>Ni7</i>	20.00±10.33	10.00±5.16
<i>Ni8</i>	33.33±27.22	16.67±13.61
<i>Ni9</i>	11.63±4.89	5.81±2.44
<i>Ni10</i>	33.33±27.22	16.67±13.61

Table 6-5. A table shows peak Ni concentrations of four clusters marked in Figure 6-25.

6.4.4 Dislocation in post-phosphorus diffusion gettering sample

6.4.4.1 *Electron Beam Induced Current analysis*

An EBIC map of a region of the post-PDG mc-Si sample is shown in Figure 6-26 (a). A dislocation marked by the red rectangle was chosen for APT analysis. The recombination strength of the defect is about 4%. Unfortunately, the recombination activity of the defect was not measured prior to PDG due to the difficulty of the fabrication method.

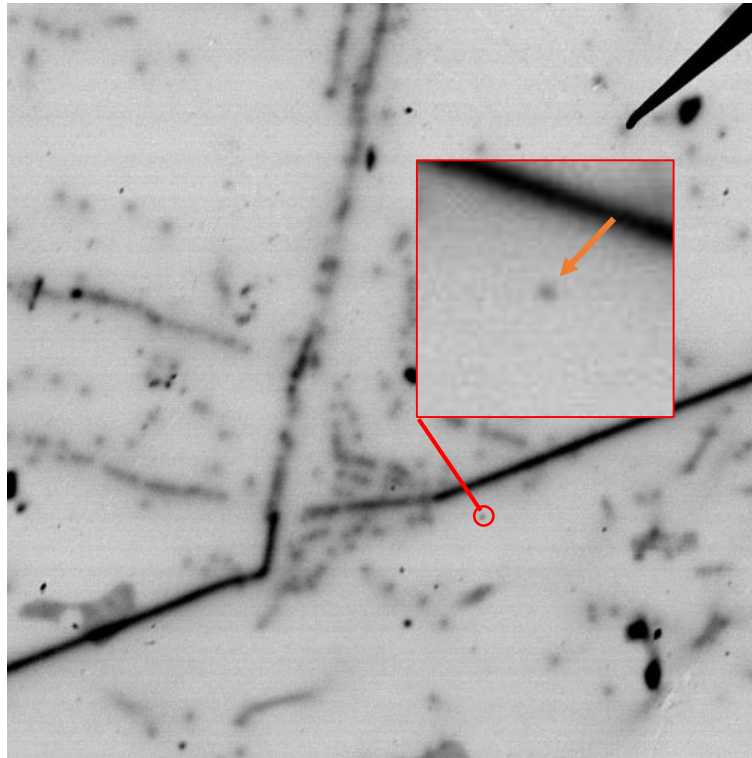


Figure 6-26. An EBIC map of the PDG mc-Si sample. The image was taken at 1000x magnification with a beam size of 110nm and accelerating voltage of 20kV. Inset: a high magnification EBIC image shows the selected dislocation marked by the orange arrow.

6.4.4.2 Transmission Electron Microscope analysis

TEM analysis was performed on the APT specimen containing the dislocation. Figure 6-27 shows a dark dot with the bright region on one side and dark region on the side, which is similar to TEM images of edge dislocations in [8] and [9]. Unfortunately, it was extremely difficult to characterise the dislocation because the specimen only contains a small section of the defect (about 100-150nm). The dislocation intersects with the specimen at a specimen height about 350nm from the tip. The height of the specimen was reduced by about 250nm in the low-energy ion beam cleaning stage in order to reduce the amount of time taken for the APT analysis to reach the dislocation while allowing sufficient time to perform the laser and local electrode alignment procedures.

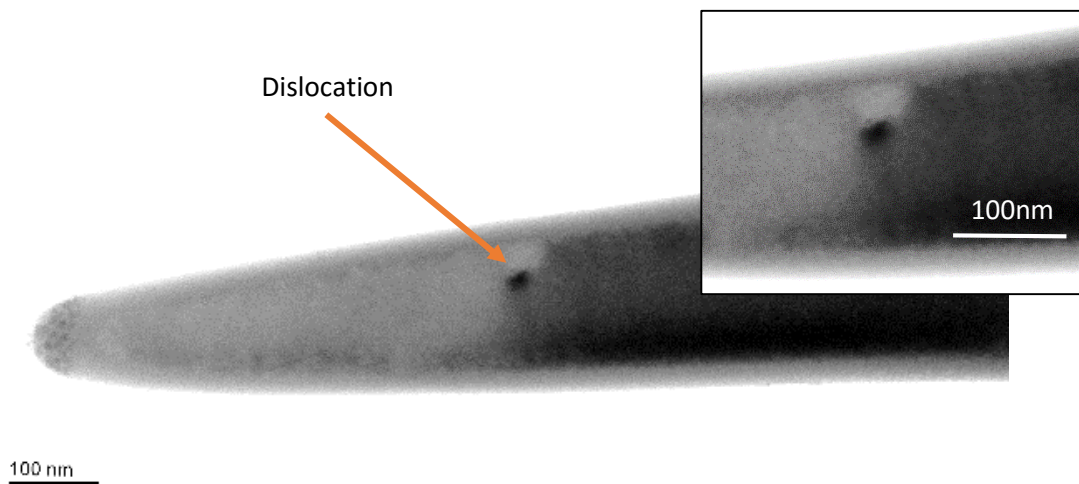
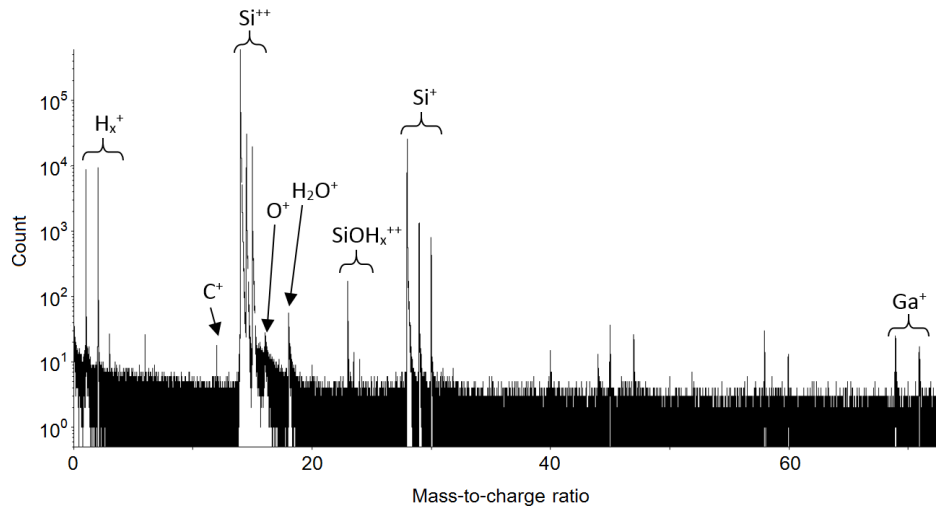


