Abstract

Hafnia and hafnium silicate are leading high-κ materials to replace SiO₂ in CMOS devices. In this thesis the results of a study of bulk powders and thin films of these materials are reported.

Bulk powders were investigated to provide a greater understanding of the crystallisation process by which HfO₂ and HfSiO₄ are formed. Investigation using thermal analysis, x-ray diffraction and electron microscopy techniques revealed that starting materials, heating conditions and atmosphere significantly affected the crystallisation pathway. In particular three mechanisms for tetragonal hafnia (t-HfO₂) stabilisation were identified: (1) oxygen vacancies; (2) the critical particle size effect; and (3) the surface energy effect.

Electron energy-loss spectroscopy (EELS) was used to try to obtain a standard O K edge for t-HfO₂ from the powders and to better understand experimental EELS spectra obtained from thin films. A standard t-HfO₂ edge was not found and many of the spectra obtained did not match existing standard edge shapes. The local atomic environment has a large effect on the edge shape in these samples, leading to the conclusion that a ‘standard’ edge shape may be impossible to obtain. Combining the EELS spectra from bulk and thin film samples, with modelled data it was found that the atoms within ~6Å from the excited atom had the largest effect on the edge shape. Consequently EELS spectra taken at a distance from an interface greater than ~6Å will give a bulk-like signal.

20nm HfxSi1-xO₂ thin films were also investigated using TEM having been subjected to different thermal anneals and deposition conditions. It was found that the electron beam caused significant growth of SiO₂ layers due to oxygen diffusion, and crystallisation within the high-κ layer. Furthermore, the higher the SiO₂ content in the sample the more crystallisation was inhibited, though segregation into HfO₂ and SiO₂ rich regions occurred in all samples.
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Author’s Declaration

This thesis is a record of the work carried out by me in the Department of Materials Science and Engineering at Imperial College London and in the Department of Physics at the University of Glasgow. The work described herein is my own with the exception of: XRF analysis carried out by Andrew Payzant at the CNMS at Oak Ridge National Laboratory, USA; collection of standard HfSiO$_4$, m-HfO$_2$, HfN, TiN, SiO$_2$, $\alpha$-Al$_2$O$_3$ and a-Al$_2$O$_3$ EELS spectra, and the spectrum in Fig 2.10 was carried out by Maureen MacKenzie at the University of Glasgow; the TEM image in Fig 8.1(d) was collected by Samuel McFadzean.

Some of the results reported in this thesis have been published in the following papers:


Chapter 1 - Introduction

1 Introduction

In this chapter an introduction to the project will be presented. The predictions made by Moore’s law and the consequences for CMOS devices will be discussed – particularly in relation to the insulating SiO$_2$ layer. The problems associated with the SiO$_2$ layer will be outlined and some of the possible solutions discussed. The advantages and disadvantages of the implementation of HfO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ as high-$\kappa$ alternatives to SiO$_2$ will be considered. Materials incorporation into gate stacks will be reviewed. To try to further understand thin films the chemistry of the materials in bulk form is also discussed.

1.1 Background

Complementary metal-oxide semiconductors (CMOS) field effect transistors (FET) have become particularly important electronic devices. Made of silicon they have been improved over the last three decades according to Moore’s Law$^1$. This law, first published in 1965$^2$ says that the number of devices on a chip will double every 2-3 years. Until recent times Moore’s law has been achieved by device scaling, and maintaining progress at this rate has been the driving force for both the electronics and semiconductor industries since the 1970’s. However, there is a great deal of concern over the future growth of the industry. Device scaling is reaching atomic limits and it will be no longer possible to reduce the size of the CMOS device. Moore’s law will continue for a number of years yet but only if new materials and techniques are introduced into the device manufacturing process. Some of these problems are related to the limitation of lithographic techniques in being able to etch features small enough to meet the requirements – very small wavelengths of light are required. Another problem occurs with the interconnects though this has been partially solved by replacing aluminium with copper as the interconnect material, which lowers the resistance allowing higher conductivity. Related to this is the production of heat within the integrated circuit and new ways to increase heat dissipation are currently being developed.
However, by far the largest challenge is to find a replacement dielectric material for the insulating Si(O,N).

![Figure 1.1: Schematic of CMOS device gate stack](image)

Figure 1.1: Schematic of CMOS device gate stack

A schematic of a typical CMOS gate stack is illustrated in Fig 1.1. Currently the SiO$_2$ or Si(O,N) layer is about 1.2 nm wide (about 5 Si atoms thick)$^3$. To continue device scaling this layer will need to be replaced, as making SiO$_2$ any thinner results in an unacceptably high leakage current due to tunnelling of electrons through the SiO$_2$ barrier, leading to dielectric breakdown. Until now SiO$_2$ or Si(O,N) have been the dielectrics of choice, mainly because of the excellent interfaces formed with the silicon substrate and poly-silicon (poly-Si) gate electrode. Its amorphous nature up to high temperature results in no crystallinity or phase segregation which would provide a path for diffusion of atoms; there are few defects and trapped charges at the interface due to the good match in structure. Because of these properties it is difficult to find a suitable Si(O,N) replacement.

### 1.2 Replacement materials: requirements and concerns

The criteria for replacement materials are that they have: a high dielectric constant of 15-30, so that a physically thicker layer can be used whilst still having the same capacitance; must have good interfaces with the substrate and gate electrode materials such that interface layers do not form; have a low charge defect density; the material
should be either single crystal or amorphous to reduce leakage current and diffusion at
grain boundaries; and be stable under current annealing temperatures (up to ~1000°C).
The materials most suitable for these devices are metal oxides, nitrides, oxynitrides and
silicates though most binary nitrides have been eliminated due to their thermal
instability under device processing conditions. We will briefly consider some of these
materials parameters and their consequences for device incorporation.

1.2.1 Dielectric constant ($\kappa$)

The dielectric constant is a measure of the strength of the electric field in a material and
is directly related to the capacitance, $C$, of a parallel plate capacitor (Equation 1.1):

$$ C = \frac{\kappa \varepsilon_0 A}{t} \quad \text{Eqn. 1.1} $$

where $\kappa$ is the dielectric constant, $\varepsilon_0$ = permittivity of free space = $8.85 \times 10^{-12}$ C$^2$N$^{-1}$m$^{-2}$, $A$ is the area of the capacitor and $t$ the thickness of the dielectric.

In the case of SiO$_2$, because both the gate electrode and substrate are made of silicon,
the bonding at the interface is excellent and no interface layer or interfacial defects are
found. Most alternative dielectric materials will form unwanted interface layers in
contact with Si due to the mismatch in crystal structure between the two materials. The
schematic in Fig 1.2 illustrates this point.
Figure 1.2: Schematic of (a) ideal gate stack (b) gate stack with replacement high-k material

The interface layers that form are typically 0.5-1.0 nm thick. These interface layers are usually insulating themselves and have a dielectric constant lower than that of the high-k layer. This results in an overall reduction of the effective dielectric constant for the material between the gate electrode and substrate. From Equation 1, the dielectric constant scales with capacitance and the total capacitance follows the relationship in Equation 1.2:

$$\frac{1}{C_{TOT}} = \frac{1}{C_1} + \frac{1}{C_2} = \frac{1}{\varepsilon_0 A} \left( \frac{1}{\kappa_1} + \frac{1}{\kappa_2} \right)$$

Eqn. 1.2

where $C_{TOT}$ is the total capacitance, $C_1$ and $C_2$ and $t_1$ and $t_2$ are the capacitance and thickness of materials 1 and 2 respectively. The total capacitance across the layer is dominated by the material with the lowest capacitance, hence also the lowest dielectric constant. Equation (1) shows that as well as materials with a lower dielectric constant reducing capacitance, having a wider dielectric layer has a similar effect. By adding a small thickness, $t_2$, of low dielectric constant $\kappa_2$, the capacitance can be substantially lowered. Therefore the formation of interface layers increases the gate width and also contributes to the reduction of the total capacitance across the gate. Hence, as the material with the lowest capacitance dominates, the total capacitance across the gate stack is reduced. These observations lead to the conclusion that not only is a material
with a dielectric constant higher than that of SiO₂ required ($\kappa \sim 3.9$ for SiO₂⁴), but the
dielectric constant must be sufficiently high such that the overall dielectric of the high-$\kappa$
layer plus the interface layers is also greater than that of SiO₂.

Equation 1.3 can be used to establish the ‘equivalent (SiO₂) oxide thickness’ (EOT) of
the potential gate material.

$$t_{eq} = \frac{3.9t_{high-\kappa}}{\kappa_{high-\kappa}}$$  \hspace{1cm} \text{Eqn. 1.3}

t_{eq}$ and $t_{high-\kappa}$ are the equivalent oxide thickness and thickness of the high-$\kappa$ material and
$\kappa_{high-\kappa}$ is the dielectric constant of the high-$\kappa$ material. A high-$\kappa$ material is desired so
that scaling can continue to lower EOT’s. With this in mind it is most desirable to have
a material where $\kappa$ is greater than 12 and ideally in the 25-30 range⁵. Therefore, suitable
candidate materials include Ta₂O₅ ($\kappa \sim 22$), TiO₂ ($\kappa \sim 80$), HfO₂ ($\kappa \sim 25$), ZrO₂ ($\kappa \sim 25$)
and La₂O₃ ($\kappa \sim 30$). However there is a trade off with other parameters as discussed
below.

### 1.2.2 Film morphology

Control of film morphology is also important. SiO₂ remains amorphous above 1000°C,
the highest temperature reached in device manufacture. However, most replacement
gate dielectrics studied crystallise or phase segregate after annealing at this temperature.
As a result, finding a suitable oxide compatible with processing conditions is a
challenge. Poly-crystalline species are not suitable as the grain boundaries provide a
diffusion pathway through the dielectric layer. The diffused species, as well as resulting
in leakage current, also often cause or widen unwanted interface layers. Most suitable
oxide or oxynitride materials crystallise after heating to 1000°C though HfO₂ and ZrO₂
are both being considered despite this. There have however been reports of thin, 1-2nm
HfO₂ layers which are resistant to this crystallisation⁶⁻⁷. One solution to the problem of
crystallinity is to alloy the metal oxide with SiO₂ so as to make an HfₓSi₁₋ₓO₂ (or ZrₓSi₁₋ₓO₂) compound, since SiO₂ is known to increase the crystallisation temperature of the
material⁸. With this comes a lowering of the dielectric constant. For example, alloying
HfO₂ with SiO₂ lowers the dielectric constant from ~25 to ~11⁵. The compromise
between thermal stability and dielectric constant may result in a material that is more
suitable and remains amorphous after heating. An alternative solution is to deliberately
deposit a thin amorphous interfacial layer, usually of SiO₂ (channel layer – see Fig 1.2) that is stable in contact with both the dielectric and silicon. This would help stop diffusion across the grain boundaries of a crystalline dielectric material. However this may greatly affect the capacitance of the system⁹. This chemical oxide layer also allows for better bonding between the dielectric and the silicon substrate.

1.2.3 Defects

Defects within the structure often occur, especially at interfaces. For SiO₂ as the insulating layer, defect concentration was low due to the low co-ordination number of Si. This results in a flexible network which can relax and repair broken bonds so as not to allow many defects at the interface. Many other replacement materials have a high co-ordination number resulting in impurities or oxygen deficiency at the interfaces. If the replacement material is crystalline this may become even more pronounced due to strain and lattice mis-match. These defects result in charge being trapped at the interface which in turn affects carrier mobility in the channel, leading to a change in the threshold voltage of the transistor and can result in unreliability which leads to dielectric breakdown. The ‘charge trapping’ or ‘charge defects’ are due to a mismatch in the number of electrons contributing to the bonding from each side of the interface. These reduce mobility of the electrons by causing scattering at the interface. For example, Misra et al.¹⁰ quote the fixed charge at an Si/SiO₂ interface as being ~0.1% of the interface atoms compared with a silicon/high-κ interface where the fixed charge is ~1%. During processing forming gas (90%N₂:10%H₂)⁹ may be used to help passivate these interfacial traps. One consequence is that the nitrogen can react with the dielectric or interface materials to form new materials. This is not necessarily bad, as it has been shown that nitrogen inhibits crystallisation and oxygen diffusion⁵. Excess oxygen is sometimes used to passivate dangling bonds but this easily diffuses to react with the silicon, forming SiO₂.

1.3 Processing conditions

With a change of dielectric material there are problems associated with the current wafer processing conditions which have to be resolved. SiO₂ was grown using a simple thermal oxidation process. New materials have required new means of growth or
deposition of the oxide which are being investigated and developed. An earlier method for deposition was physical vapour deposition (PVD) where metals are evaporated onto the surface of the dielectric. But, because of the force with which the metal ions reach the surface, damage induced by sputtering, occurs. This can result in unwanted interfacial states and so this is not the deposition method of choice.

Both atomic layer deposition (ALD) and chemical vapour deposition (CVD) are the preferred methods and can be more easily incorporated into the preparation process industrially. In ALD, pulses of the precursor gases are allowed into the reaction chamber sequentially. The first reactant aligns itself on the substrate. The second pulse of gas then reacts with the first gas to form a fraction of a monolayer on the silicon substrate. Hence the number of layers can be monitored closely and ALD is therefore useful in obtaining accurate deposition. This method has mainly been adopted for deposition of HfO$_2$, ZrO$_2$ and Al$_2$O$_3$ but brings with it the added problems of having a slow growth rate$^{5,11}$. The ALD process also works better on an oxygen terminated surface and so a ‘chemical oxide’ layer of SiO$_2$ is first deposited on the silicon substrate to aid the formation of the high-$\kappa$ layer.

In CVD (and metal-organic CVD (MOCVD)) the reactant gases are passed over a heated substrate. As they come into contact with the substrate, the gases react and the product is deposited on the wafer. The temperature of the wafer is critical for the reaction to take place and using this technique uniform coverage of the wafer is possible. Depending on the reactants used the CVD technique (as well as ALD) can result in unwanted impurities such as C, H or Cl hence the reactants have to be chosen with care$^5$. The advantage of this technique is that the electronics industry already use it widely and so it is a well known and developed technique.

### 1.4 Hafnia containing gate stacks

HfO$_2$ has been the leading candidate as an SiO$_2$ replacement material for a number of years and in 2007 Intel announced its incorporation into their most recent 45nm technology$^{12}$. Though now used to produce 45nm devices, many fundamental questions remain as to its stability and crystallisation pathway under the required fabrication
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conditions. Hf$_{x}$Si$_{1-x}$O$_2$ has also been studied due to its higher crystallisation temperature as previously mentioned. In this section both HfO$_2$ and Hf$_{x}$Si$_{1-x}$O$_2$ materials will be considered. Thin films are generally made by MOCVD or ALD and temperatures of up to 1000°C are typically used during the annealing of the wafers.

1.4.1 Crystallisation and phase segregation

Monoclinic HfO$_2$ (m-HfO$_2$) is the stable room temperature phase of HfO$_2$ when it crystallises. In the bulk m-HfO$_2$ transforms into tetragonal HfO$_2$ (t-HfO$_2$) at temperatures of about 1750°C which then changes to the cubic phase at 2600°C, finally melting above 2800°C. If pressure is applied (e.g. >3.5GPa) the orthorhombic phase can also form though this has rarely been observed experimentally in bulk samples$^{13-17}$.

The temperature at which HfO$_2$ is deposited effects the layer morphology. For example Aarik $et$ $al.$$^{18}$ note that deposition by ALD at 225°C resulted in an amorphous film, while deposition at temperatures of 300°C or above resulted in crystalline films as-deposited. Others confirm this$^{19}$. Triyoso $et$ $al.$$^{20}$ observe that subsequent crystallisation of a film deposited at 300°C does not occur until an annealing temperature of 800-900°C for 2.5-25nm films. However, contradictory results indicate that 20nm films deposited at 300°C are polycrystalline after deposition$^{21}$, while Bohra $et$ $al.$$^{22}$ find that as-deposited samples remain amorphous up to 600°C. The discrepancy in findings indicate that there are factors other than temperature which contribute to the crystallisation of the film: reactants, thermal history, and the presence of a capping layer being some of these.

There is also some debate regarding the phase into which the thin film first crystallises. Because m-HfO$_2$ is the stable room temperature phase, it is assumed that m-HfO$_2$ forms on crystallisation, and in many cases this is reported (see references $^{18,21-24}$) either on deposition or after a high temperature anneal. However orthorhombic, tetragonal and cubic phases have also been observed$^{18,21,22,25,26}$ by grazing incidence x-ray diffraction (XRD) and electron diffraction. Maria $et$ $al.$$^{8}$ suggested that film thickness (5, 10 and 20nm) did not affect the phase of the first crystalline product.

Alloying HfO$_2$ with another compound such as SiO$_2$ can suppress crystallisation of HfO$_2$. The HfO$_2$-SiO$_2$ phase diagram (Appendix 1) is incomplete since little work had been carried out on Hf$_{x}$Si$_{1-x}$O$_2$ compounds until recent years. Because Zr and Hf are
isomorphous it has been assumed that their phase diagrams are similar and so the crystallisation pathway has often been deduced from the ZrO$_2$-SiO$_2$ phase diagram (also found in Appendix 1). However experimental data shows that Hf$_x$Si$_{1-x}$O$_2$ and Zr$_x$Si$_{1-x}$O$_2$, and similarly HfO$_2$ and ZrO$_2$, do behave differently when subjected to heat.

Results for thin film Hf$_x$Si$_{1-x}$O$_2$ samples in terms of crystallisation temperatures and phase formation are varied and primarily dependent on the film composition. It is known that SiO$_2$ can increase the crystallisation temperature of HfO$_2$ and also stabilise the high temperature t-HfO$_2$ phase at lower temperatures$^{8,27}$. For example Stemmer et al.$^{28}$ note that their 4nm ALD samples Hf$_x$Si$_{1-x}$O$_2$ (x = 0.8, 0.6 and 0.4) all contain crystalline particles after annealing at 1000°C. While the x = 0.8 sample has fully crystallised, this is not the case for x = 0.6 and 0.4 where amorphous phase segregation is also present. Maria et al.$^8$ also note this amorphous phase separation for x = 0.5 samples. This separation occurs between 700-800°C before starting to nucleate HfO$_2$ at ~800°C. Crystallisation temperature also increases with increased SiO$_2$ content, varying from ~550°C where x = 1.0 to ~1000°C when x = 0.3, but for x = 0.25 no crystallisation was found. Similar phase separation is found in HfSiON films$^7$ though Ikarashi et al.$^{26}$ note that whilst phase segregation and crystallisation have occurred within Hf$_{0.5}$Si$_{0.5}$O$_2$, the same sample that has been nitrided only shows a hint of phase segregation in a HAADF-STEM image and no crystallisation has occurred after annealing at 1000-1100°C. The explanation given for this is that diffusion of Hf allows the Hf$_x$Si$_{1-x}$O$_2$ layer to segregate into HfO$_2$ and SiO$_2$ rich regions, resulting in crystallisation. They hypothesise that when N is present, N-Si bonds form within the layer, inhibiting diffusion of Hf and hence no crystallisation is observed in these films under identical annealing conditions.

Crystallisation of Hf$_x$Si$_{1-x}$O$_2$ samples is reported as monoclinic, tetragonal$^{7,8,28}$ or orthorhombic$^{26,29}$. Though the data is limited, one report indicates that when the percentage of HfO$_2$ is high, crystallisation directly into m-HfO$_2$ occurs$^{28}$. Where the HfO$_2$ ratio was lower (i.e. x = 0.6 or less), t-HfO$_2$ was the first to form. This then transforms to m-HfO$_2$ after heating to higher temperature$^8$. Whilst in most cases m-HfO$_2$ is the dominant phase, there are also reports of orthorhombic being the only phase present in Hf$_x$Si$_{1-x}$O$_2$ samples$^{26}$. 

To try to understand the variation in crystallisation temperatures, phases and dependence on composition, work has recently been carried out by Maria et al.\textsuperscript{8} and Stemmer et al.\textsuperscript{28} to extend the current HfO\textsubscript{2}-SiO\textsubscript{2} phase diagram using experimental results (see Appendix 1). The HfSiO\textsubscript{4} crystalline phase, though predicted by the current HfO\textsubscript{2}-SiO\textsubscript{2} phase diagram, has only been observed twice at 1100°C\textsuperscript{30} and 1400°C\textsuperscript{23}, but in the latter case not without the sample being heated for a prolonged period of time. With this phase effectively missing the phase diagram can be considered as metastable. Stemmer et al.\textsuperscript{28} argue that spinodal decomposition can be assumed in the phase diagram and accounts for the experimental observations. An updated phase diagram for HfO\textsubscript{2}-SiO\textsubscript{2} can be found in reference \textsuperscript{8}. Their study is particularly in relation to Hf\textsubscript{x}Si\textsubscript{1-x}O\textsubscript{2} thin films which have undergone a rapid thermal anneal, though the interpretation can also be extended to bulk materials. Their premise is that an initially amorphous sample consisting of some ratio of HfO\textsubscript{2}:SiO\textsubscript{2} will try to lower its free energy by crystallising into its constituent phases. Within the amorphous material the Hf rich regions will expel Si from them until they reach the composition defined by the extension of the spinodal. If the temperature at which this occurs is above the glass transition temperature of the HfO\textsubscript{2}, the HfO\textsubscript{2} rich regions will crystallise. If the annealing temperature is below the glass transition temperature the film will remain in a chemically separated state with HfO\textsubscript{2} and SiO\textsubscript{2} rich regions. The crystallisation mechanism outside of the miscibility gap differs in that crystallisation is controlled by nucleation and growth of the phase if the temperature is above the glass transition temperature. Below this temperature the film will be homogeneous and no separation of the phases will have occurred. From the phase diagram in Ref\textsuperscript{28} this will occur when the sample is HfO\textsubscript{2} rich (\textasciitilde80\% HfO\textsubscript{2}).

1.4.2 Interfaces and changes in layer thickness

It is not easy for a good interface to form between a high-\(\kappa\) material and the silicon substrate. To aid this process a thin (usually \textless1nm) chemical oxide layer (SiO\(_x\)) is deposited on top of the Si substrate and the high-\(\kappa\) material deposited on top. During processing this SiO\(_x\) layer may grow, most likely due to oxygen diffusion\textsuperscript{23,31} and Bohra et al.\textsuperscript{22} note that as the annealing time is increased the SiO\(_x\) layer thickness also increases in the case of an HfO\(_2\) film. Oxygen diffusion has been considered in density functional theory (DFT) calculations\textsuperscript{31} as well as Hf, where Hf also found to diffuse towards the interface to satisfy dangling bonds. Others\textsuperscript{19} suggest that Si diffuses from the Si substrate into the HfO\(_2\), again resulting in a widening of the SiO\(_2\) layer. However
care is needed in the interpretation of SiO$_2$ layer widths from TEM images as studies have found that electron beam irradiation significantly widens the SiO$_2$ layer and induces crystallisation$^{32,33}$.

After annealing the width of the high-κ layer is also reported to change$^{20}$. Samples exposed to a higher deposition temperature result in a smaller change in width after annealing. The change in layer width is thought to be due to densification of the film as the amorphous-to-crystalline transition takes place. Samples which are already partially crystalline (i.e. those that were deposited at higher temperature) have less change in film thickness after annealing. Roughening of interfaces is also reported, particularly at the HfO$_2$/TiN interface, but also to a lesser extent at the SiO$_2$/HfO$_2$ interface$^{21,33,34}$. This is also related to the degree of crystallinity – the more crystalline, the rougher the interface – or of new phases forming$^{35}$.

Electron energy-loss spectroscopy (EELS) and x-ray photoelectron spectroscopy (XPS) are being used to probe interfaces on the atomic level. One of the challenges of this work is to be able to distinguish between overlapping grains of different materials due to a rough interface, intermixing between constituent materials or whether in fact a new ‘phase’ has formed. To try to better understand these effects it is necessary to combine experimental work with modelling of these spectra$^{24,32,35,36}$.

### 1.4.3 Dopants and Defects

A number of defects can be found within the gate stacks. Firstly impurities may result from the preparation method used. Triyoso et al.$^{21}$ report the presence of Cl$^-$ impurities which result in void formation within the films. The lower the deposition temperature the more Cl$^-$ ions there are incorporated into the high-κ layer. Voids are clearly not desirable due to them being a key source for diffusion of ions and a leakage current pathway. Chlorine impurities are found in films deposited by Atomic Layer Deposition (ALD), but high quantities of C are found in Metal Oxide Chemical Vapour Deposition (MOCVD) prepared samples. Docherty et al.$^{33}$ report the presence of excess oxygen resulting from the glue used to make TEM cross-sections. This causes widening of the SiO$_2$ layer.

Another area of interest is nitrogen incorporation in the thin film. Nitrogen may be incorporated into the film intentionally or unintentionally due to the N$_2$ or NH$_3$ purges
that take place between depositions. This may be responsible for some of the interface phases that form. It has been found that as annealing temperature is increased, N incorporation increases\textsuperscript{19}. It was also found that N incorporation occurs with Si diffusion. However, N incorporation is sometimes wanted as it has been found to inhibit crystallisation\textsuperscript{26,37}.

Modelling of interfaces is of great importance for understanding what is actually occurring at them\textsuperscript{31,38}. The HfO$_2$/gate or Hf$_x$Si$_{1-x}$O$_2$/gate interfaces are poorly understood and little modelling work has been carried out on them. In contrast the Si/HfO$_2$ or SiO$_2$/HfO$_2$ interface has been studied in greater detail. For example Hakala et al.\textsuperscript{31} have modelled both stoichiometric and non-stoichiometric Si-SiO$_x$-HfO$_2$ interfaces. They find that by modelling a non-stoichiometric interface containing defects, that the bonding of the Hf atoms is insufficient resulting in diffusion of the Hf towards the Si surface. This results in Hf-Si bonds which are metallic in nature and dangling bonds of Hf. These dangling bonds are ideal for trapping of interfacial charge and result in the defect states appearing in the band gap. This can be partially overcome by passivating this layer with oxygen such that a wider band gap is formed where there are not defect states. Defect free interfaces are much more stable but they are still able to form SiO$_x$ easily.

1.4.4 Influence of gates

With the introduction of Hf-containing gate dielectrics it has become necessary to change the gate material used from poly-Si. Poly-Si is incompatible with HfO$_2$ as a gate oxide material due to formation of interfacial silicides which result in high leakage current, and the poly silicon results in Fermi level pinning which is undesirable. It has become necessary to replace both the gate and the gate oxide at the same time. Of the possible metals and metal composite possibilities, TiN has become a leading candidate as a suitable gate material.

It has been noted by some that the crystallisation behaviour of the gate stacks differs according to high-\kappa layer thickness and whether a gate is present during processing or not. Triyoso et al.\textsuperscript{21} carried out a study on 3nm and 20nm HfO$_2$ films, looking at the effect of a 7nm TiN cap on the HfO$_2$ layer after annealing to 1000°C for 5s. It was found that samples which had been uncapped produced films that contained lots of voids, but those that had had their caps removed were smooth and were free of voids.
Annealing without a capping layer resulted in crystallisation of m-HfO$_2$. However, with a capping layer, t-HfO$_2$ also crystallised. The tetragonal phase increased with decreasing deposition temperature. It is suggested that due to the 3-5% volume expansion that occurs during the tetragonal to monoclinic phase transformation, the presence of a capping layer provides a mechanical stress that stops that transformation occurring and stabilises the tetragonal phase. The physical barrier of the gate prevents any particular grains from growing upwards which would result in voids.

Though a replacement gate has had to be found for HfO$_2$, poly-Si is still compatible with Hf$_x$Si$_{1-x}$O$_2$ as the gate oxide material. Because silicon is incorporated into the oxide, the problems associated with the interfaces in HfO$_2$ are not such a problem in Hf$_x$Si$_{1-x}$O$_2$. However, a compromise between dielectric constant and good interfaces may need to be found.

### 1.5 Bulk Powders

To aid interpretation of results from thin films, it is important to gain an understanding of the material as it behaves in bulk form and hence use these results to understand the crystallisation of thin films.

Because of this increased and widespread interest in HfO$_2$ containing compounds it has become increasingly important to gain a detailed understanding of the chemistry involved in the crystallisation of HfO$_2$. Although in many respects similar to ZrO$_2$, the HfO$_2$ system has not been characterised extensively. The information available in the literature is contradictory for Hf-containing bulk samples. Starting materials, temperature, heating rate, heating environment and pH are all factors affecting the crystallisation process.

The phase changes occurring for HfO$_2$ and ZrO$_2$ in the bulk are
The monoclinic phase is stable at room temperature, transforming into tetragonal hafnia via a martensitic phase transformation and then cubic at higher temperatures\textsuperscript{39}. This transformation results in all the atoms in the structure moving simultaneously without any change in connectivity between them. On cooling the transformation is reversed, the tetragonal phase transforming to monoclinic with a $\sim$5\% volume expansion\textsuperscript{15}. There are also two orthorhombic phases which form when subjected to high pressure\textsuperscript{13,15,17}. In the discussion of HfO$_2$ it is often reported that because HfO$_2$ is isomorphous with ZrO$_2$, that their behaviour is similar. It is therefore assumed that HfO$_2$ and ZrO$_2$ exhibit near identical properties. However, a simple comparison of the crystallisation pathway immediately reveals there are differences that must be taken into account when interpreting data. Though the crystalline phases formed are the same, HfO$_2$ is more stable with a much higher temperature required before phase transformations take place. Because ZrO$_2$ has been studied extensively – interest in HfO$_2$ has been much more recent – it is still necessary to look at ZrO$_2$ as a comparison, so long as the differences in crystallisation pathway are kept in mind.