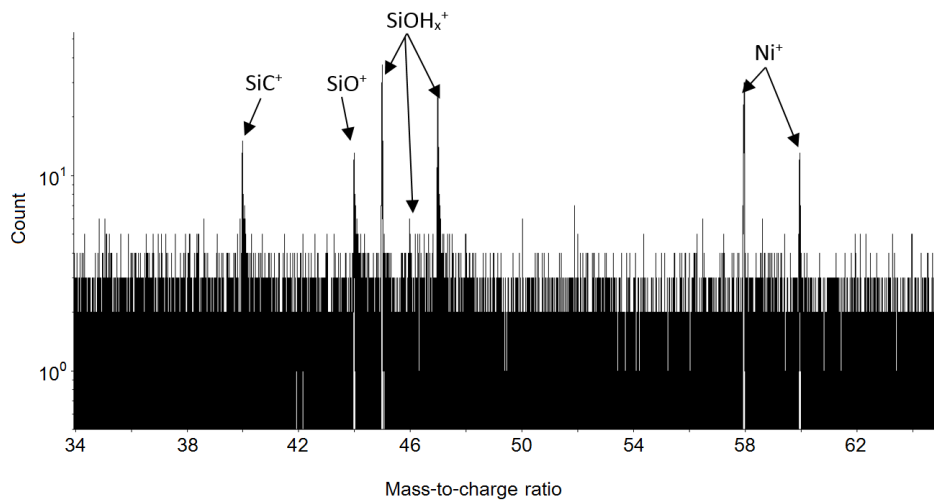
Figure 6-27. A BF TEM image of the atom probe specimen containing the selected dislocation. Inset: a high magnification BF image of the dislocation shows the characteristic bright and dark regions above and below the defect, respectively.

6.4.4.3 Atom Probe Tomography analysis

APT analysis of the specimen produced a dataset containing about 12 million atoms. The mass spectrum of the specimen, Figure 6-28 (a), contains similar chemical species to those found in the post-PDG specimen. The only metal impurity in the specimen was Ni, as shown in Figure 6-28 (b).



(a)



(b)

Figure 6-28. The mass spectrum of the post-PDG APT specimen containing an isolated dislocation with mass peaks assigned to chemical species: (a) and (b) show sections of the mass spectrum with amu ranging from 0amu to ~70amu and ~35amu to ~65amu, respectively.

The reconstruction in Figure 6-29 shows the segregation of Ni at two particular locations along the dislocation.

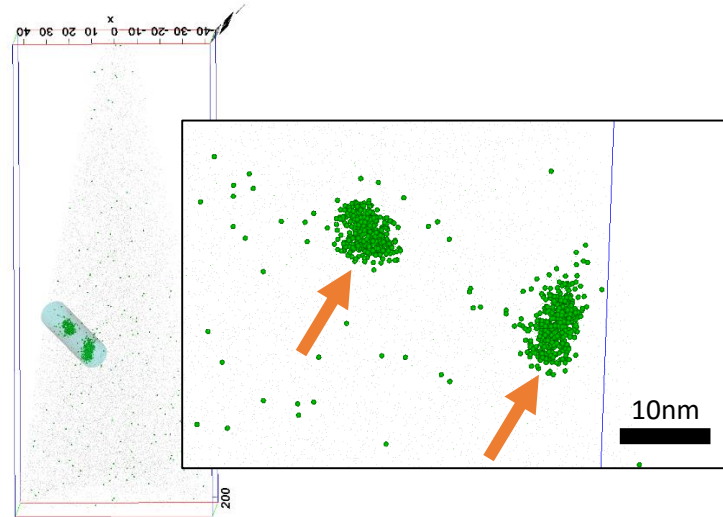


Figure 6-29. An atom map of the post-PDG specimen showing two Ni clusters (green) decorating the along the dislocation line. The defect is encapsulated in the cylindrical object. Inset: a magnified atom probe map the Ni clusters (marked by orange arrows) with the dislocation line running parallel to the imaging plane.

6.4.4.3.1 Bulk concentration

Table 6-6 shows the bulk composition of the specimen obtained from a dataset with a sample size of about ten million ions. The concentrations of C and Ni were found to be comparable to their detection sensitivities of 3.00×10^{18} atom/cm³ and 1.35×10^{18} atom/cm³ and hence they were regarded as background noise. Similar to other specimens, the O concentration is much higher than that expected in mc-Si. The element was found to distribute homogeneously throughout the reconstruction.

Ion type	Concentration (10^{19} atom/cm ³)
C	n/a
Ni	n/a
O	4.79±0.05

Table 6-6. The bulk composition of the post-PDG specimen containing a dislocation. The concentrations were obtained with the complex ions being decomposed into their associated solute atoms. The solute atoms with the concentration less than their detection sensitivities are in bold.

6.4.4.3.2 Ni clusters

Two Ni clusters, referred to hereafter as Ni1d and Ni2d, were encapsulated in iso-concentration surfaces with a Ni concentration threshold of 2.8at%, as shown in Figure 6-30. The diameter of both clusters was about 10nm. The average Ni peak concentrations of the clusters were 19.89at% or 9.94×10^{21} atom/cm³.

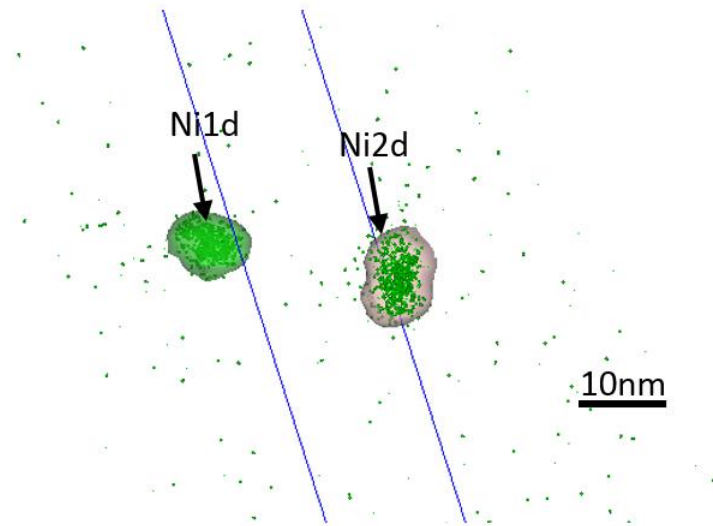


Figure 6-30. An atom map of the post-PDG specimen containing a dislocation. Shown here are two nickel clusters (green) encapsulated in iso-concentration surfaces with the nickel concentration threshold of 1.80at%.

Cluster	Concentration	
	at%	$\times 10^{21}$ atom/cm ³
Ni1d	25.00 $\pm$ 15.31	12.50 $\pm$ 7.65
Ni2d	14.78 $\pm$ 2.34	7.39 $\pm$ 1.17

Table 6-7. A table shows the peak concentrations of two Ni clusters. The concentrations were obtained with the complex ions being decomposed into their associated solute atoms.

6.5 Discussion

This section discusses the results from the atom probe analysis of the various mc-Si specimens in terms of the solute atoms, and their associated molecular ions, that were found or expected to decorate the defects present in the specimens.