Firstly a brief review of the structures being investigated is required (Fig 1.3). The cubic phase of HfO$_2$ has the fluorite (CaF$_2$) structure: the metal atom sits at the centre of a cube in 8-fold coordination to 8 oxygen atoms. The tetragonal structure is a distorted cube with Hf still having 8-fold coordination, whereas the monoclinic and orthorhombic phases have Hf$^{4+}$ in 7-fold coordination\textsuperscript{17,40}. 

\[\begin{array}{ccc}
\text{HfO}_2 & \text{monoclinic} & 1720^\circ\text{C} & \text{tetragonal} & 2600^\circ\text{C} & \text{cubic} \\
\text{ZrO}_2 & \text{monoclinic} & 1170^\circ\text{C} & \text{tetragonal} & 2370^\circ\text{C} & \text{cubic} \\
\end{array}\]
From the phase diagram in Appendix 1 m-HfO₂ is the stable room temperature phase due to the covalent nature of the Hf-O bond favouring 7-fold coordination. Transformation to the tetragonal phase on heating is generally attributed to the formation of oxygen ion vacancies in the lattice which stabilise the tetragonal phase. The cubic phase is stabilised by a higher concentration of O vacancies. In both cases the oxygen vacancies form as the lattice expands due to heating. In this situation, while the structure is tetragonal or cubic, the Hf⁴⁺ retains a coordination number of ~7, due to the oxygen vacancies. A number of orthorhombic structures are also found in the literature, all of which were formed under high temperature and pressure (see Tang et al.¹⁶, Haines et al.⁴¹ and Ohtaka et al.¹⁴). The corresponding temperature-pressure phase diagram can be found in Appendix 1.

Though the m-HfO₂ → t-HfO₂ → c-HfO₂ transformation is the expected crystallisation pathway, results from bulk samples differ somewhat. We will consider both HfO₂ and ZrO₂ in the discussion. For ZrO₂, though the first phase to crystallise on heating is expected to be m-ZrO₂, there are many reports of t-ZrO₂ forming at low temperatures, directly from the amorphous material⁴²-⁴⁷. Some observe t-ZrO₂ formation at low temperatures (~400°C) which then transforms to the monoclinic phase on heating⁴⁴-⁴⁷. It is suspected that this will subsequently transform into a high temperature tetragonal phase on further annealing.
The alternative method to induce tetragonal stabilisation in ZrO\textsubscript{2} at low temperatures is by doping with a trivalent cation such as Y\textsuperscript{3+}. This effectively creates an oxygen vacancy within the lattice which has the same effect as described above in terms of the structure\textsuperscript{40,48}. There are many more effects observed in ZrO\textsubscript{2}, but those mentioned here show that the ZrO\textsubscript{2} system is complicated and not as simple as is sometimes perceived. Since the main focus of this thesis is on Hf-containing oxides, the discussion will now focus more on those materials.

### 1.5.1 HfO\textsubscript{2} bulk powders

The work carried out on HfO\textsubscript{2} and Hf\textsubscript{x}Si\textsubscript{1-x}O\textsubscript{2} in bulk materials in the past has been limited, though because of interest in the semiconductor industry, there is a greater need to understand their bulk properties. As with ZrO\textsubscript{2}, HfO\textsubscript{2} is a complicated system and not well understood. Although expected to follow the monoclinic-to-tetragonal-to-cubic crystallisation pathway, in reality factors such as starting materials, pH and thermal history greatly affect this. Ushakov \textit{et al.}\textsuperscript{23} present results for HfO\textsubscript{2} bulk powders. They show from XRD and differential scanning calorimetry (DSC) results that starting materials have a significant effect on both the crystallisation temperature and phase, increasing the crystallisation temperature by \textasciitilde370°C and forming the tetragonal rather than monoclinic phase on crystallisation. The t-HfO\textsubscript{2} crystals are found to have a smaller crystallite size and larger surface area than the m-HfO\textsubscript{2} crystals. (Different preparation routes were used in each case). The t-HfO\textsubscript{2} forms under normal ambient and is retained after cooling to room temperature. This is contrary to many of the results found for ZrO\textsubscript{2}. As the sintering temperature of the amorphous material is increased the crystallite size (if the monoclinic phase forms first) increases\textsuperscript{49}. Štefanić \textit{et al.}\textsuperscript{50,51} studied crystallisation during hydrothermal analysis and find that the pH of the starting materials also influences the temperature and crystalline phase formed on crystallisation. Unlike sol-gel preparation methods, when t-HfO\textsubscript{2} is the first phase to form on crystallisation, the sample needs to be held at temperature for much less time than if m-HfO\textsubscript{2} is the first phase to form at the same temperature. However, tetragonal formation only occurs when the pH = 13. At all pH values below this, the monoclinic phase always forms first. The tetragonal phase then transforms into the monoclinic phase if held at temperature for longer.
1.5.2 $Hf_xSi_{1-x}O_2$ bulk powders

Whilst $Hf_xSi_{1-x}O_2$ has also been studied, the main advantage over $HfO_2$ is that it increases the crystallisation temperature of $HfO_2$ and hence is more stable at higher temperatures\(^8\). According to the $HfO_2$-$SiO_2$ phase diagram, $HfSiO_4$ should be stable at temperatures below 1400°C, however only Kanno\(^30\) has observed this at 1100°C and Ushakov et al.\(^23\) observed it after heating to 1400°C for a prolonged time. Surprisingly, the main phase to form at all lower temperatures is $t$-$HfO_2$\(^23;27;39;52\) though some also report $m$-$HfO_2$\(^52\). Ushakov et al.\(^27\) find that the main crystalline phase for all samples containing $SiO_2$ is $t$-$HfO_2$. As the percentage of $SiO_2$ in the sample is increased the crystallisation temperature also increases from \(~750°C\) at $Hf_{0.9}Si_{0.1}O_2$ to \(~1100°C\) at $Hf_{0.1}Si_{0.9}O_2$ compositions. Only the $Hf_{0.9}Si_{0.1}O_2$ sample transforms into the $m$-$HfO_2$ on cooling, the samples with $x<0.9$ retain their tetragonal structure. As the $SiO_2$ content is increased, the crystallite size decreased. They also note that while crystallisation has a specific onset temperature from both XRD and DSC analysis, TEM images of these samples, heated below their crystallisation onset temperature, exhibit crystallinity within the sample, not detected by the other two techniques. Mountjoy et al.\(^53\) also note no crystallinity up to \(~750°C\) when $SiO_2$ is in abundance, and Neumayer and Cartier\(^52\) demonstrate that crystallisation is directly into the tetragonal phase at \(~900°C\) which then transforms into the monoclinic phase on heating to 1100-1200°C.

1.6 Project Outline

With this in mind it is clear that a more detailed understanding of the chemistry of $HfO_2$ and $Hf_xSi_{1-x}O_2$ is required both in bulk and thin film environment. Firstly, the main experimental techniques used to achieve this are outlined in Chapter 2. These are employed to achieve the results in Chapters 3, 4, 7 and 8.

The chemistry and in particular crystallisation pathways of $HfO_2$ and $Hf_xSi_{1-x}O_2$ are investigated in Chapters 3 and 4. Bulk powders were prepared using two different sol-gel preparations routes. These are described and the results from each presented in Chapters 3 and 4 respectively.
Chapters 5-7 cover electron energy-loss spectroscopy – both in the form of modelling and experimental results. The theory surrounding the two modelling techniques implemented is discussed and the specifics of Feff8 and Wien2k packages are outlined (Chapter 5). Materials modelled are those relevant to this thesis and also for wider CMOS applications. These include investigation into bulk materials, interface reaction products and what happens to the EELS spectra at interfaces between gate and high-κ material (Chapter 6). These are then used for comparison with EELS results from the bulk Hf containing samples from Chapters 3 and 4 (Chapter 7).

The effects on Hf$_x$Si$_{1-x}$O$_2$ thin films of different processing conditions is then discussed in Chapter 8.

Each chapter contains discussion and conclusions, which are then brought together in Chapter 9. Areas for further work are mentioned following on from the conclusions.
2 Instrumentation and Theory

2.1 Thermal Analysis

“Thermal analysis” covers a number of techniques where a physical property of a specimen, such as mass loss, is measured as a function of temperature or time. The three main techniques used in this investigation were differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) which measure the temperature difference, heat flow and mass change, respectively.

2.1.1 Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)

In DTA the difference in temperature of a sample relative to that of an inert reference material is measured as a function of temperature or time. The sample and reference material are heated simultaneously, at a constant rate. If phase changes, decomposition reactions or any other event requiring a change in thermal energy take place, an exotherm (positive peak) or endotherm (negative peak) will appear on the graph. This is dependent on the temperature difference between the reference material and the sample. The area under a DTA peak is proportional to the change in enthalpy and the mass of the sample taking part in that particular thermal event. A schematic of a typical thermal analysis setup is found in Fig 2.1. An inert reference material, in our case alumina (Al₂O₃), and a quantity of sample are measured into either platinum or alumina crucibles and placed on the balance with a thermocouple located underneath each crucible. The balance is surrounded by a furnace such that the whole of the sample is heated simultaneously. Flowing gas may also be passed through the furnace depending on the experimental requirements.

A DSC works on a similar basis but the design differs from DTA. Both samples (and crucibles) sit on a heat flux plate. When a thermal event occurs, the difference in temperature between the sample and the reference results in a flow of heat across the plate. By careful calibration of the system the signal can be converted to measure the
quantity of heat flow and therefore enthalpies can be measured directly using Equation 2.1:

$$\text{Area} = \frac{m\Delta H}{K}$$  \hspace{1cm} \text{Eqn. 2.1}$$

where $m$ is the mass, $\Delta H$ is the change in enthalpy and $K$ a constant. For DSC $K$ is independent of temperature, but in DTA it is temperature dependent.

![Schematic of thermal analysis set-up](image)

**Figure 2.1:** Schematic of thermal analysis set-up

### 2.1.2 Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) measures the difference in mass that occurs during a heating process. Heat is applied at a constant rate to a sample and reference simultaneously and the mass is measured as a function of time or temperature. Mass loss provides information on decomposition or loss of volatile species in the sample. The temperature range over which the mass change occurs is dependent on the heating rate, crystallite size and atmosphere, although the initial and final weights are independent of this. In this work the TGA was recorded simultaneously with the DTA or DSC.
2.2 X-ray diffraction (XRD)

X-ray diffraction is a technique used to determine the crystal structure of a compound. The elastic scattering of x-rays by a crystal results in a diffraction pattern. X-rays have a wavelength of the order of 1Å which is close to the atomic spacing in a crystal lattice which is ~2-3Å. Because the wavelength of the x-rays and the lattice spacing of the crystal are similar, elastic scattering of x-rays from the repeating structure of the crystal lattice will result in a diffraction pattern from the diffracted beam. X-rays are generated by accelerating electrons from a filament (often tungsten) towards a metal target at 30-40kV. Copper is the target of choice due to its penetration depth and high intensity per yield of copper. These electrons have sufficient energy to ionise the 1s electrons in copper leaving behind a hole in the 1s shell. Electrons from the 2p or 3p states drop into the 1s vacancy emitting a photon in the process. The wavelength of the photon emitted during the $2p \rightarrow 1s$ transition gives rise to the Cu K$_\alpha$ radiation (illustrated in Fig 2.2) and similarly the photon emission from the $3p \rightarrow 1s$ transition is Cu K$_\beta$. K$_\beta$ radiation is less intense and so is filtered out to avoid confusion between the two wavelengths. K$_\alpha$ radiation has much greater intensity as the probability of this transition occurring is much higher. The K$_\beta$ radiation is removed by passing the x-ray beam through a filter - the K$_\beta$ and ‘white’ radiation is absorbed but allows K$_\alpha$ to pass through. The K$_\alpha$ peak in the diffraction pattern is sometimes observed as having a shoulder on it or the peak is split. This occurs because K$_\alpha$ radiation resulting from the $2p \rightarrow 1s$ transition has two different wavelengths due to the transition by electrons from the two different spin states within the 2p energy level. This results in a slight difference in wavelength – $K_{\alpha 1}\ (\lambda=1.54051\text{Å})$ and $K_{\alpha 2}\ (\lambda=1.54433\text{Å})$ – which causes peak splitting in the diffraction pattern. Sometimes the diffractometer can resolve these two lines – $K_{\alpha 1}$ is always the more intense line at slightly lower angles. If this is the case the $K_{\alpha 2}$ line can be removed from the diffraction pattern and only the $K_{\alpha 1}$ wavelength used. If, however, they cannot be resolved then the average wavelength of K$_\alpha$ ($\lambda=1.5418\text{Å}$) is used to determine peak positions, lattice spacing, strain and crystallite sizes.
Once generated the x-rays leave the x-ray tube via a beryllium window. Only a small proportion of the energy of the electron beam is converted into x-rays; most of the beam is turned into heat which means that the x-ray tube has to be continually cooled. The x-rays then hit the sample and are diffracted if the sample is crystalline.

In its simplest form diffraction from crystalline material follows Bragg’s Law:

\[ n\lambda = 2d \sin \theta \] \hspace{1cm} \text{Eqn. 2.2}

where \( n \) is the number of wavelengths (\( \lambda \)); \( d \) is the spacing between lattice planes and \( \theta \) is the Bragg angle.
The incident x-rays are scattered from adjacent planes within the crystal and an interference pattern formed. The x-rays interfere constructively if scattered at the Bragg angle, allowing the d-spacing for the crystal to be calculated (Fig 2.3). Each crystal structure has a characteristic ‘fingerprint’ diffraction pattern due to the different space groups, lattice spacing and atoms present in the system. For this thesis the powder diffraction technique was employed. Because the grains within the powder are oriented randomly in the sample, all of the allowed reflections will be probed.

The following explanation of how diffractometers work will concentrate on the specific instruments used to gather the results presented in this thesis.

### 2.2.1 Ambient XRD

The diffractometer is first calibrated using the (111) peak from a polycrystalline silicon standard. For the experiments a thin layer of powder is deposited on a silicon single crystal disc which is cut in such a way that no silicon peak appears in the XRD scan. A little acetone or isopropanol is used to help adhesion of the powder to the disc. An X-ray diffraction pattern is then collected after specifying the step size and time per step. It is assumed that the crystals are in a random orientation. However, if the crystals are in a specific orientation on the silicon the peak intensities of the diffraction pattern will not reflect that of a randomly oriented powder. It is therefore important that the powder is very fine to stop this happening. Analysis of the diffraction pattern allows us to identify crystalline phases of a sample by comparison with already existing experimental and calculated powder diffraction files.