6.5.1 Gold

It was initially thought a surprising result that no Au was observed either at the GB or the associated dislocations in the gold-contaminated specimen. The mc-Si sample was quenched after Au in-diffusion to stop any chance of precipitate formation or substantial loss of Au to the specimen surface. Thus, the conditions used should have produced a Au concentration in the bulk equal to the solid solubility at 1000°C which is about 1×10^{16} atom/cm³ [10]. A similar method had been used by Douglas Jordan¹¹ in the Oxford Semiconductor Group to introduce Au into Si and had been found to work effectively.

The most likely reason for the lack of gold being observed is that the binding energy of Au to the defect is low. The binding energy can be estimated as follows:

Equation 6-3
$$[Au_{defect}] = [Au_{bulk}] \exp\left(\frac{\Delta G}{kT}\right)$$

where Au_{defect} and Au_{bulk} are the concentrations of gold at the defect and in the bulk, respectively. ΔG is the binding energy of Au to the defect, k is the Boltzmann constant ($\sim 8.617 \times 10^{-5}$ eV/K) and T is the temperature in K which is assumed to be 1273K because of the quench that was used. Au_{bulk} can be estimated from the solid solubility ($\sim 1 \times 10^{16}$ atom/cm³) and the upper limit of Au_{defect} can be inferred from the LEAP data as $\sim 2.48 \times 10^{18}$ atom/cm³, so the highest ΔG can be is 0.63eV. Note that Au_{defect} is defined as the detection sensitivity of Au which was determined using Equation 2-8 with N_{noise} being the noise counts between 98.3amu to 98.7amu, i.e., $^{197}Au^{2+}$ peak. This particular noise range was chosen for two reasons; (a) Au is expected to become field evpaorated either as singly-charged or doubly-charge ions according to the Kingham diagram of the element in [12]; and (b) the noise counts at lower amu are expected to be higher and would therefore give the minmium gold detection sensitivity, which is essential when determining the upper limit of ΔG .

There is only one report in the literature of the quantitative value for the binding energy of an impurity species to a dislocation in silicon which shows that the binding energy of O to dislocations is 0.74eV at high temperatures and 0.2eV at low temperatures¹³. The maximum value of the binding energy of gold

to the defect found in this work is thus lower than that of O to dislocations. However, the binding energy of oxygen to dislocations includes a chemical component of bonding between the O and the otherwise unsatisfied silicon bonds at the dislocation core. It is likely that this component of the binding energy is not present for Au. Conversely, because Au is a bigger atom than O the strain energy component of the binding energy may well be higher. However this work indicates that, for whatever reasons, the binding energy of Au to the dislocations (and the grain boundary in which they lie) is lower than 0.63eV ensuring that the Au concentration at the defects is below $\sim 3 \times 10^{18} \text{ atom/cm}^3$ and thus not seen in this experiment.

6.5.2 Iron

Iron was not observed in any of the specimens despite being considered one of the most prominent impurities in solar grade silicon^{14,15,16}. This result implies that its concentration was below the iron detection limit. Table 6-8 contains the Fe detection sensitivities determined for all the analysed specimens using Equation 2-8. Since the $^{56}\text{Fe}^+$ peak was not present in any mass spectra, the noise count (N_{noise}) was measured between 55.8 and 56.2. Although these values are much higher than the iron concentration in the bulk of commercial mc-Si ingot (between 10^{14} - $10^{16} \text{ atom/cm}^3$ [17,18]), the iron concentration at the defects was expected to be significantly higher. A factor that further limits the iron detection efficiency is the overlapping of the Fe_{56}^{2+} peak with the Si_{28}^+ peak in the mass spectra. APT analysis of the Fe calibration specimen in Section 5.7 has shown that about 35% of Fe ions are singly-charged. In other words, more than half of the Fe ions evaporated from the specimen will not be detectable because they cannot be distinguished from the silicon ions.

Sample	Iron detection sensitivity	
	ppm	atom/cm ³
Gold-contaminated GB / dislocations	34	1.68E+18
As-grown GB / dislocations	56	2.82E+18
Post PDG GB / dislocations	40	2.01E+18
Post PDG isolated dislocation	53	2.67E+18

Table 6-8. The Iron detection sensitivity of analysed specimens.

With regard to the fast quenched gold contaminated specimen the same arguments may be applied as those used for Au. However, in the case of Fe, the bulk impurity concentration is not known accurately. The specimen was taken from the top red-zone of the ingot and so the Fe concentration will have been high by mc-Si standards. If an estimate of the Fe concentration being higher than 10^{15} atom/cm³ is used together with a detection sensitivity for Fe of 1.68×10^{18} atom/cm³ then it can be estimated that the binding energy of Fe to dislocations and to this particular grain boundary in Si is less than 0.81eV.

With the exception of the gold contaminated specimens all the specimens had relatively slow cools from elevated temperatures. In the case of the as-grown specimen the cool will have taken many hours. Thus in these specimens the analysis of the ratio of the defect impurity concentration to the bulk concentration in terms of the impurity defect binding energy is not appropriate. However, the slow cools should have given sufficient opportunity for impurities to be gettering to and hence decorate the defects. Equation 6-3 shows that at low temperatures even relatively small values of binding energy would generate significant impurity concentrations at the defects. Thus, the absence of Fe in the APT specimens which had a slow cool may be due to the fact that the iron was present mainly in the form of precipitates and that these precipitates were so far apart as not to be found in the APT specimens. A number of studies^{19,20} have shown that Fe forms precipitates along grain boundaries in mc-Si with the typical distance between precipitates being in the range of several microns, which is much larger than the length of the grain boundary being analysed in the LEAP (200nm-500nm). In addition, no atomic scale decoration of the grain boundaries or dislocations was detected. The detection limit is of the order of one impurity atom every 8-9nm. The iron detection sensitivities were determined using Equation 2.9.9 with N_{noise} being the noise counts between 55.8amu and 56.2amu. Previous work²¹ showed that an impurity concentration of approximately one atom every 5nm along a dislocation core gave rise to EBIC contrast of 10%. Unfortunately, a direct quantitative comparison cannot be made between that work and this because the impurity species are likely different and the geometry of the EBIC contrast measurements is also different. However,

in general terms, it does show that substantial electrical activity might be produced at dislocations by concentrations of impurities below the detection threshold obtained in this work. Further work would be required to determine if this is in fact the case.

6.5.3 Copper

Copper atoms were found to segregate to the grain boundary of the as-grown specimen as either individual atoms or small clusters. The former is unexpected for Cu because this solute generally forms precipitates with diameters of tens to hundreds of nanometres^{22,23,24,25} due to its high diffusivity and long cooling time during the ingot cooling stage.

The Cu/Si phase diagram in [26] shows several intermetallic phase between the two elements. However, many studies^{27,28,29} have shown only the most silicide-rich phase (Cu_3Si) is present in mc-Si. The concentration of Cu in Cu clusters at the grain boundary in the as-grown specimen are much lower than this phase. This can be explained by the local magnification effect³⁰; the evaporation field of the clusters is lower than the bulk, thus resulting in Si ions being focused inwards towards the centre of the clusters. This behaviour was observed in [31], where Fe ions were projected into oxide precipitates in steel alloy specimens. The magnification effect can also be used to explain the distribution behaviour of Cu atoms at the grain boundary.

6.5.4 Nickel

Nickel clusters were found in both the grain boundary and the isolated dislocation specimens taken from the PDG mc-Si sample. Many studies in the literature have confirmed the segregation of Ni at grain boundaries^{32,33,34} and dislocations^{35,36}. However, the peak Ni concentrations in most Ni clusters in both post-PDG specimens are about 50% lower than the stable form of nickel silicide (NiSi_2 [37,38]) often found in mc-Si. This could be due to a proportion of Ni ions are field evaporated as Ni^{2+} . Since the two major peaks associated with the charge state (Ni_{58}^{2+} and Ni_{60}^{2+}) overlap with the silicon peaks (Si_{29}^{+} and Si_{30}^{+}), it was difficult to distinguish all the Ni evaporated, and so the measured Ni concentration is always expected to be below the true value.

In order to prove this hypothesis, the differences between the measured counts and the expected count in three Si⁺ mass peaks, i.e., ²⁸Si⁺, ²⁹Si⁺ and ³⁰Si⁺, in the mass spectra of both specimens were determined. The expected counts for an isotope, N_{isotope}, is given by:

Equation 6-4
$$N_{isotope} = \frac{NA_{isotope}(\%)}{NA_{reference}(\%)} \times N_{reference}$$

where NA_{reference} and NA_{isotope} are the natural abundance of the reference and the expected isotopes, respectively, and N_{reference} is the measured counts of the reference isotope. The equation assumes that the mass peak of the reference isotope only is not contaminated with other chemical species. By using ²⁸Si as the reference isotope, the results, summarised in Table 6-9 (a) and (b)), reveal higher measured ²⁹Si⁺ and ³⁰Si⁺ counts than the expected counts in both specimens.

<i>Si count</i>			
	²⁸ Si ⁺	²⁹ Si ⁺	³⁰ Si ⁺
<i>Measured</i>	653561	34074	22194
<i>Expected</i>	653561	33186	21877
<i>Difference</i>	0	888	317

(a) Grain boundary

<i>Si count</i>			
	²⁸ Si ⁺	²⁹ Si ⁺	³⁰ Si ⁺
<i>Measured</i>	669443	36617	23362
<i>Expected</i>	669443	33993	22408
<i>Difference</i>	0	2624	954

(b) Dislocation

Table 6-9. Tables show differences between the measured and the expected counts in three mass peaks associated with ²⁸Si⁺, ²⁹Si⁺ and ³⁰Si⁺ in the spectra of (a) the grain boundary and (b) the dislocation. Both specimens were taken from the PDG mc-Si sample.

Interestingly, if one were to use Equation 6-4 to calculate the expected ⁶⁰Ni²⁺ counts by assuming that the difference between the measured and the expected counts of ²⁹Si⁺ is made up entirely of ⁵⁸Ni²⁺, then the values, which represent the expected ⁶⁰Ni²⁺ counts, would be similar to the differences between the measured and the expected counts of ³⁰Si⁺ for both specimens, i.e., 348counts and 1028counts for the grain boundary and the dislocation specimens, respectively. In other words, the additional ²⁹Si⁺ and ³⁰Si⁺ counts in Table 6-9 (a) and (b) are likely to be ⁵⁸Ni²⁺ and ⁶⁰Ni²⁺ ions.

This assumption was used to determine $\text{Ni}^+:\text{Ni}^{2+}$ ratios of both specimens. The ratios for the grain boundary and the isolated dislocation specimens were 0.44 and 0.56, respectively. These results imply that roughly half of Ni atoms were field evaporated as Ni^{2+} , which would account for the missing Ni atoms in most Ni clusters in both specimens.

The average Ni concentration of the Ni clusters decorating the isolated dislocation was found to be lower than the Ni clusters at the grain boundary even after Ni concentrations have been corrected according to the $\text{Ni}^+:\text{Ni}^{2+}$ ratios calculated earlier. This is rather unexpected since the isolated dislocation was surrounded by larger volume of materials than the grain boundary, which should allow more impurities to segregate to the defect. A possible explanation is that the isolated dislocation was located near a grain boundary, see Figure 6-26. Since the grain boundary also provides gettering sites for impurities, there was ‘impurity gettering’ competition between the grain boundary and the dislocation, resulting in a lower impurity concentration at the dislocation than expected.

Nickel also forms NiC molecular ions at dislocations in the gold-contaminated specimen. Although this complex has not been reported in the literature, it could have been induced by the high laser beam energy employed in these analyses.

In any case, the presence of Ni in both defects after PDG suggests strong binding of this solute atom to these defects. Nickel is also known to enhance the electrical activity of extended defects in silicon^{39,40} and hence is expected to contribute to the electrical activity of the both the isolated dislocations and the grain boundaries in post-PDG specimens.

6.5.5 Oxygen

The oxygen concentration in the bulk was found to be at least two orders of magnitude higher than what is expected in commercial mc-Si ingots (about 3×10^{17} atom/cm³ [41,42]). This can be explained by (a) the field evaporation of residual gas (O_2) in the analysis chamber at the specimen surface during the APT analysis; and (b) the migration of surface contamination along the shank of the specimen

during the APT analysis. Still, the oxygen concentration at the grain boundary in the gold-contaminated specimen is still higher than in the bulk, thus suggesting the enrichment of solute atoms at the defect. Oxygen decorates these defects in the form of SiO which is known to enhance the electrical activity of defects^{43,44} and thus is expected to contribute to the electrical activity of the defect.

6.5.6 Carbon

The concentrations of C in bulk were found to be higher than the expected concentration in the commercial mc-Si ingots (about $5 \times 10^{17} \text{ atom/cm}^3$ [45]) for the as-grown and the post-PDG specimens with both containing a grain boundary. The same explanations as used for O can be used to explain this effect, which are (a) the field evaporation of residual gas (CO_2) inside the analysis chamber at the specimen apex and (b) the migration of surface contamination along the shank of the specimen.

The SiC molecular ion was also found to decorate the grain boundaries in the gold-contaminated and the post-PDG specimens. However, the molecular ion forms a uniform layer at both grain boundaries as opposed to a more commonly observed filament-like structure^{46,47}. Still, the SiC is known to act as a shunting path⁴⁸ through the p-n junction, resulting in the reduction in the solar cell performance.

6.5.7 Chemical compositions at the grain boundary before and after PDG

The APT specimens in Section 6.4.2 and 6.4.3 were taken from the same grain boundary before and after PDG. The grain boundary in the as-grown specimen was enriched with Cu while the same defect in the post-PDG specimen were decorated with Ni and C. The gettering process has led to significant reduction in the recombination strength of the defect from about 58% to about 22%, but the difference in the chemical compositions of these specimens cannot be simply explained by the removal of impurities during phosphorus diffusion since Ni and C are found after the gettering process and weren't in the specimen analysed before the gettering process. It is thus likely that different positions on the grain boundaries in these specimens were decorated with different solute atoms. The

distance between the two specimens taken from the same grain boundary was determined by taking two thickness measurements of the same sample at two different stages; one after the fabrication of the as-grown specimen and another after the fabrication of the post-PDG specimen. The thicknesses of the sample at these stages were $121\pm 1\mu\text{m}$ and $109\pm 1\mu\text{m}$. The distance between the two APT specimen along the grain boundary is therefore about $11\pm 1\mu\text{m}$.