---

**Figure 2.4: Schematic of XRD set-up**
Chapter 2 Instrumentation and Theory

The set up of the equipment is slightly different for each of the experiments so it is worth mentioning how these work. Fig 2.4 shows a schematic of the 0-20 ambient XRD setup as implemented on the Philips PW1200 series diffractometer. In this set up, the x-ray tube is not moved. The angle between the incident x-rays and the sample, and the outgoing x-rays and the sample, must be kept constant. To maintain this both the sample and the detector move, the sample by θ and the detector by 2θ (known as a 0-20 scan).

\subsection*{2.2.2 HTXRD – CNMS}

High temperature x-ray diffraction can be carried out on dedicated instruments. Two of these were used for this project with most of the data being recorded at the Centre for Nanophase Materials Science (CNMS) at Oak Ridge National Laboratory (ORNL). Instead of the detector and sample moving during the experiment as with the ambient XRD setup, the sample is kept horizontal and both the x-ray tube and detector are moved through the same angle (θ-θ configuration).

![CNMS HTXRD setup](image)

The sample itself is contained within an alumina holder of diameter 15mm and depth 2.5mm. The sample is fully enclosed within the heater so the whole of the sample is heated simultaneously. It is possible to pass gas through the chamber to study the
effects of heating in the presence of an inert environment. The heating and data collection is computer controlled using the Philips X’Pert Data Collector software. Using temperature controlled XRD the evolution and crystallisation of a species can be monitored as the temperature is varied. If the same sample were heated in a furnace and then cooled before an XRD scan then some of these features may not be observed. Using this technique many features can then be correlated with DTA results. For all experiments carried out on this instrument an automatic divergence slit was used causing the area of the sample irradiated to remain the same throughout the course of the experiment.

**2.2.3 HTXRD – Imperial**

The Imperial XRD system is similar to that at the CNMS. The crucial difference is in how the sample is heated. Here the powder sample is mounted on a thin piece of platinum foil (0.05mm in thickness) which is placed on a platinum-rhodium heating strip. This is then placed inside the XRD chamber and similarly controlled using the Philips software ‘X’Pert Data Collector’. This method allows the sample to be heated to higher temperatures. There are however, a number of problems associated with this set up. Firstly this equipment is older and not fitted with a fast acquisition scanner as the CNMS equipment is. This means that to gain a good signal to noise ratio the scans require a much longer time to complete. A sample being held at temperature for a long time whilst a scan is taken can alter the crystallisation pathway if a sample is affected by its thermal history. The other problem is in the temperature control and is related to the type of heater used which can result in large errors in temperature. This is discussed more in Chapter 3. In this experimental set up a fixed divergence slit was used which results in the area of sample irradiated varying as the angle changes.

**2.2.4 Particle Sizing**

Calculation of the crystallite size can be done either manually or using the Rietveld Refinement technique. Rietveld Refinement was originally developed for the refinement of neutron diffraction data which is of far superior quality than XRD data. Whilst it can be used to determine some parameters from XRD data such as lattice parameters, its estimate of crystallite sizes or strain is not particularly accurate. Rietveld refinement was carried out using the X’Pert Highscore Plus software and was only used to estimate crystallite sizes from data taken using the fast acquisition scanner
at the CNMS. Crystallite sizes were also calculated manually for comparison and for data sets where Rietveld refinement was not possible.

The two equations used to calculate crystallite sizes manually are:

\[ t = \frac{0.9\lambda}{B \cos \theta_B} \]  \hspace{1cm} \text{Eqn. 2.3}

\[ B^2 = B_M^2 - B_S^2 \]  \hspace{1cm} \text{Eqn. 2.4}

where  
- \( t \) = thickness of crystal (Å),  
- \( \lambda \) = wavelength of the incident x-rays (Å)  
- \( B \) = line broadening (rad)  
- \( B_M \) = measured peak width (rad)  
- \( B_S \) = peak width of standard (rad)

When calculating crystallite sizes, instrumental broadening must first be taken into consideration. From this the line broadening due to crystallite size effects can be calculated using the Warren Formula (Eqn. 3) if the peak width of a standard, mixed with the powder, can be measured. The wavelength of the incident radiation is known and so together with the calculated line broadening and the Bragg angle, the average crystal thickness, \( t \), can be calculated (Eqn. 2). Broadening increases at higher angles and so to obtain a realistic value for thickness, the standard material must have a peak close to the peak of interest in the powder scan. Depending on the XRD technique employed either the silicon (111) peak was used or the platinum (111) peak.

### 2.3 Electron microscopy

#### 2.3.1 The Electron Microscope

Three microscopes were used to carry out the work in this thesis: an FEI Tecnai F20 (University of Glasgow), a JEOL 2010 and a monochromated FEI Titan 80/300 (both Imperial College London). Very little comment will be made about the JEOL 2010 instrument - it was only used for a small amount of imaging. The majority of the discussion will be based around the Tecnai microscope with comment on how the Titan differs.
A diagram of the upper column of the Tecnai is shown in Fig 2.6. The electron source in both the Tecnai and Titan is a field emission gun (FEG) which consists of a fine tungsten tip oriented in the [100] direction, covered with a thin layer of ZrO$_2$ which helps reduce the work function of the material allowing electrons to tunnel out of the tungsten. This type of electron emitter is known as a “Schottky” emitter (or ‘thermally assisted field emission gun’). The electric field ($\varepsilon$) applied to the tip follows the equation:

$$\varepsilon = \frac{V}{r}$$

where $V$ is the voltage applied to the tip and $r$ the spherical radius (~1$\mu$m) of the tip. The field emission tip sits above a double anode. To the first anode a positive voltage is applied whereby electrons are extracted (literally pulled) from the tip. A typical operating voltage for our experiments was between 3.8-4.5kV. The second anode acts as an accelerator, to accelerate the electrons through the applied field. The Titan was typically operated with an accelerating potential of 300kV and the Tecnai and JEOL at 200kV. The combination of the two anodes effectively acts as an electrostatic lens, focusing the electron beam to the gun cross-over point. The tip plus two anodes make up the gun lens system. This determines the beam position and the effective size of the source.
The Schottky tip is kept under ultra high vacuum (UHV) at $\sim 7 \times 10^{-9}$ Torr and typically reaches temperatures of $1800^\circ$C during operation. The heating of the tip helps to keep the surface defect free. One must always be careful when increasing the extraction voltage of the tip. The voltage must be increased very slowly so as not to induce mechanical shock which can cause the tip to fracture. So long as it is treated with care a tip can typically last for 6000 working hours.

The JEOL 2010 on the other hand uses a LaB$_6$ filament known as a thermionic emission source. In this case the tip is heated sufficiently that the electrons overcome the work function of the material and are emitted from the tip. The electrons are accelerated through a potential difference by the anode. Between the tip and the anode is the Wehnelt which acts as a lens, focusing the electron beam to a point (gun crossover point) between the Wehnelt and the anode, by applying a small negative bias to the Wehnelt. This region is referred to as the gun lens system. Thermionic sources give a less coherent electron beam than the FEG hence why the FEG is more suitable for detailed STEM and EELS work.
The gun lens system in the Titan microscope differs from the Tecnai in that a monochromator sits within the lens system. The monochromator selects a narrow energy range of the emitted electrons. This reduces the energy spread of the electron beam hence increasing the energy resolution, before it is then accelerated through the anode. Use of the monochromator results in a loss in beam intensity and a balance needs to be found between intensity and energy resolution depending on the experiment being carried out. If the beam intensity is greater then more electrons are allowed to contribute to the beam, but in turn these have a larger energy spread. Alternatively, fewer electrons are allowed through, reducing the energy spread but also reducing the intensity of the beam. In the Titan the beam always passes through the monochromator but it is only when the monochromator is in an excited state that the beam is referred to as being monochromated. The energy resolution of a monochromated beam is typically below 0.2eV with 0.12eV possible on the Imperial College Titan. The monochromator was not used in its excited mode for any of the results presented in this thesis.

The electron beam then passes through a series of condenser lenses and apertures, the main purpose of which is to turn the electron beam into either a parallel or convergent beam depending on whether TEM or STEM mode are required. The C1 lens forms a demagnified image of the gun crossover which in turn defines the diameter of the electron beam (or probe). This is referred to as the ‘spot size’. The C1 aperture, which sits above the C1 lens, is used to remove any stray scattering from the electron source. The C2 lens is used to produce illumination of the sample controlling the size and brightness of the illuminated area: parallel illumination in TEM; a converged beam for STEM. The C2 aperture sits inside the C2 lens field and is used to define the convergence angle of the beam on the sample. In the Titan there is an additional condenser lens (C3) situated below the C2 aperture. This lens allows greater functionality in the illumination of the sample, and a combination of C2 and C3 working together varies the beam diameter and convergence angle.

The double deflection coils are used to translate or tilt the beam before it reaches the sample. The scan coils apply a magnetic field which in turn deflects the electron beam. When the microscope is operating in scanning transmission mode (STEM) an additional set of scan coils are used. These tilt the beam twice such that the electron beam path is parallel to the optic axis. These move the electron beam so that it scans across the sample.
The specimen itself sits within the objective lens system – marked on Fig 2.6 as the ‘objective TWIN lens’. This is where the height of the sample is set such that it does not shift along the optic axis when the sample is tilted. The plane where this occurs is called the eucentric plane, where the specimen will be in focus and is positioned at the eucentric height on the optic axis. The eucentric plane is the point at which both TEM and STEM are imaged.

The mini condenser lens is used to operate the beam in either TEM or STEM mode (TEM mode or probe mode). A schematic of this is found in Fig 2.7. When operating in microprobe mode (TEM) the mini condenser lens focuses the beam to produce a cross-over point above the objective lens (pre-specimen). The objective lens then focuses the beam onto the sample with parallel illumination. If operating in nano-probe mode for STEM the mini condenser lens is effectively switched off and the pre-specimen objective lens focuses the electron beam down to a spot on the sample.

The lower column (see schematic in Fig 2.8) is used to form the TEM images and diffraction patterns. Below the post-specimen objective lens is the objective aperture. This is situated in the back focal plane where a diffraction pattern forms before being recombined to form an image in the image plane (i.e. where the screen is situated). For viewing a diffraction pattern the back focal plane (objective aperture removed) becomes the object for the diffraction lens, the strength of which can be altered to give a diffraction pattern on the viewing screen. Similarly, if an image is required the SAD aperture is removed and the intermediate lenses adjusted such that the image plane of

Figure 2.7: Schematic of mini-condenser lens system (a) TEM mode, (b) STEM mode
the objective lens becomes the object plane for the diffraction lens and hence an image is projected onto the viewing screen using the projector lens system.

The image double deflection coils are used to move the image of the sample, or position the beam in the centre of the EELS spectrometer. As well as projecting the image onto the screen the projector lens system allows magnification of the image. A CCD camera is used to record images on both Tecnai and Titan microscopes, and diffraction patterns on the Titan, though great care has to be taken in the latter case so as the intense, non-diffracted beam does not damage the CCD detector. In contrast, photographic film is used to collect diffraction patterns in the Tecnai. In STEM mode images are collected in the high angle annular dark field (HAADF) detector which sits above the viewing screen on the optic axis. This collects electrons that have been scattered to high angles, incorporating electrons where mainly incoherent and elastic scattering events have
occurred. The scattering cross section and therefore resulting contrast is directly proportional to the thickness, \( t \), and \( Z^2 \), with \( Z \) being the atomic number:

\[
Q_{\text{nucleus}} t = 1.62 \times 10^{-24} \left( \frac{N_0 \rho t}{A} \right) \left( \frac{Z}{E_0} \right)^2 \cot^2 \left( \frac{\theta}{2} \right)
\]

**Eqn. 2.6**

where \( Q_{\text{nucleus}} \) is the number of scattering events, \( N_0 \) is Avogadro’s number, \( \rho \) is the density, \( E_0 \) the beam energy and \( \theta \) the scattering angle of the electron.

It is assumed that for TEM samples the sample thickness is fairly uniform hence the contrast observed is mainly due to variation in the atomic number. In STEM the higher the atomic number the brighter that element appears in the STEM image. The HAADF detector has a hole in the centre of it which allows electrons scattered at low angles, not used for STEM imaging, to pass through to other analytical devices such as the EELS spectrometer.

![Figure 2.9: Schematic of EELS spectrometer](image)

The analytical technique of most interest for this thesis is EELS. A schematic of the EELS spectrometer is found in Figure 2.9. The beam passes through the entrance aperture to the spectrometer where any electrons still outwith the required angular range are discarded. The focusing coils consist of a number of quadrupole and sextupole lenses which focus the beam onto the detector. The electrons pass through a magnetic prism which deflects the electrons by 90° and disperses them according to their energy...
– electrons with the greatest energy-loss are deflected the most. This is analogous to white light splitting into its constituent wavelengths as it passes through a prism. A voltage is applied to the drift tube, which is electrically isolated, and allows the energy range collected by the CCD (charge coupled device) detector to be tuned. The beam then passes through a set of multipole lenses which effectively magnify the energy dispersion of the beam before hitting the YAG scintillator which is coupled to a CCD detector. Magnification of the energy dispersion is essential for recording the signal on the CCD detector. The CCD detector is an array of pixels which record information from the incident electron beam. This signal is converted into a voltage which can then be digitised into the required form. The charge that is stored in each pixel in the CCD detector is proportional to the intensity of the incident electron beam. For EELS detection the CCD detector consists of an array of 1024 pixels (for the Enfina) which detect the signal simultaneously (2048 x 2048 pixels for the Tridium). This is known as parallel EELS (PEELS) detection as opposed to serial EELS detection where the signal is recorded pixel by pixel. CCD detectors also pick up ‘dark-current’. This is due to electrons hitting the detector from the surroundings even when no signal is being read. A dark current is usually collected when the shutter to the detector is closed and then subtracted from the acquired signal. The Gatan Enfina 1000 spectrometer is fitted on the Tecnai F20 and the Gatan Tridiem is fitted on the Titan (the JEOL instrument has no EELS capabilities).

2.3.2 Electron Energy-Loss spectroscopy (EELS)

Electron energy-loss spectroscopy (EELS) is a spectroscopic technique carried out in the electron microscope. Analogous to X-ray absorption spectroscopies carried out at a synchrotron where x-rays are used to probe the local atomic structure of a crystal or molecule, electrons are used in-situ in the TEM to determine similar properties – such as local atomic environment, co-ordination number and quantification. Electrons emitted from the gun pass down the column and interact with the specimen. The electron passing through the other side of the specimen may have lost energy due to interactions with the sample. This loss of energy is measured and gives detailed information on the local chemistry, structure and bonding of the sample being analysed.

A number of interactions can occur as the electron passes through the sample for a sample thickness of less than 1 mean free path (mfp) for inelastic scattering (typically less than 100nm for a 100keV electron)\(^55\). The mean free path is different for each
material as it is a measure of the average distance that the electron travels between scattering events. Figure 2.10 shows a typical energy loss spectrum highlighting the main scattering events that occur due to the incident electron which result in a change/loss of energy by this electron. The most common event is for the electron to pass through the specimen having undergone elastic scattering – that is, no energy has been lost by the incident electron though it may have undergone a change in direction. This results in a sharp intense feature at 0eV on the energy-loss spectrum as illustrated in Fig 2.1, known as the zero-loss peak (zlp). The full width half maximum (FWHM) of the peak is determined by the spread of energies of the electrons transmitted from the electron source. This is dependent on the type of emitter used. The spectrometer itself may also affect this energy spread. The FWHM of the zero loss peak (zlp) is quoted as the resolution of the spectrum. The typical working energy resolution from the Glasgow Tecnai F20 is ~ 0.75eV. From the Titan: unmonochromated ~0.6eV and monochromated 0.12eV.

![EELS Spectrum](image)

**Figure 2.10**: EELS spectrum (acknowledgement: M MacKenzie, University of Glasgow)

The area on an EELS spectrum between 0-50eV is known as the low-loss region and includes the zlp. In the energy range ~10-100meV, the vibrations of the atoms in the solid, known as phonons, are detected. However, because of the energy resolution these
features are usually incorporated into the zlp and not observed experimentally. The low-loss region is dominated by the plasmon peak which results from collective oscillations of the valence electrons – the density of the valence electrons determine the energy at which the peak is found, and the plasmon peak width is a function of the rate of decay of the excitation. In thick samples additional peaks at multiples of the plasmon energy are observed which occur after other scattering events. For example these may occur at \(~15-20\text{eV}\) beyond the edge onset of a core-loss excitation and result from more than one excitation by the incoming electron. Other features in the low-loss region, for insulators in particular, are due to interband transitions which arise from a valence electron being promoted to a low-energy state above the Fermi level. By combining the zero-loss peak and low-loss region information on the sample thickness, dielectric function and band-gap can be studied. The thickness of the sample can be calculated from the area’s under the low-loss peaks using the equation:

\[
I_0 = I_e \exp\left(-\frac{t}{\lambda}\right)
\]

Eqn. 2.7

where \(I_0\) and \(I_e\) are the area under the zlp and the total area under the low-loss region respectively, \(t\) is the specimen thickness and \(\lambda\) is the mean free path for the energy loss. Thickness is often quoted as a \(t/\lambda\) value as this is a parameter that can be compared between materials, since \(\lambda\) itself is dependent on the type of material. For EELS a \(t/\lambda\) value of between 0.3 and 0.6 is used. With a value as high as 1 the thickness effects are too large for detailed analysis to be possible.

The core-loss region starts at about 50eV. Typically energy losses up to \(~2000\text{eV}\) can be measured before the signal becomes too weak. Sharp features appear on the decreasing background due to interactions of the incident electron with core-electrons within the atom. These features are known as ionisation edges as they relate to the energy required to promote electrons from the inner shells of the atom to the unoccupied states above the Fermi level (unoccupied density of states (DOS)).

Each core atomic shell has a different binding energy and hence the incident electron loses a different amount of energy depending on the position of the electron it interacts with in the atom. This in turn affects the position in energy of the resultant ionisation edge in the EELS spectrum. This allows the type of atom being probed to be identified. The intensity under the ionisation edge is proportional to the number of atoms present in
the sample and, so long as effects of plural scattering are accounted for, this can be used for quantitative analysis.

Plural scattering can be removed, however this step is not always possible due to difficulties in collecting both low and core loss spectra under the same acquisition conditions. The conditions required for core-loss acquisitions often results in the ZLP being too intense for the detector. Hence the multiple scattering effects cannot always be removed. This is one reason why the dual EELS detector and fast beam switch now being implemented at the University of Glasgow (mentioned in Chapter 2) is of such importance allowing both low-loss and core-loss regions to be collected simultaneously from the same point. This also means that real shifts in edge onsets resulting from changes in local environment can be probed, whereas currently, because the low and core-loss spectra are collected separately, one can never be 100% sure that a shift in the edge onset is real or whether it is due to drift causing a shift in the energy.

Background subtraction from the core-edge is carried out following an inverse power law. An energy window of about 30eV before the edge onset is selected with which to fit the background, illustrated in Fig 2.11. To determine whether a good fit is achieved the residuals must fluctuate evenly around the zero intensity mark without any large positive or negative intensity values. The background is then subtracted.

![Figure 2.11: O K edge fitted with background model using Digital Micrograph](image-url)
Ionisation edge | Atomic shell | Probe of DOS
--- | --- | ---
K | 1s | p
L₁ | 2s | p
L₂ 2p₁/₂ | s+d
L₃ 2p₃/₂ | s+d
M₁ 3s | p

Table 2.1: Ionisation edge information for EELS interpretation

Only certain transitions from core to unoccupied states are allowed as specified by the dipole selection rule, where electrons can only go into states with orbital angular momentum of \(l \pm 1\) (where \(l\) is the orbital angular momentum of the ground state). This means that electrons in an s ground state can only probe the p states of the unoccupied DOS. Similarly, if the initial ground state is p-like then both the s and d unoccupied states can be probed by the excited electron, but the greatest contribution to the edge will be from the d states. Some of the most common transitions are outlined in Table 1. Because each of the s, p, d states in an atom have different binding energies, the energy at which each of the ionisation edges appears for a single atom will vary. The same transition in different atoms will also cause the ionisation edge to change in energy.

The position of the states above the Fermi level will vary depending on the specific atomic environment being probed. For example the DOS of a single atom will be different from the DOS of an atom, X, co-ordinated to another atom X, because by the very act of adding another atom to the system the electronic configuration is affected, altering the DOS. Adding an atom Y instead of X will also affect the DOS but in a different way. Therefore we can see that as the local atomic environment changes, the unoccupied DOS is also altered. This manifests itself in the fine structure on the ionisation edge. The first 30eV above the edge onset is known as the energy-loss near-edge structure (ELNES). Taking a multiple scattering approach this results from the degree of overlap of the atomic wavefunctions scattered from the surrounding atoms and is hence modified by the local environment. The fine structure of the ELNES can be used as a ‘fingerprint’ to determine the atomic environment. However advances in the understanding of the ELNES means that features within the near-edge structure can be attributed to specific transitions in terms of the crystal field splitting for crystal structures.

The region over 40eV above the edge onset is known as the extended energy-loss fine structure (EXELFS). This region arises from single scattering events. The period of the
oscillations allow bonding distances to be measured and the amplitude of the oscillations, the co-ordination number.

As mentioned earlier, if the sample is thick extra plasmon peaks appear about 15-20eV above the ionisation edge onset. These affect the near-edge structure by masking the true structure for a more intense plasmon peak. We therefore want to be able to remove the thickness effects by subtracting the low-loss from core-loss regions. To carry out this deconvolution both the low and core loss must be taken under identical acquisition conditions (though the time/spectrum may be varied). The zlp and plasmon region is then removed from the core-loss spectra to allow for further analysis – especially for quantification. However, this is not always possible due to the intensity of the zlp under the conditions required to collect core-loss spectra, as already mentioned. To obtain both under the same acquisition conditions a compromise usually has to be made. Again the fast beam switch will be of great advantage here. If this becomes available commercially it will have a dramatic effect on EELS analysis in the future.
3 Powder Synthesis and Characterisation – Oxychloride

3.1 Sol-gel preparation

HfO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ powders were prepared using a sol-gel technique. The Hf$_x$Si$_{1-x}$O$_2$ sample was prepared from a solution of hafnium oxychloride (HfOCl$_2$·xH$_2$O, Sigma-Aldrich 99.99%, Fluorochem 99.23%), water and hydrochloric acid having the molar ratio 1:30:1. The HCl acts as a catalyst for the reaction. One mole equivalent of tetraethoxyorthosilane (TEOS, Si(OC$_2$H$_5$)$_4$, Sigma-Aldrich, 98% solution) was added to this. The solution was mixed at room temperature using a magnetic stirrer until viscosity increased, then left to dry at 45°C-50°C for 2-7 days. The resulting amorphous powder contains HfO$_2$ and SiO$_2$ in a 50:50 ratio. The two different HfOCl$_2$·xHfO$_2$ precursors, from Sigma-Aldrich and Fluorochem, were quite different in texture. The former was a white powder, while the latter was wet and sticky and consisted of fine, rectangular splinters of material. HfOCl$_2$ can have 4-8 H$_2$O molecules co-ordinated to it. Where 8 water molecules are present, in solution four of these molecules join together to form the [Hf$_4$(OH)$_8$(H$_2$O)$_{16}$]$^{8+}$ cation$^{59}$. The texture of the Fluorochem sample is consistent with a higher percentage of water compared with the Sigma-Aldrich sample, probably close to 8 moles to each HfOCl$_2$ molecule. The Hf$_x$Si$_{1-x}$O$_2$ samples were prepared using both precursors. Slight differences in the products formed are attributed to the difference in hydration state which led to slightly incorrect quantities being used in the preparation using the Sigma-Aldrich powder. This was because a hydration state of 8 was assumed. Hence the results that are presented in this thesis are for the samples prepared from the Fluorochem powder.

Hf$_x$Si$_{1-x}$O$_2$ samples with x = 0.7 and x = 0.3 were prepared in the same way with the ratio of reactants adjusted accordingly. HfO$_2$ powders were made in an identical manner except that the TEOS was omitted. All other reactants and quantities were kept constant so that direct comparison could be made between the Hf$_x$Si$_{1-x}$O$_2$ and non-SiO$_2$ containing samples, without any differences in results being attributable to parameters other than the SiO$_2$ content.
Aliquots of sample were heated in a furnace to temperatures of 800, 1000 and 1400°C for 24 hours and to 1650 or 1700°C for 12 hours. This reduction in time at the highest temperature was to stop damage occurring to the furnace. The samples were then crushed to a fine powder using an agate mortar and pestle for x-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis. Powders were also used for high temperature XRD (HTXRD) and thermal analysis.

3.2 Experimental Parameters

3.2.1 Thermal Analysis

Two instruments were used for thermal analysis. The first was a Stanton Redcroft STA 780 series Simultaneous Thermal Analyser. Approximately 40mg of powder sample was heated in a platinum crucible to 1250-1350°C. A heating rate of 10°C/min was used. Alumina (Al₂O₃) was used as the inert reference material and experiments were conducted in either flowing air or argon. Unless otherwise stated it can be assumed that the experiment was conducted in an argon environment. Thermal-gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out simultaneously.

The second instrument, a Netzsch DSC (Differential Scanning Calorimetry) 449C Simultaneous Thermal Analyser (STA), was used to measure the DSC and TGA simultaneously. Samples were heated from room temperature to 1450°C at 10°C/min in alumina crucibles. An empty alumina crucible was used as the reference. Because the same heating conditions were used in both instruments, direct comparison between the two instruments can be made. 60-80mg of sample was used for each experiment. Experiments were conducted in either flowing air or nitrogen. Results presented were gained from a nitrogen environment unless otherwise stated. Many of the spectra had a reference scan removed from them to help improve the baseline. However this did not always result in an improvement due to the length of time between collection of the reference scan and the actual data. This results in some of the data presented with no reference subtraction carried out. Where applicable, this is mentioned in the text.

The temperature at which a thermal event occurs is taken as the peak maximum/minimum in the DTA or DSC graphs.
3.2.2 X-ray diffraction (XRD)

3.2.2.1 Ambient XRD

Ambient XRD was recorded at room temperature using a Philips PW1700 series automated powder diffractometer with a secondary graphite crystal monochromator and Cu $K\alpha$ (1.5418Å) x-ray beam. After samples had been heated either in the furnace or after thermal analysis their diffraction pattern was recorded at room temperature. Typical collection conditions were: step size 0.04°2$\theta$, 2s/step, range 10-90°2$\theta$. Crystallite sizes were calculated using the Scherrer equation as described in Chapter 2. The line broadening was calculated from the Warren formula using the (111) peak at 28.48°2$\theta$ of a silicon single crystal standard.

3.2.2.2 High temperature XRD (HTXRD) – Imperial

HTXRD was carried out in still air on a Philips X'Pert MPD with a Buhler HDK 2.4 environmental chamber, operating at 40mA and 40kV. This uses Cu $K\alpha$ radiation and has a secondary graphite crystal monochromator. A 5mm mask was used at the divergence slit to keep the beam width fixed and therefore concentrated in the centre of the width of the Pt/Rh heating strip. The length irradiated varied as the diffractometer angle changed. The powder sample was placed on a piece of platinum foil, approximately 1cm x 1cm, which then sat on top of the Pt/Rh strip. Diffraction patterns were taken of the powders at room temperature. The precursors were then heated at a rate of 60°C/min and a number of scans recorded at temperatures up to ~1200°C. Once at temperature a fast scan was taken (~5mins, step size 0.04°, dwell time 0.5s), the sample was then held at temperature for 1hour before a slow scan was obtained (~55mins to complete, step size 0.04°, dwell time 5s). The total dwell time was about 120min. The same sample was then heated to the next temperature and the process repeated. This allowed the crystallisation pathway to be monitored as a function of both time and temperature, with the effects of time at temperature also being considered.

There are a number of errors associated with the experimental setup, most stemming from the fact that the sample is mounted on a piece of platinum foil. The foil is difficult to get flat resulting in poor thermal contact between it and the Pt/Rh heating strip. This causes a difference in temperature between the sample and the heater itself which will vary for each sample depending on the area of thermal contact achieved. The difference in temperature will also depend on the thickness of the powder on the foil. The thinner
the powder the closer it is to the correct temperature but this significantly reduces the number of counts in the XRD scan and so a compromise has to be made. As well as this there is a large temperature gradient across the area of platinum foil occupied by the sample - the temperature of the sample being lower at the edges of the foil than in the centre above temperatures of 600°C. The temperatures recorded have been adjusted according to calibration data obtained using thermal paint and are thought to have an error of ±10°C for sample situated at the centre of the foil. However, the sample was not restricted to the centre of the foil and so it is not clear exactly what the temperature error on each scan is. Using calibration data and by comparison with samples heated on other instruments the temperatures below ~600°C are thought to have an error of ±10°C, samples heated to the higher temperatures may have an error of as much as ±40°C. However this was also difficult to judge as each sample is different due to the thermal contact and thickness effects. Because of the errors involved it is more important to look at the general trend of the HTXRD results for comparison with thermal analysis and ambient XRD rather than the absolute temperatures.

Crystallite sizes for scans taken from furnace heated samples and from HTXRD (Imperial) analysis, were calculated from the full-width half-maximum (FWHM) as described in Chapter 2.