6.6 Conclusion

The APT specimen fabrication process developed in Chapter 3 and 4 together with the optimisation of LEAP's parameters in Chapter 5 have for the first time allowed the distribution of impurities at dislocations in a grain boundary and an isolated dislocation in mc-Si to be observed. The results indicate that the binding energy of gold to dislocations and grain boundaries in the gold-contaminated specimen is less than 0.63eV. Atomic scale decoration of grain boundaries by Ni and C was detected and possibly by C, Ni, O and N for dislocations. Whilst clustering/ precipitation of Ni and Cu was found at grain boundaries and Ni at dislocations. The increase in impurities at the defects relative to the bulk is very likely the cause of the electrical activity associated with them which is so damaging to the performance of solar cells. However, the present work although producing the first ever atomic analyses of selected defects in silicon has produced several surprises, namely the lack of Fe in all the specimens and the atomic decoration of Cu atoms in most part of the grain boundary in the as-grown specimen, and much more work is required before the decoration of defects by impurities, their impact on electrical properties, and the effect of gettering in mc-Si is understood.

6.7 References

¹ Miller, M. K., & Hetherington, M. G. (1991). Local magnification effects in the atom probe. *Surface Science*, 246(1), 442-449.

² Marquis, E. A., & Vurpillot, F. (2008). Chromatic aberrations in the field evaporation behavior of small precipitates. *Microscopy and microanalysis*, 14(06), 561-570.

³ Miller, M. K. (1987). The effects of local magnification and trajectory aberrations on atom probe analysis. *Le Journal de Physique Colloques*, 48(C6), C6-565.

- ⁴ Hellman, O. C., Vandenbroucke, J. A., Rüsing, J., Isheim, D., & Seidman, D. N. (2000). Analysis of three-dimensional atom-probe data by the proximity histogram. *Microscopy and Microanalysis*, 6(05), 437-444.
- ⁵ Vaumousse, D., Cerezo, A., & Warren, P. J. (2003). A procedure for quantification of precipitate microstructures from three-dimensional atom probe data. *Ultramicroscopy*, 95, 215-221.
- ⁶ Cerezo, A., & Davin, L. (2007). Aspects of the observation of clusters in the 3-dimensional atom probe. *Surface and interface analysis*, 39(2-3), 184-188.
- ⁷ Crimp, M. A., Simkin, B. A., & Ng, B. C. (2001). Demonstration of the $g \cdot b_{\text{ex}} = 0$ edge dislocation invisibility criterion for electron channelling contrast imaging. *Philosophical magazine letters*, 81(12), 833-837.
- ⁸ Menter, J. (1956, July). The direct study by electron microscopy of crystal lattices and their imperfections. In *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* (Vol. 236, No. 1204, pp. 119-135). The Royal Society.
- ⁹ Yang, H., Lozano, J. G., Pennycook, T. J., Jones, L., Hirsch, P. B., & Nellist, P. D. (2015). Imaging screw dislocations at atomic resolution by aberration-corrected electron optical sectioning. *Nature communications*, 6.
- ¹⁰ Stolwijk, N.A., et al., Diffusion and solubility of gold in silicon. *Physica B*, 1983. 116: p. 335.
- ¹¹ Jordan, D.M. (2011). Semi-insulating silicon. Published DPhil thesis, University of Oxford, Oxford, United Kingdom.
- ¹² Kingham, D. R. (1982). The post-ionization of field evaporated ions: A theoretical explanation of multiple charge states. *Surface Science*, 116(2), 273-301.
- ¹³ Senkader, S., Giannattasio, A., Falster, R. J., & Wilshaw, P. R. (2002). On the dislocation–oxygen interactions in Czochralski-grown Si: oxygen diffusion and binding at low temperatures. *Journal of Physics: Condensed Matter*, 14(48), 13141.
- ¹⁴ Coletti, G., Kvande, R., Mihailetchi, V. D., Geerligs, L. J., Arnberg, L., & Øvrelid, E. J. (2008). Effect of iron in silicon feedstock on p-and n-type multicrystalline silicon solar cells. *Journal of applied physics*, 104(10), 104913.
- ¹⁵ Istratov, A. A., Buonassisi, T., McDonald, R. J., Smith, A. R., Schindler, R., Rand, J. A., ... & Weber, E. R. (2003). Metal content of multicrystalline silicon for solar cells and its impact on minority carrier diffusion length. *Journal of applied physics*, 94(10), 6552-6559.
- ¹⁶ Bentzen, A., Holt, A., Kopecek, R., Stokkan, G., Christensen, J. S., & Svensson, B. G. (2006). Gettering of transition metal impurities during phosphorus emitter diffusion in multicrystalline silicon solar cell processing. *Journal of Applied Physics*, 99(9), 093509.
- ¹⁷ Istratov, A. A., Buonassisi, T., McDonald, R. J., Smith, A. R., Schindler, R., Rand, J. A., ... & Weber, E. R. (2003). Metal content of multicrystalline silicon for solar cells and its impact on minority carrier diffusion length. *Journal of applied physics*, 94(10), 6552-6559.
- ¹⁸ Kvande, R., Geerligs, L. J., Coletti, G., Arnberg, L., Di Sabatino, M., Øvrelid, E. J., & Swanson, C. C. (2008). Distribution of iron in multicrystalline silicon ingots. *Journal of applied physics*, 104(6), 064905.
- ¹⁹ Seifert, W., Vyvenko, O., Arguirov, T., Kittler, M., Salome, M., Seibt, M., & Trushin, M. (2009). Synchrotron-based investigation of iron precipitation in multicrystalline silicon. *Superlattices and Microstructures*, 45(4), 168-176.

- ²⁰ McHugo, S. A., Thompson, A. C., Perichaud, I., & Martinuzzi, S. (1998). Direct correlation of transition metal impurities and minority carrier recombination in multicrystalline silicon. *Applied physics letters*, 72(26), 3482-3484.
- ²¹ Wilshaw, P.R. (1984). *An EBIC Study of Dislocations in Silicon*. Published DPhil thesis, University of Oxford, Oxford, United Kingdom.
- ²² Buonassisi, T., Istratov, A. A., Heuer, M., Marcus, M. A., Jonczyk, R., Isenberg, J., ... & Weber, E. R. (2005). Synchrotron-based investigations of the nature and impact of iron contamination in multicrystalline silicon solar cells. *Journal of Applied Physics*, 97(7), 074901.
- ²³ Buonassisi, T., Istratov, A. A., Pickett, M. D., Heuer, M., Kalejs, J. P., Hahn, G., ... & Weber, E. R. (2006). Chemical natures and distributions of metal impurities in multicrystalline silicon materials. *Progress in Photovoltaics: Research and Applications*, 14(6), 513-531.
- ²⁴ Kajbaji, M. E., & Thibault, J. (1995). Platelet copper precipitates in silicon: a high-resolution electron microscopy study. *Philosophical magazine letters*, 71(6), 335-339.
- ²⁵ Jendrich, U., & Möller, H. J. (1990). TEM investigation of copper precipitation at grain boundaries in silicon. *Le Journal de Physique Colloques*, 51(C1), C1-197.
- ²⁶ Kaufman, L. (1979). Coupled phase diagrams and thermochemical data for transition metal binary systems-VI. *Calphad*, 3(1), 45-76.
- ²⁷ Buonassisi, T., Marcus, M. A., Istratov, A. A., Heuer, M., Cizek, T. F., Lai, B., ... & Weber, E. R. (2005). Analysis of copper-rich precipitates in silicon: chemical state, gettering, and impact on multicrystalline silicon solar cell material. *Journal of applied physics*, 97(6), 063503.
- ²⁸ Solberg, J. K. (1978). The crystal structure of Cu₃Si precipitates in silicon. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography*, 34(5), 684-698.
- ²⁹ Seibt, M., Griess, M., Istratov, A. A., Hedemann, H., Sattler, A., & Schröter, W. (1998). Formation and properties of copper silicide precipitates in silicon. *physica status solidi (a)*, 166(1), 171-182.
- ³⁰ Lasagni, F. (2011). *Fabrication and characterization in the micro-nano range new trends for two and three dimensional structures* (pp. 209-210). Berlin: Springer.
- ³¹ London, A. J., Lozano-Perez, S., Moody, M. P., Amirthapandian, S., Panigrahi, B. K., Sundar, C. S., & Grovenor, C. R. M. (2015). Quantification of oxide particle composition in model oxide dispersion strengthened steel alloys. *Ultramicroscopy*.
- ³² Buonassisi, T., Istratov, A. A., Marcus, M. A., Peters, S., Ballif, C., Heuer, M., ... & Weber, E. R. (2005, January). Synchrotron-based investigations into metallic impurity distribution and defect engineering in multicrystalline silicon via thermal treatments. In *Photovoltaic Specialists Conference, 2005. Conference Record of the Thirty-first IEEE* (pp. 1027-1030). IEEE.
- ³³ Rizk, R., Portier, X., Allais, G., & Nouet, G. (1994). Electrical and structural studies of copper and nickel precipitates in a $\Sigma=25$ silicon bicrystal. *Journal of applied physics*, 76(2), 952-958.
- ³⁴ Buonassisi, T., Istratov, A. A., Pickett, M. D., Marcus, M. A., Cizek, T. F., & Weber, E. R. (2006). Metal precipitation at grain boundaries in silicon: Dependence on grain boundary character and dislocation decoration. *Applied Physics Letters*, 89(4), 042102.
- ³⁵ Tang, W., Picraux, S. T., Huang, J. Y., Gusak, A. M., Tu, K. N., & Dayeh, S. A. (2013). Nucleation and atomic layer reaction in nickel silicide for defect-engineered Si nanochannels. *Nano letters*, 13(6), 2748-2753.
- ³⁶ Seibt, M., Kveder, V., Schröter, W., & Voß, O. (2005). Structural and electrical properties of metal impurities at dislocations in silicon. *physica status solidi (a)*, 202(5), 911-920.

- ³⁷ Heuer, M., Buonassisi, T., Marcus, M. A., Istratov, A. A., Pickett, M. D., Shibata, T., & Weber, E. R. (2006). Complex intermetallic phase in multicrystalline silicon doped with transition metals. *Physical Review B*, 73(23), 235204.
- ³⁸ Choi, J. H., Kim, S. S., Park, S. J., & Jang, J. (2003). Polycrystalline silicon prepared by metal induced crystallization. *Thin Solid Films*, 440(1), 1-4.
- ³⁹ Walz, D., Joly, J. P., Falster, R., & Kamarinos, G. (1995). Characterization of nickel contamination in float zone and Czochralsky silicon wafers by using electrolytic metal tracer or microwave photoconductivity decay measurement. *Japanese journal of applied physics*, 34(8R), 4091.
- ⁴⁰ Rizk, R., & Nouet, G. (1997). Electrical activity and structural configuration of transition metals (Cu, Ni, Fe) in silicon bicrystals. *Interface Science*, 4(3-4), 303-316.
- ⁴¹ M. Di Sabatino, S. Binetti, J. Libal, M. Acciarri, H. Nordmark, E.J. Øvrelid, Oxygen distribution on a multicrystalline silicon ingot grown from upgraded metallurgical silicon, *Solar Energy Materials and Solar Cells*, Volume 95, Issue 2, February 2011, Pages 529-533
- ⁴² Trumbore, F. A. (1960). Solid solubilities of impurity elements in germanium and silicon. *Bell System Technical Journal*, 39(1), 205-233.
- ⁴³ Borghesi, A., Pivac, B., Sassella, A., & Stella, A. (1995). Oxygen precipitation in silicon. *Journal of Applied Physics*, 77(9), 4169-4244.
- ⁴⁴ Maurice, J. L. (1987). On the origin of the electrical activity in silicon grain boundaries. *Revue de Physique Appliquée*, 22(7), 613-621.
- ⁴⁵ Teng, Y. Y., Chen, J. C., Lu, C. W., & Chen, C. Y. (2010). The carbon distribution in multicrystalline silicon ingots grown using the directional solidification process. *Journal of crystal growth*, 312(8), 1282-1290.
- ⁴⁶ Breitenstein, O., Bauer, J., & Rakotoniaina, J. P. (2007). Material-induced shunts in multicrystalline silicon solar cells. *Semiconductors*, 41(4), 440-443.
- ⁴⁷ Bauer, J., Breitenstein, O., & Rakotoniaina, J. P. (2007). Electronic activity of SiC precipitates in multicrystalline solar silicon. *physica status solidi (a)*, 204(7), 2190-2195.
- ⁴⁸ Breitenstein, O., Rakotoniaina, J. P., Al Rifai, M. H., & Werner, M. (2004). Shunt types in crystalline silicon solar cells. *Progress in Photovoltaics: Research and Applications*, 12(7), 529-538.

7 Summary and future work

Table of Contents

7.1	Introduction	- 228 -
7.2	The development of the atom probe tomography specimen fabrication process.....	- 228 -
7.2.1	Defect delineation by wet chemical etching.....	- 228 -
7.2.2	Defect marking techniques	- 229 -
7.2.3	APT specimen fabrication methods	- 230 -
7.3	Summary of the optimisation of LEAP's parameters	- 231 -
7.4	Summary of defect characterisation results.....	- 231 -
7.5	Suggestions for further work	- 232 -
7.5.1	Determine the binding energy of metal impurities to extended defects.....	- 233 -
7.5.2	Correlation between chemical compositions at defects and their electrical activities -	233 -
7.5.3	Further studies on etch pit geometry	- 233 -

7.1 Introduction

The performance of mc-Si solar cell is limited by the presence of metal decorated defects (dislocations and grain boundaries). They act as recombination sites for minority carriers. In the solar cell industry, this effect is minimised by introducing performance enhancement steps in to solar cell processing: phosphorus diffusion gettering (PDG), aluminium gettering (AG) and hydrogenation via surface passivation. However, despite improvements in the solar cell performance, some defects remain electrically active. In this project, LEAP is used together with EBIC to establish the correlation between impurity compositions at defects with their electrical activity, which would then allow us to determine which impurities are mainly responsible for the electrical activity of defects.