3.2.2.3 HTXRD – Oak Ridge National Lab (ORNL)

HTXRD work was carried out at Oak Ridge National Laboratory (ORNL) in the Centre for Nanophase Materials Sciences (CNMS). The CNMS was equipped with an X’Pert PRO PANalytical high temperature x-ray instrument with an Anton Paar XRK-900 environmental heater reaching a maximum temperature of 900°C. The operating current and voltage were 40mA and 45kV respectively. X-rays pass through a nickel filter before hitting a copper target causing Cu Kα radiation emission (λ = 1.5418 Å). A fixed mask of 10mm was used at the divergence slit. The diffractometer had been calibrated with an NIST LaB₆ standard. The sample was held in an alumina holder of diameter 15mm and depth 2.5mm and sitting on an alumina disc containing holes to allow gas to flow through the whole sample. The sample was heated at a rate of 30°C/min to a temperature of 300°C and a scan taken. The sample continued to be heated at this rate to 900°C with a scan taken every 20°C. Each scan was taken over the range 20-40°C using an automatic divergence slit so as to have a fixed irradiation length of 8mm on the sample. A step size of 0.017°2θ with a time per step of 60s was used.
Experiments were carried out in flowing N\textsubscript{2} and repeated in still air. The expected error in the temperature is ±2°C. As the temperature increases it takes longer to stabilise the heater at each temperature. This introduces additional errors as the effective time the sample is held at the high temperatures is greater than at the low temperatures.

Rietveld refinement was carried out using X’Pert HighScore Plus. Fitting was done using a Pseudo-Voigt function and for all calculations a $\chi^2$ value of less than 4% was achieved with most less than 3%. This value is quite high due to the short angular range over which data was collected resulting in it being difficult to get a better fit with the data. The main use of Rietveld refinement was to calculate rough crystallite sizes for the crystalline phases present. Because a Pseudo-Voigt function was used, the peak shape can be varied to be anything between its Lorentzian and Gaussian form which represent each end of the ‘shape’ scale. Accurate crystallite sizes can only be trusted for neutron data. However where reasonable fits with XRD data are obtained the average crystallite sizes can be taken as reasonable, to within a few nanometres. Of more interest than the crystallite size itself is how the crystallite size changes with temperature and whether a general trend is observed.

Many of the XRD graphs displayed in this thesis have had an offset applied in the y direction so as the scans can are more easily distinguishable from each other.

### 3.2.3 X-ray Fluorescence (XRF) Spectroscopy

XRF was used for rapid elemental analysis. Analysis was carried out at the CNMS using a Shimadzu, µEDX-1300, energy dispersive, micro, X-ray fluorescence spectrometer. Elements with an atomic number lower than fluorine cannot be detected but both hafnium and chlorine, the elements of particular interest, are within the detection limit of the technique.

### 3.2.4 TEM imaging

Powder samples used for TEM were prepared by crushing the powder and suspending it in isopropanol. The solution was then dropped onto either a holey or lacy carbon grid. Two microscopes were used to image the samples – the FEI Tecnai F20 at the University of Glasgow and the FEI Titan at Imperial College London. No standard set of imaging conditions were used for imaging these samples. However typical conditions for parallel beam illumination are as follows:
Tecnai: HT = 200kV, FEG = 4.5kV, I = 55μA, spot 3, C1 = 2000μm, C2 = 100μm, O = 50μm

Titan: HT = 300kV, FEG = 3.8-4.5kV, I = 55-60μA, spot 3, C1 = 2000μm, C2 = 150μm, C3 not inserted, O = 60μm

where HT = high tension; FEG = field emission gun; I = current; C1, C2 and C3 = condenser apertures 1, 2 and 3; O = objective aperture.

### 3.3 Hafnia results

#### 3.3.1 Air Environment

HTXRD results are displayed in Fig 3.1 for a sample heated and analysed in air. The two most intense peaks situated at about 28 and 31°2θ are the (-111) and (111) reflections respectively of m-HfO2. m-HfO2 is the stable, room temperature phase which is expected to transform to t-HfO2 at 1720°C and then the cubic phase at 2600°C\(^\text{39}\). It is difficult to distinguish the orthorhombic and cubic phases from t-HfO2 by XRD. We have therefore adopted the convention that features coinciding with the tetragonal/orthorhombic/cubic phases in the XRD will be named t-HfO2 throughout this thesis.
Considering m-HfO$_2$ first, from XRD results (Fig 3.1) this phase has formed by a temperature of 460°C. A weak feature at ~28°2θ can be observed in the 440°C scan, suggesting that m-HfO$_2$ has started to form by this temperature (Fig 3.1b). Data showing the crystallisation temperatures for each phase determined from XRD are displayed in Table 3.1. Here the temperature at which there is first a hint of a peak in the scans, is indicated as well as the temperature at which the phase is clearly observed. Crystallite sizes for m-HfO$_2$ as determined by Rietveld refinement are presented in Fig 3.2 showing a comparison between the air and N$_2$ heating environments. Crystallite sizes increase steadily from ~18-31nm over the 500-900°C temperature range. An error of ±2-5nm is expected for the crystallite sizes, similar to the errors calculated manually for the furnace heated samples below (see Table 3.2). There may also be a systematic error in the data resulting in the data points having been shifted in the y direction. However, since it is only general trends that are of interest from this data, a systematic shift should not affect the observations. These errors also apply to Fig 3.10.
Table 3.1: Summary of temperatures at which phases appear and disappear for HfO₂ and HfₓSi₁₋ₓO₂ (x = 0.7, 0.5 and 0.3). 'Hint of phase' is where a very small feature appears in the position where the crystalline feature is expected; 'Clear' is where the feature can clearly be assigned to a phase; 'Phase decrease' is the temperature at which the peak intensity for that phase starts to decrease; 'Phase disappeared' is the temperature by which the phase is no longer detected.

<table>
<thead>
<tr>
<th></th>
<th>N₂ m</th>
<th>Clear (°C)</th>
<th>Phase decrease (°C)</th>
<th>Phase disappeared (°C)</th>
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<tr>
<td>HfO₂</td>
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<td>x = 0.7</td>
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Figure 3.2: Changing crystallite size with temperature for m-HfO₂ and t-HfO₂ heated in air or nitrogen
m-HfO$_2$ is the dominant phase but at 480°C a weak feature indicative of t-HfO$_2$ (011) peak (labelled t in Fig 3.1b) is observed at ~30°2\(\theta\), with some evidence of a similar feature in the same position at 440°C and 460°C. This peak disappears on heating to 500°C.

Samples heated in the furnace to temperatures of 800, 1000, 1400 and 1700°C show only the presence of m-HfO$_2$ (Fig 3.3). Crystallite sizes were calculated manually using the Scherrer equation, from the full-width half-maximum’s (FWHM) of the (111) and (-111) peaks (Table 3.2). At 1700°C the peak intensity is much lower than expected compared with scans taken at other temperatures. This is most likely due to there being less sample as some sample was bonded to the alumina crucible after heating to this temperature.

![Figure 3.3: Ambient XRD of HfO$_2$ powder after heating to 800-1700°C](image)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>800</th>
<th>1000</th>
<th>1400</th>
<th>1700</th>
</tr>
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<tbody>
<tr>
<td>Crystallite size (nm)</td>
<td>19.8 ± 1.3</td>
<td>26.9 ± 1.9</td>
<td>43.2 ± 2.5</td>
<td>31.9 ± 5.9</td>
</tr>
</tbody>
</table>

Table 3.2: Crystallite sizes of furnace heated HfO$_2$ samples calculated using the Scherrer equation

Fig 3.4 shows the thermal analysis results from the Netzsch DSC STA after heating samples in air and nitrogen environments separately. Considering the air environment the DSC shows a sharp exotherm at 564°C and two smaller peaks at 497 and 521°C.
respectively (more clearly shown in the inset of Fig 3.4). There is a mass loss of ~45% after heating from room temperature to 600°C where the mass loss then levels off. The changes in slope in the mass loss corresponds to the endotherms in the DSC between room temperature and 400°C. These are attributed to the loss of HCl, water and chlorine from the structure\textsuperscript{59}. There is also a mass loss of ~1.5% coinciding with the features in the DTA between 497-564°C. (The N\textsubscript{2} results will be discussed later). The particle size of the amorphous powder may affect the crystallisation temperature as deduced from thermal analysis; the smaller the average particle size, the lower the crystallisation temperature. The particle size was not taken into consideration in these experiments. This should be remembered during data interpretation and its influence should be investigated in future experiments.

The most intense exothermic peak at 564°C is thought to be representative of the main crystallisation event occurring within the sample – i.e. crystallisation of the m-HfO\textsubscript{2} phase. However, this temperature does not correspond to the crystallisation temperature observed by XRD. The first of the two smaller features at 497°C in the DSC is closer to the crystallisation temperature observed by XRD. It is possible that different heating
rates between DSC and XRD could induce crystallisation at different temperatures but as we will see later, this is not thought to have a large effect on this sample.

### 3.3.2 Nitrogen Environment

It was found that the crystallisation pathway of the amorphous powders on heating is different when heated in N\(_2\). Fig 3.5 shows a selection of the HTXRD results for a HfO\(_2\) powder heated in flowing nitrogen. Here we observe formation not only of m-HfO\(_2\) but also t-HfO\(_2\), by 480°C with a hint of each phase in the 460°C XRD scan (Fig 3.5b). Both t-HfO\(_2\) and m-HfO\(_2\) peak intensities increase until 580°C where t-HfO\(_2\) starts to decrease in intensity. It has disappeared completely by 800°C. The remaining amorphous material continues to crystallise into the m-HfO\(_2\) phase up to 900°C. The prominence of t-HfO\(_2\) was also observed when a similar experiment was carried out under vacuum on the Imperial HTXRD system. Because of the experimental set-up, exact temperatures could not be assigned and so the results are not shown here. However, the main point is that a similar effect is observed in vacuum and so the effect is not due to incorporation of nitrogen into the structure.

![Figure 3.5](image-url)  
*Figure 3.5: HTXRD results for HfO\(_2\) precursor after heating in an N\(_2\) environment  (a) Selected scans after heating, showing the main crystallisation features  (b) magnification of features in 460-480°C scans*
It was noticed that on cooling from 900°C to room temperature using the Oak Ridge XRD set-up, the m-HfO$_2$ peak intensities decreased whilst there was little variation in the FWHM of the peak. This indicated that there was a sample height effect due to thermal expansion and densification of the sample on cooling to room temperature which may affect the peak intensities. This was the same for all samples no matter what the heating environment, although the effect was more pronounced in an N$_2$ environment due to some sample being “blown away” by the gas flowing through the holder. The change in sample height was visible to the eye after the experiment had been completed.

All samples heated in nitrogen had turned a grey colour by the end of the experiment. This colouring has previously been attributed to substoichiometry and oxygen vacancies within the HfO$_2$ (ZrO$_2$) structure$^{60}$. Livage et al.$^{60}$ found that heating in an oxygen free environment produced a black powder, but when reheated in oxygen the powder changed back to a white colour. Similarly, Collins and Bowman$^{61}$ observe a colour change to black after heating in a nitrogen environment. They attribute this to either sub-stoichiometry or incomplete combustion of carbon species in the powder due to an organic precursor being used. The first suggestion is the most likely for this sample. From results in Fig 3.2 we see that the m-HfO$_2$ crystallite size increased from ~20nm @ 500°C to 35nm @ 900°C. Similarly the t-HfO$_2$ particles changed from 18nm @ 500°C to 28nm @ 660°C. The m-HfO$_2$ crystals are slightly larger when grown in N$_2$, compared with the air environment, however, the similar gradients on the graph are an indication that there is little difference in the rate of crystallite size increase. There is no crystallite size information for temperatures higher than 900°C as the furnace heating experiments were carried out in air only. It is assumed, due to lack of features in the DSC (Fig 3.4) above this temperature, that only m-HfO$_2$ is present over the temperature range studied.

To investigate the effects of heating rate the same HTXRD experiment was carried out under a nitrogen environment using a 5°C/min heating rate instead of 30°C/min. The results at the slower heating rate were identical to those of the sample analysed with a 30°C/min heating rate (results not shown here). The two heating rates investigated did not have any detectable effect on the experimental results.
The DSC results for a nitrogen environment in Fig 3.4 are similar to those for air. The exothermic peaks have shifted to lower temperature by about 2°C and the endothermic peaks are at higher temperature by about 8°C. The two distinct features at 497 and 521°C in the air sample are replaced by one broad peak covering the same temperature range. After repeated experiment under identical conditions in both the DSC and DTA with the samples from the same batch, this peak was sometimes resolved clearly into two separate peaks, and sometimes only one was present. It is not clear why this occurs. After the main exothermic peak, finishing at about 595°C, there is a lot of roughness in the DSC trace. This was not observed for the air environment.

The mass loss follows a similar pattern to that in oxygen up to a temperature of 500°C. At 554°C there is an abrupt step in the mass loss of ~3% ending at around 595°C, the end point of the main exothermic peak. This was observed but to a much lesser extent in the DTA/TGA under an argon or air environment but was repeatedly observed in the DSC/TGA in an N₂ atmosphere. The mass loss is most likely due to loss of oxygen from the material. Up to about 850°C there are small fluctuations in the TGA, ending where the corresponding fluctuations in the DSC end. This DSC/TGA experiment was repeated and although the same trend was observed in the mass as temperature increases, the overall mass loss varied (37% c.f. 45%). It is unclear why this variation between samples should occur as the samples were taken from the same vial and had been exposed to air for roughly the same length of time. After heating the sample in nitrogen, a residue was deposited on the metal surrounding the crucible. It is not known what compounds or elements this contains. This was only observed towards the end of the DSC experiments so it is not known whether the residue was also left after heating in air. Karapetrova et al.⁴⁸ also found a white condensate after heating in a tube furnace. This was found only in the samples that had a high concentration of chlorine in the original sample as found a large quantity of chlorine in the condensate.

**3.3.3 Kinetics experiment**

An investigation was carried out to examine the effect of time at temperature on the sample. The sample was heated in flowing nitrogen to 440°C then held at temperature with XRD scans continually taken. Selected results are shown in Fig 3.6. The sample appears amorphous until after the second scan at 440°C after which both m-HfO₂ and t-HfO₂ peaks start to form. The m-HfO₂ peak increases in intensity and decreases in width over the time held at temperature, indicating an increase in crystallite size. In
contrast, the t-HfO$_2$ peak forms but reaches an optimum peak width and intensity and remains at this for the duration of the experiment. Both phases are still present after cooling to room temperature without any apparent change in crystallite size from their final state at 440°C.

![Graph showing XRD scans of HfO$_2$ sample.](image)

**Figure 3.6:** HfO$_2$ sample heated to 440°C then held at temperature with XRD scans being continually taken. Experiment was carried out in an N$_2$ environment.

### 3.3.4 XRF

XRF analysis was used to determine whether chlorine was present in the t-HfO$_2$ containing samples after heating in nitrogen. XRF analysis was carried out at room temperature on samples before and after heating to 900°C and on the sample heated to 480°C where both m-HfO$_2$ and t-HfO$_2$ were present. As expected, the sample before heating showed both Hf and Cl content. Both the 480°C and 900°C samples showed only Hf with no detectable chlorine in the sample by the time m-HfO$_2$ or t-HfO$_2$ has crystallised – it has all be burned off at lower temperatures.

### 3.3.5 TEM images

TEM was used to investigate the morphology of the samples. Figure 3.7 shows a selection of images from three samples heated in air to 1000°C and 1700°C, and in N$_2$ to 440°C. Fig 3.7a-c were taken of the powders after heating to 1000°C. Fig 3.7a,b show crystalline particles of size ~ 50-150nm. The particles are often found as agglomerates with the individual particles having well defined shapes. Whilst at
1000°C the particles were more agglomerate-like, in the 800°C and 1700°C samples the particles were often found dispersed individually on the grid. This may be the result of how the sample was prepared. At 1700°C some of the particles were less angular and when imaged at higher magnification, contained smaller crystalline particles within their structure. An example of this is Fig 3.7d where small particles can be seen within the large particle, at the top right of the image. The lattice fringes are seen more clearly in Fig 3.7e. Also, in the 1000°C sample there were large areas of the grid covered in small, spherical, 2-5nm sized particles, such as those in Fig 3.7c. These are faint in the TEM images. A STEM image of a similar sample is found in Fig 4.11. Here the particles are easily distinguished. In this sample these were often found near larger particles. There was no indication from the images that the particles present on the holey carbon in Fig 3.7c were surrounded by any of the remaining amorphous material though it is possible that this was the case.

From XRD of either 1000°C or 1700°C samples we would expect to find only m-HfO₂ present. This implies that both the large and small particles have the m-HfO₂ phase. This may help explain the discrepancy between crystallite sizes as calculated from XRD.
and measured from TEM images. There may in fact be a large number of small particles which cause the XRD peak to broaden and therefore the average crystallite size calculated is between the two size regimes evident in the images. Why these two size regimes exist with few particles with sizes in-between, is not yet clear.

Figure 3.7(f)-(g) were taken from a HfO$_2$ sample which had been heated in nitrogen to 440°C then held at this temperature where growth of both m-HfO$_2$ and t-HfO$_2$ crystallites was induced. This sample contained many particles that looked like those in Fig 3.7(a)-(c), both larger, angular particles and also small, spherical particles dispersed across the holey carbon grid. Particles such as those in Fig 3.7(f) and (g) were also observed where whole particles were made up of small (2-10nm), spherical crystals.

Figure 3.8: HfO$_2$ precursor powders

Imaging of the starting powder, before any heating had taken place, was also carried out. Some typical images are displayed in Fig 3.8. Fig 3.8(a)–(c) are typical of this sample. Though it looks, especially in Fig 3.8(b) that there are a number of particles, when imaged at higher magnification these are amorphous. Particle in Fig 3.8(d) was an anomaly and is crystalline. From XRD the sample is actually crystalline at room
temperature however it has not been possible to index the diffraction peaks. On heating to 100°C the sample becomes completely amorphous. It is thought that the crystallinity is due to water present in the system which, when heated, disappears making the sample amorphous. It is suggested that this is what causes the crystallinity observed in Fig 3.8(d). The particles damaged very quickly under the beam and sometimes disappeared altogether. There were also problems with the sample charging which made it difficult to get images at high magnification.

### 3.4 Hafnium silicate $\text{Hf}_{0.5}\text{Si}_{0.5}\text{O}_2$

#### 3.4.1 Low Temperature Region $<900^\circ\text{C}$

Results from samples heated to temperatures below 900°C are almost identical to those for HfO$_2$ with a maximum difference of ~40°C for the crystallisation temperature. As with the HfO$_2$ samples heating in air results in m-HfO$_2$ crystallisation and heating in N$_2$ gives both m-HfO$_2$ and t-HfO$_2$ (Fig 3.9). As with the HfO$_2$ samples, there is a small t-HfO$_2$ feature in the XRD scans between 440 and 540°C after heating in air. The feature remains small and disappears above 540°C. In the sample heated in nitrogen both the m-HfO$_2$ and t-HfO$_2$ phases grow at the same time with t-HfO$_2$ initially having a much greater crystallisation rate, observed from the t-HfO$_2$ peak intensity initially being much greater than that of m-HfO$_2$. By ~540°C the m-HfO$_2$ peak intensities are greater than the t-HfO$_2$ peaks and the t-HfO$_2$ peak intensity starts to decrease. By 800°C the t-HfO$_2$ peak has decreased such that it is difficult to distinguish it from the background.
The crystallite sizes were determined by Rietveld refinement and are displayed in Fig 3.10. Results show that the m-HfO$_2$ crystallite size is independent of heating environment. The crystallite sizes are also very similar to those in the SiO$_2$ free sample (Fig 3.2). The t-HfO$_2$ crystallite size appears to initially increase and then decrease above about 550°C (Fig 3.10). It is unlikely that the crystallite sizes did actually decrease. Above temperatures of ~550°C data fitting for the t-HfO$_2$ peak was not good due to the decreased peak intensity, and the fit gets worse with each data set. Hence, the crystallite sizes for t-HfO$_2$ are not accurate.
Figure 3.10: $m$-HfO$_2$ and $t$-HfO$_2$ crystallite sizes for Hf$_{0.5}$Si$_{0.5}$O$_2$ powder heated under different environments

The thermal analysis data shown in Fig 3.11 is again taken from the Netzsch DSC STA. Below 900°C the results are almost identical to those for HfO$_2$. In the air environment the three peaks observed in Fig 3.4 are again observed at nearly identical temperatures, 497, 521 and 567°C (Fig 3.11 peaks marked 1-3 in insert). The sample heated in nitrogen did not have as much powder in the crucible to start with and so the features are not as clear as for the air sample. The main peak is still observed at 567°C. This peak is much broader than for the air environment and has a shoulder (possibly another peak?) to the high-temperature side of the peak. Before this there is a feature at 500°C. This is similar to the case of HfO$_2$ where, when heated in nitrogen again only one peak was observed before the main exotherm. However, over a number of experiments in the two thermal analysers, when heated in nitrogen or argon either one or two peaks were observed, even under the same experimental conditions. The mass loss is almost identical at ~36.5% in the two environments. A small variation is observed over the 490-570°C range. The mass loss for the nitrogen sample is not as great over the region of the features before the main crystallisation peak at 567°C. This may be another indication of the difference in crystallisation pathway between the two samples. As with the HfO$_2$ results the crystallisation temperatures do not match up between the thermal analysis and XRD.
Between 1200-1400°C another feature is observed in the DSC. There is a clear peak at \(\sim 1330°C\) in the air environment with a much less intense peak starting at the slightly lower temperature of 1295°C in the nitrogen environment. Although we have XRD data for samples heated in the furnace in air up to this temperature (see below) there is no data for the nitrogen environment so it is not clear whether this apparent difference in the feature is due to the heating environment, or not. There is a small mass loss of 0.2 and 0.4% in the air and nitrogen samples, coinciding with the peak onset in the DSC at 1260 and 1210°C respectively.

### 3.4.2 High Temperature region – 900-1700°C

The high temperature region was probed using thermal analysis (as described above) and XRD, and by correlation with TEM imaging.

#### 3.4.2.1 Furnace Heated results

Samples were heated in the furnace, cooled to room temperature then investigated using XRD. The results are illustrated in Fig 3.12. As has already been seen from the
HTXRD results, only m-HfO$_2$ is observed at 800°C. After heating at 1000°C a broad peak, indicative of t-HfO$_2$, is observed at $\sim$30°2θ. This peak becomes sharper and more intense as the temperature is increased to 1400°C. The width of the peak indicates that the particles grow from $\sim$5nm to $\sim$20nm. The m-HfO$_2$ peaks behave in a similar manner over the same temperature range. At 1400°C some SiO$_2$ has crystallised into the cristobalite form. Cristobalite has both a high and low phase. The high phase converts to the low phase on cooling and the peak at $\sim$21.5°2θ corresponds to the low-cristobalite phase. A small feature is observed at the low angle side of the (-111) m-HfO$_2$ peak at 1400°C which may be the start of the HfSiO$_4$ phase forming. By 1700°C the t-HfO$_2$ phase has completely disappeared, m-HfO$_2$ has reduced significantly in intensity and HfSiO$_4$ has formed. All the peaks in the 1700°C scan are slightly asymmetric. It is not clear what may have caused this. It is possibly a problem with the diffractometer, as a similar effect is observed in the sub-stoichiometric $x=0.3$ and 0.7 samples below. Alternatively, it may be due to a substoichiometry of the HfSiO$_4$ and m-HfO$_2$ phases at these high temperatures.

![Figure 3.12: Hf$_{0.5}$Si$_{0.5}$O$_2$ samples heated to 800-1700°C](image)

### 3.4.2.2 TEM imaging

The powders that had been heated in the furnace to 800 - 1700°C were examined using TEM. Fig 3.13a is a typical image of the sample heated to 800°C. This sample consists mainly of chemically separated dark and light, HfO$_2$ and SiO$_2$ rich regions. These are
mainly amorphous with a few crystalline regions. At 1000°C particles such as 13b were found which contain many nanoparticles ~2-5nm in size. Particles more typically observed at this temperature are those in Fig 3.13c. These larger, angular, crystalline particles were also observed for HfO₂ in Fig 3.7a+b. Because of their abundance and size (20-100nm) these are expected to be m-HfO₂. Around the edge of many of these particles a thin amorphous region was observed which contained nanocrystals (2-10nm) dispersed in it. On average the crystallite size was about 5nm. These larger particles with surrounding amorphous regions were also observed at 1400°C sample. At 1400°C areas where chemical separation had occurred, but on a larger scale than in Fig 3.13a, were commonly observed.

Particles in the 1700°C sample were not particularly similar to each other. Particles such as those in Fig 3.14a were found where a large crystalline particle is observed. Here the area to the left of it initially appears to have phase separated, but on closer inspection has crystallised though not into discrete particles such as in Fig 3.13c. Particles that on first inspection look fully crystalline, such as Fig 3.14b, when looked at in more detail, reveal phase separated and crystallised on a fine scale. This effect had not been observed in any of the other samples. At this temperature (1700°C) the majority of the sample is HfSiO₄ and so these particles may be representative of that phase.
Figure 3.13: TEM images of Hf$_{0.5}$Si$_{0.5}$O$_2$ samples after heating to (a) 800°C (b)-(c) 1000°C.
3.5 Hafnium silicate $\text{Hf}_0.3\text{Si}_{0.7}\text{O}_2$ and $\text{Hf}_0.7\text{Si}_{0.3}\text{O}_2$

To investigate further the influence of the SiO$_2$ content on the samples, the HfO$_2$: SiO$_2$ ratio was varied. Samples with composition $\text{Hf}_{0.3}\text{Si}_{0.7}\text{O}_2$ and $\text{Hf}_{0.7}\text{Si}_{0.3}\text{O}_2$ were prepared and studied by thermal analysis and XRD.

3.5.1 Thermal Analysis

Fig 3.15 shows the thermal analysis results. As with previous results the base line of the DSC is not horizontal as it should be. Some of the previous results had a reference
subtracted from them to improve the base line but in this case a background subtraction did not enhance any of the features on the graph and did not improve the baseline. Therefore a background subtraction was not used here. For an accurate background subtraction the background would have had to be taken each day the DSC was used. Since only two experiments could be conducted in a day it was impractical to also take a background scan so this may account for the poor baseline in these results. However, because a good background has not been included in the results some features are not very clear, especially for the x = 0.3 sample. To assist in interpretation the equivalent results from the Stanton Redcroft STA instrument for the DTA part of the scan have been displayed in Fig 3.15b and c. Care has to be taken when comparing these results as the analysis was carried out under different heating environments – the DSC under N₂ and the DTA under Ar. This should not cause any significant difference to the results. However, slight differences in crystallisation temperatures may be attributed to this. All the main features are present in both sets of results.

The DSC results (Fig 3.15a), reveal that the sample containing the higher percentage of SiO₂ has very weak features in comparison to the Hf₀.₇Si₀.₃O₂ sample where the exotherms at ~ 600°C are strong. This is consistent with the earlier observation (Fig 3.4) that the thermal events occurring in this region are predominantly due to the Hf
atoms and their interaction. Although difficult to distinguish from the graph above, two very weak features are present at 523°C and 568°C. These are clearer in the DTA data, marked 1 and 2 in Fig 3.15(b). From the HfO₂ and Hf₀.₅Si₀.₅O₂ data we would expect to see crystalline features in this region. For the Hf₀.₃Si₀.₇O₂ sample these features are more clearly resolved when carried out in the Ar environment (Fig 3.15b). The temperatures at which they occur (509°C and 552°C) are slightly lower than in the nitrogen environment. In the temperature range 900-1400°C there is a broad feature in the DSC, which is clearer in the DTA covering a temperature range of ~890-1075°C. The total mass loss is ~24% over the duration of the experiment. This was the same for both DTA and DSC.

For the Hf₀.₇Si₀.₃O₂ sample an exotherm at ~580°C is observed in the DSC with a shoulder on it at the slightly lower temperature of 567°C. In the DTA (Fig 3.15c) this becomes clearer, two peaks are resolved (marked 1 and 2). The main crystallisation peak is at 553°C (peak 3) with two small thermal events occurring at 491°C and 514°C. The total mass loss was ~40% which was consistent between instruments. There is a step in the mass loss of ~2.5% coinciding with the main exotherm in the DTA.

### 3.5.2 HTXRD

HTXRD was carried out at the CNMS as for previous experiments. The temperatures at which different phases appeared and disappeared are presented in Table 3.1. As with previous samples t-HfO₂ forms in an N₂ environment but only a small amount of t-HfO₂ is observed in the air environment. Generally, for samples heated in nitrogen, the temperature at which m-HfO₂ crystallises (i.e. is clearly observed) increases as the percentage of HfO₂ in the system increases. An exception to this is that the crystallisation temperature for x = 1 and 0.7 is the same. The trend follows through to the SiO₂ free sample where the crystallisation temperature for both m and t phases is 480°C.