7.2 The development of the atom probe tomography specimen fabrication process

A major challenge when using the LEAP is that the instrument requires the specimen to be in the shape of a needle with an apex radius of 100nm or less. Despite numerous APT specimen fabrication strategies reported in the literature, none has the precision to fabricate a specimen containing a specifically selected defect such as a dislocation. It was initially thought that this could be overcome by making relatively small changes to an existing method. However, numerous technical difficulties were encountered during the development process. This eventually led to the development of a new entire fabrication process. This section summarises important stages of the development process.

7.2.1 Defect delineation by wet chemical etching

Preferential etching was developed as a precursor step to APT specimen fabrication in the Nvision. The technique uses etch pits to reveal where extended defects intersect the sample surface. Three potential etchants were explored for defect delineation, namely Dash, Sirtl and Secco, from which Secco was selected. Three parameters of the Secco etch process were then optimised to produce circular dislocation pits with an average diameter of about 100nm. The optimum parameters were 0.05M potassium dichromate at 20°C and 30sec etch time. Repeated etching on five samples showed that dislocations with similar etch pit diameters could be produced. Hence, these parameters were

used for the APT specimen fabrication method in Section 2.7.4. Depth measurement results show that the average defect etch pit depth was 170nm across five samples, which is within the 100nm and 1000nm range required for APT specimen fabrication and thus, these etch parameters were used to etch samples for the APT specimen fabrication methods developed in Chapter 4. The optimum parameters were also used to study the propagation behaviours of defects through the sample thickness. The investigated defects were found to propagate at inclined angles to the surface normal and their propagation directions were unpredictable.

7.2.2 Defect marking techniques

The chances of successfully fabricating an APT specimen containing a defect rely heavily on the ability to locate the defect in the Nvision. The etch pit created by the preferential etchant is prone to the ablation effect of the ion beam which intensified during APT specimen fabrication. Hence, a marking technique was developed for each defect type. The fabrication procedures of these techniques are described below.

7.2.2.1 *Dislocations*

A tungsten dot is deposited over the selected defect, i.e., a single dislocation or a specific point on a grain boundary, using EBID at 5kV accelerating voltage and 30 μ m objective aperture size. The deposition time is the time taken for the tungsten dot to fill the cavity plus 50sec deposition time to produce a tungsten dot with a height of about 200nm above the specimen surface. A 15 μ m by 4 μ m carbon strip is then deposited over the tungsten dot using the FIB at 90sec deposition time. The misalignments between the crosshair in spot mode and the tungsten dot in the image are corrected by moving the crosshair to the centre of the dot. This process is performed every ten seconds.

7.2.2.2 *Grain boundaries*

A tungsten line is deposited over the grain boundary using the FIB at 1pA beam current. The length of the tungsten line can be adjusted depending on the length of the grain boundary wanted to be analysed. The deposition time can also vary depending on the depth of the etched grain boundary.

The general idea is to deposit until the tungsten line is observed. A carbon strip, 10 μ m long and 4 μ m wide, is then applied over the tungsten marker using the FIB at 20sec deposition time.

7.2.3 APT specimen fabrication methods

Initially, the marking techniques described in the section above were used together with the standard lift-out and annular milling methods described in Section 2.7.4 to fabricate APT specimens for the defects. However, it was later discovered that extended defects do not run normal to the surface of mc-Si samples, rendering the fabrication method unusable. An alternative approach to APT specimen fabrication approach was proposed, based on which the APT fabrication methods for dislocations and grain boundaries were developed. The fabrication procedure of both methods is shown in Figure 7-1.

Note that the figure also shows the type of specimen holder being used for each process.

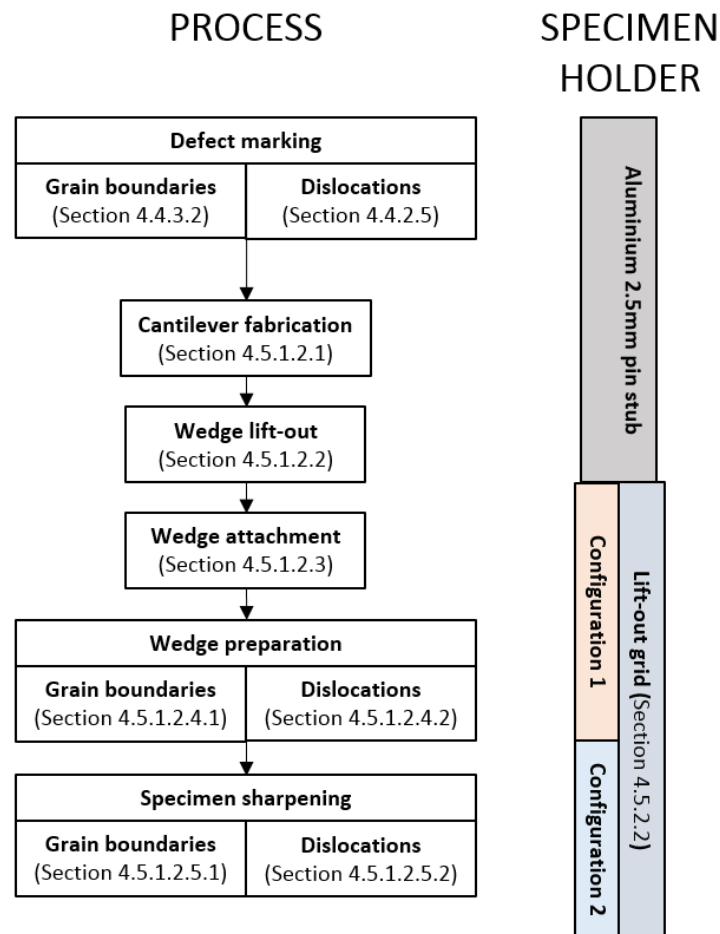


Figure 7-1. A schematic shows the APT specimen fabrication procedure for grain boundaries and dislocations, including the specimen holder used during each process (see right-hand side). The sections containing additional information on the corresponding processes or specimen holder configurations are enclosed in brackets where applicable.

7.3 Summary of the optimisation of LEAP's parameters

The LEAP parameters were optimised to maximise the Fe detection sensitivity. A matrix of pre-sharpened specimens was analysed using a variety of LEAP parameters. The optimum parameters were determined to be 0.5nJ laser beam energy, 55K specimen temperature, 160kHz repetition rate and 0.3% evaporation rate. The average iron detection sensitivity for these parameters was determined across five pre-sharpened specimens to be about 53ppm or 2.65×10^{18} atom/cm³. A specially prepared iron calibration specimen was then analysed using the optimum parameters. The result gave an iron detection efficiency of 35% and an iron detection sensitivity of 54ppm or 2.70×10^{18} atom/cm³, which is similar to the value obtained from pre-sharpened specimens.

7.4 Summary of defect characterisation results

The APT specimen fabrication methods and the optimisation of the LEAP parameters from Chapter 3 to chapter 5 allowed, for the first time in the world, four defects to be successfully characterised in accordance with the procedure described in Section 2.2. The results are summarised in this section.

The first specimen analysed was a grain boundary taken from the gold-contaminated mc-Si sample. The electrical activity of the grain boundary in this specimen was not determined by EBIC because its main purpose was to assess the effectiveness of the APT specimen fabrication method developed in Chapter 4. The TEM images of the specimen show a grain boundary runs almost along the centre of the specimen. Dislocations were also found at the grain boundary running approximately normal to the specimen axis. APT analysis of the specimen reveals enrichment of both Ni and C at the grain boundary. Furthermore, the grain boundary area also contains three dislocations. These dislocation were enriched with Ni, C, O and N. One of the dislocations was found to have significantly lower concentrations of these solute atoms than the other two dislocations. Surprisingly, no gold was observed in the specimen and this might be due to the low binding energy of the solute atoms to the defect. The upper bound binding enthalpy of Au to the defect was determined to be 0.63eV.

The second specimen was a grain boundary taken from the as-grown mc-Si sample. The recombination strength of the defect is about 58%, which is considered to be moderately active among all the defects in the sample. The specimen reconstruction reveals the enrichment of Cu at the grain boundary. Surprisingly, Copper atoms are homogeneously distributed at the grain boundary with only four Cu clusters being detected at the bottom section of the defect. The diameters of these clusters are between 4nm and 9nm with an average peak Cu concentration is 26.46at% or 1.32×10^{22} atom/cm³.

For the third specimen, the same grain boundary as that in the as-grown specimen was characterised. The recombination strength of the defect has been reduced by 36% to 22%. The specimen reconstruction shows that grain boundary is decorated with Ni clusters as well as C. Most Ni clusters have platelet structures with diameter and thickness ranging from 4nm-7nm and 2nm-4nm, respectively, with an average Ni peak concentration of about 1.14×10^{22} atom/cm³. In contrast, carbon is uniformly distributed along the grain boundary.

The last specimen was an isolated dislocation taken from the PDG mc-Si sample. The recombination strength of the isolated dislocation was determined using EBIC to be about 4%. The specimen reconstruction shows two Ni clusters decorating the dislocation. They are spherical with diameter of about 10nm and an average peak Ni concentration of 1.14×10^{22} atom/cm³. The distance between the centres of these clusters is about 35nm.

7.5 Suggestions for further work

The atom probe fabrication methods developed in this work allow impurities presence at a specific extended defect, be it a section of a grain boundary or an isolated dislocation, to be determined in the LEAP. The result can be used together with other instruments, such as EBIC and TEM, to correlate the impurity composition at defects with their electrical activity and characteristic. Here is a list of possible studies that can be carried out using these methods.

7.5.1 Determine the binding energy of metal impurities to extended defects

The APT specimen fabrication methods can be used to determine the binding energy of an impurity to the defect by performing APT analysis on the same defect taken from sister Si wafers contaminated with the impurity at different temperatures. The binding energy of the impurity can then be determined using the Arrhenius equation. However, it might be necessary to optimise the LEAP's parameters in order to maximise the detection sensitivity of that particular impurity. Otherwise, issues with mass peaks overlapping in the mass spectrum, surface migration and local magnification could potentially limit the result accuracy.

7.5.2 Correlation between chemical compositions at defects and their electrical activities

The defect characterisation procedure described in Section 2.2 can be used to study the effect of PDG parameters on the electrical activity and chemical composition of extended defects. This type of study can also be extended to other performance enhancement processes such as aluminium gettering, and surface passivation.

7.5.3 Further studies on etch pit geometry

Two interesting features were observed during the optimisation of Secco etch parameters that can be further studied: (a) some dislocation pits were found to be significantly smaller compared to the rest of the dislocations, see Figure 3-7; and (b) trail-like features were attached to some dislocation pits, see Figure 3-10. The characterisation procedure described in Section 2.2 can be used to correlate the chemical composition and the morphology of the dislocation pits. The results could potentially allow chemical etching to give a quick indication of the electrical activity or impurity composition of the defect.

3 Appendix

3.1 Dislocation pit diameter measurement program for optical micrographs

```
I = imread('OPTICAL MICROGRAPH');
A = rgb2gray(I);
A = imadjust (A);

Scaling factor (pixel/nm)
pixelnm = NUMBER;

%Dislocation selection criteria
Sensitivity= NUMBER;
EdgeThreshold= NUMBER;

%Find circle algorithm
[centers1, radii1, metric1] = imfindcircles(A,[1
8], 'Sensitivity',Sensitivity, ...
    'EdgeThreshold',EdgeThreshold, 'ObjectPolarity','dark');

%Display output
imshow(A)
viscircles(centers1, radii1, 'EdgeColor','b');

%Convert radius to diameter
diameter = (2*radii1)/pixelnm;
```

3.2 Dislocation pit diameter measurement program for electron micrographs

3.2.1 Automated dislocation pit selection

```
%IMPORT IMAGE%
I = imread('ELECTRON MICROGRAPH');

%Scaling factor (pixel/nm)
pixelnm = NUMBER;

%Image processing
I = rgb2gray(I);
I = imadjust (I);
Ibw = imcomplement (I);

%Criteria
Ibw = I < NUMBER;
A_min= NUMBER;

%Show image
imshow(Ibw);

%Discard region with area below A_min
Ibw = bwareaopen(Ibw, A_min);
```

```

CC = bwconncomp(Ibw);

%Display results as binary image
[L,num] = bwlabel(Ibw);
imshow(Ibw)

%measure area of segregated white pixels
for i=1:num
area(i) = bwarea(L==i);
end

%Convert area to diameter
diameter= (sqrt(area/pi)*2)/ pixelnm;

```

3.2.2 Manual dislocation pit selection

```

%IMPORT IMAGE%
I = imread('ELECTRON MICROGRAPH');

%VARIABLES%
pixelnm = NUMBER; %number of pixel per nm (scale)
Area = [] %empty array for dislocation area
Diameter = [] %empty array for calculated dislocation diameter

%Image processing%
I = rgb2gray(I);
I = imadjust(I);
Ibw = imcomplement(I);

%Criteria
Ibw = I < NUMBER;
A_min= NUMBER;

%Discard region with area below A_min
Ibw = bwareaopen(Ibw, A_min);
CC = bwconncomp(Ibw);

%Show image
imshow(Ibw);

H = msgbox('Click on Object of Interest');
uiwait(H);

while 1
while 2
[x y] = ginput(1);
Pxidx = sub2ind(size(Ibw),round(y),round(x)) %pixel linear index
Objidx = cellfun(@(x) any(x==Pxidx),CC.PixelIdxList) %what object?
if ~any(Objidx)
H = errordlg('Doh! You didn''t select a valid object');
uiwait(H);
H = msgbox(sprintf('Let''s try again\nClick on Object of
Interest'));
uiwait(H);
else
break;

```

```
end

end
ObjArea = numel(CC.PixelIdxList{Objidx}); %get area
Area(end+1) = ObjArea %input area
Diameter(end+1) = (sqrt(ObjArea/pi)*2)/ pixelnm; %find & input diameter
end
```