Similarly, for the nitrogen environment, as the percentage of SiO₂ increases t-HfO₂ crystallises at the lower temperature of 440°C compared with 460°C (though in this case x = 0.7 and x = 0.5 are roughly the same). This is contrary to the literature where an increase in the SiO₂ content usually increases the crystallisation temperature$^{8,23,27}$. As the percentage of SiO₂ decreases the temperature at which the t-HfO₂ phase disappears also increases. The SiO₂-free sample does not fit this trend.
No trend is observed for the crystallisation temperatures for the samples heated in air. Crystallisation occurs somewhere between 420 and 460°C for m-HfO₂ with t-HfO₂ generally observed in the 460°C scan. t-HfO₂ disappears again between 500 and 540°C.

### 3.5.3 Furnace Heated Results

The results obtained for ~800-1000°C agree with those of the same temperature range in the HTXRD as to the influence of SiO₂ on crystallisation. In Fig 3.16 the 1700°C scan is missing in (a) but not for (b). This is due to the sample containing the high SiO₂ content melting in the furnace at this temperature. The diffraction peaks in Fig 3.16a are less intense than for (b) or the Hf₀.₅Si₀.₅O₂ sample due to less HfO₂ in the sample. For the Hf₀.₃Si₀.₇O₂ sample m-HfO₂ is observed at each temperature with the peak widths decreasing, and intensity increasing as temperature increases, as observed for previous samples. t-HfO₂ forms by 1000°C as a very broad peak, with small crystallite size. The particles then grow in size as the temperature is increased. As the t-HfO₂ particles increase in size with temperature, more particles form as (or transform to) m-HfO₂ as determined by the relative peak intensity of the m:t phases at 1400°C. As expected, SiO₂ has also crystallised by 1400°C into the form of cristobalite but there is no indication of the HfSiO₄ phase having formed.
The results for the $x = 0.7$ sample are almost identical to the $x = 0.5$ sample. There is a hint of t-HfO$_2$ starting to form at 1000°C though this is not clear until 1400°C where cristobalite has also formed. By 1700°C there is still a significant amount of m-HfO$_2$ remaining while HfSiO$_4$ has started to form. This is not unexpected as the sample has a much higher proportion of HfO$_2$ hence only some of the HfO$_2$ is required to form HfSiO$_4$. As with the $x = 0.5$ sample, the HfSiO$_4$ peaks are asymmetric. This implies that there is a degree of substoichiometry in this phase.
3.6 Discussion

From these results the main points to be discussed are:

**HfO\textsubscript{2} samples:**
- HfO\textsubscript{2} crystallises into the m phase in air, but both m + t if heated in an inert environment
- t-HfO\textsubscript{2} can then be stabilised at room temperature
- t-HfO\textsubscript{2} transforms into m-HfO\textsubscript{2} if the temperature is increased
- thermal analysis appears to indicate different crystallisation temperatures compared with XRD
- both m + t have similar crystallite size close to crystallisation
- both temperature and time held at temperature affect crystallisation progress

**Hf\textsubscript{x}Si\textsubscript{1-x}O\textsubscript{2}**
- two occurrences of t formation: at low temperature – depends on inert environment; at high temperature, independent of heating environment
- as the concentration of SiO\textsubscript{2} is increased, the crystallisation temperature decreases – this is contrary to the general view that SiO\textsubscript{2} results in stabilisation and hence an increase in crystallisation temperature

The main question that arises is, what causes the stabilisation of t-HfO\textsubscript{2}? Formation of t-HfO\textsubscript{2} is observed in two temperature ranges; 400-800°C and 1000-1500°C. Formation in the lower range is common to all samples while formation in the higher window only occurs in the presence of SiO\textsubscript{2}. This implies that there are two different mechanisms for stabilisation of t-HfO\textsubscript{2}. The HfO\textsubscript{2} system is very similar to that of ZrO\textsubscript{2}. Because ZrO\textsubscript{2} is understood in much more detail, it is useful to consider this system when trying to interpret results for HfO\textsubscript{2}.

### 3.6.1 Stabilisation mechanisms - theory

Stabilisation of t-ZrO\textsubscript{2} has been widely reported at both low and high temperatures (see review article by Shukla and Seal\textsuperscript{15}). There are four common theories to explain stabilisation of t-ZrO\textsubscript{2}, namely:
1. surface energy/critical crystallite size
2. ion impurities
3. local ordering
4. oxygen vacancies

Each is reviewed below as a basis to interpret the HfO₂ results presented in this chapter.

### 3.6.1.1 Surface energy/critical crystallite size

Garvie⁴³ introduced the surface stabilisation or the possibility of a ‘critical crystallite size’ effect to the case of ZrO₂ in 1965. The theory says that particles above a critical size of 30nm cannot be t-ZrO₂, and below a size of 11-17nm, only t-ZrO₂ is present. At crystallite sizes in between both monoclinic and tetragonal phases could co-exist. Moreover, it was hypothesised that the surface energy was much greater below 30nm, corresponding to a larger surface area, leading to the conclusion that the stabilisation of t-ZrO₂ is due to the high surface energy of the particle. This was in good agreement with thermodynamic calculations. When the particle reaches the size of 30nm it is more thermodynamically favourable for it to transform into m-ZrO₂ due to the greater surface area and excess energy in this size range. To minimise the surface energy below 30nm the particles must also be spherical for this to be the only source of stabilisation. However, other effects such as interfacial energy and external strain effects also play a role where particles are not found in isolation. For example if the particles grow within a matrix – amorphous or crystalline – the strain induced by the surrounding matrix may inhibit the t→m transformation (which is accompanied by a 3-5% volume expansion²³;³⁷) and cause the crystallite size to increase before transforming. In terms of external stresses being applied the simple process of grinding the sample for analysis has been shown to induce a stress such that the t→m transformation occurs before any analysis is carried out⁶². This is similar to the process used industrially for transformation toughening in ceramic steel. With t-ZrO₂ in the structure, if a crack forms it causes a t→m transformation which, due to the volume expansion on transformation, subsequently closes over the crack⁶³. This external stress may also cause defects at the surface which in turn can act as further nucleation sites¹⁵;⁶⁴.

Garvie’s theory was derived to explain the often reported observation that ZrO₂ nucleates as t-ZrO₂, which then grows, eventually transforming to m-ZrO₂. Samples were prepared using two different preparation routes. It was found that on
crystallisation, tetragonal particles always formed. Depending on which preparation route was used, these were of the order of 5-15nm in size. Between 15 and 30nm both tetragonal and monoclinic particles were found. Above 30nm only m-ZrO$_2$ was observed. This led to thermodynamic calculations being made, taking into account surface energy effects, which were in good agreement with experimental results. TEM studies support the hypothesis that particles below 30nm are spherical in nature in samples that are reported to contain t-ZrO$_2$\cite{46,65,66}. In samples where m-ZrO$_2$ is expected, the particles are much larger and more angular\cite{46,67}.

The influence of stress and strain on phase formation has been observed in thin films. A comparison of films with thickness 4 and 2nm\cite{7}, showed that the thicker film crystallised more readily under the processing conditions. This is most likely due to the stress induced on a thinner layer by the capping layer inhibiting crystallisation. When the layer thickness is such that crystallisation can occur, t-HfO$_2$ is the first phase to form. Similarly Triyoso et al.\cite{21} observe significant structural differences in the presence of a TiN capping layer on top of a 4nm HfO$_2$ film. The t-HfO$_2$ to m-HfO$_2$ phase transformation requires a volume expansion of $\sim$3-5\%\cite{23,48}. Hence the presence of a capping layer physically inhibits the transformation because it constrains the possibility of the ‘transformation+volume expansion’ occurring.

Though many agree with Garvie’s theory, some debate remains as to the value of the critical crystallite size. For example Chraska et al.\cite{46} find the maximum tetragonal size to be 18nm. Even at the time of Garvie’s theory, results by Clearfield\cite{68} indicated that the critical crystallite size may be as low as 12nm, being dismissed by Garvie as an anomaly. Shukla and Seal\cite{15}, having considered much of the available experimental data, think 10nm is a more realistic estimate. However, it is to be expected that there would be disagreement over the exact crystallite size; Garvie’s study was one of the first into this effect and ZrO$_2$ has since been investigated much more extensively.

Though there is much evidence that agrees with Garvie’s basic premise regarding crystallite size effects, there are also reports of m-ZrO$_2$ with crystallite sizes as small as 6nm being observed, which do not fit the theory\cite{69}. The occurrence of m-ZrO$_2$ particles as small as this suggests that m-HfO$_2$ particles have formed directly into m-HfO$_2$ without first forming t-HfO$_2$. This is also contrary to Garvie’s original theory which says that all particles first nucleate in the tetragonal phase.
3.6.1.2 Ion impurities

Tetragonal HfO$_2$ crystallisation has also been attributed to the presence of water$^{47,70}$ or anions either on the surface of the particles or within the crystal lattice itself which may modify the structure such that t-HfO$_2$ is the thermodynamically favoured phase$^{71}$. Anions such as OH$^{-}\text{71,72}$, Cl$^{-}\text{48,72-76}$ and CH$_3$COO$^{-}\text{71}$ have all been reported as having an effect. Equally, contradictory evidence is also presented in the literature making some of these theories inconclusive$^{43,76}$. The most likely contaminant in our HfO$_2$ system is chlorine due to the oxychloride sol-gel precursor. Chlorine contamination has been used by many groups to explain the stabilisation effects in ZrO$_2$ and HfO$_2$ systems$^{48,72,74-76}$. However Geiculescu and Spencer$^{76}$ show Cl$^{-}$ has no effect on their systems and our XRF results show there is no Cl$^{-}$ present in the t-HfO$_2$ phase. Another possibility is the effect of the heating environment and the possibility that, for example nitrogen, could be incorporated into the structure. In our case air, argon, nitrogen and vacuum were all used to varying degrees. Little is mentioned about possible nitrogen incorporation into the crystal lattice in bulk samples though it has been shown to suppress crystallisation in thin film samples$^{7,19,26,37}$.

3.6.1.3 Local ordering

A number of papers suggest that there is a similarity between the local ‘structure’ of the amorphous material with either the monoclinic or tetragonal phases, and that this in turn determines the phase on crystallisation. Evidence for local ordering similar to either the t-ZrO$_2$ or m-ZrO$_2$ has been investigated using electron density, neutron diffraction and Raman measurements among other techniques$^{53,60,77,78}$. For example, Livage et al.$^{60}$ note that the distances between neighbouring Zr atoms in the amorphous powder matched the distances between Zr atoms of the t-ZrO$_2$ environment. Conversely Yanwei et al.$^{78}$ found, using wide angle x-ray scattering techniques that the interatomic distances in their ‘amorphous’ sample matched those for m-ZrO$_2$.

Only a small amount of data is available in the literature correlating the local structure in the amorphous phase with the ordered crystalline structure after crystallisation. Results appear contradictory but, based on the evidence that is available and from results presented in this thesis a further hypothesis may be made regarding the structural similarity between the amorphous starting material and the initial crystalline phases. Both Livage et al.$^{60}$ and Keramidas and White$^{77}$ observe similarities with the t-ZrO$_2$ phase in the amorphous powder whereas Yanwei et al.$^{78}$ and Mountjoy et al.$^{53}$ observe
the monoclinic phase after heating from ZrO2 and Hf,Si1-xO2 starting powders. The first
two groups started from an oxychloride preparation whereas the latter two start from an
alkoxide preparation. We know from the discussion in Section 3.6.2 and results that
follow in Chapter 4 that these two routes give markedly different crystallisation
pathways and it is therefore not surprising that the local atomic environment within the
amorphous starting material is significantly different to bring this about. Many
questions remain as to how this comes about, but because so little data is available more
investigation is required to verify whether this is the case.

### 3.6.1.4 Oxygen vacancies

The fourth explanation for t-HfO2 formation is the presence of oxygen vacancies. In
ZrO2 oxygen vacancies are often introduced to the structure by adding a small
percentage of an aliovalent dopant. This introduces oxygen vacancies into the structure
to maintain electroneutrality causing the zirconium to move from the sevenfold, m-ZrO2
coordination environment to the eight fold, t-ZrO2 or cubic co-ordination. Where
t-HfO2 is observed at low temperatures (<1000°C) this often corresponds with a low
oxygen partial pressure, hence oxygen vacancies are also responsible for t-HfO2
formation15;48;66;79.

Oxygen vacancies in the lattice could form in one of two ways. (1) In a reducing
environment some oxygen is removed from its lattice site forming a Frenkel defect. The
resulting oxygen vacancies stabilise t-HfO2. As the temperature increases and
thermal expansion of the lattice occurs, the interstitial oxygen may move back into its
correct lattice site resulting in a phase transformation from t→m. Alternatively (2) the
reducing environment may result in a Schottky defect where the lattice becomes oxygen
deficient. The only way this could occur is if the Hf which normally sits in an oxidation
state of 4 is reduced to have an oxidation state of 3, as a result of oxygen vacancies in
the structure.

t-ZrO2 stabilisation by oxygen vacancies have been reported by Simeon et al. 80. Many
of the explanations do not account for how charge neutrality is maintained in the
structure. Osendi et al.79 partly account for this when they observe trapped electrons
using electron paramagnetic resonance analysis, which they suggest neutralise the
oxygen ion vacancies. Similarly, from modelling, Ramo et al.81, also predict that
electron trapping may occur, though in the m-ZrO2 structure. An aliovalent cation such
as $Y^{\text{III}}$ has been found to stabilise the tetragonal phase at lower temperatures. (This was discussed briefly in the Introduction (Section 1.4). Typically $6\% \ Y_2\text{O}_3$ added to $\text{ZrO}_2$ causes the tetragonal phase to form; doping with a lower percentage, the monoclinic phase is stabilised due to the lack of oxygen vacancies. Some$^{82}$ have reported the presence of $\text{Zr}$ in an oxidation state of 3, which would have a similar effect on the oxygen vacancy density as $Y^{\text{III}}$ and also balance the charge within the structure. This however, is the only report of such a species. Others have attributed stabilisation to the presence of water, due to different processing atmospheres, when in fact it is more likely due to a change in oxygen vacancy density with change in atmosphere$^{47}$.

Bearing this in mind we will now go on to consider the results.

**3.6.2 Discussion of results**

There are three temperature regimes in which $t$-$\text{HfO}_2$ formation occurs:

1. \(~1000 - 1500^\circ\text{C}\)
2. \(~400 - 900^\circ\text{C}\)
3. \(>1750^\circ\text{C}\)

The first two will be discussed here from results presented in this chapter. The latter is the expected phase transition at high temperatures. This was not observed in the experimental results and so will not be discussed here. Because, from this chapter and the one following it is clear that the starting materials play an important role in determining the crystallisation pathway, as far as is possible previous experimental work based around oxychloride precursors will be applied to the discussion below. Likewise, for Chapter 4, alkoxide preparation methods will be the main point of reference. In each case information from other sources may also have to be drawn upon as is necessary.

**3.6.2.1 Tetragonal formation in the high temperature regime \((\sim 1000 - 1500^\circ\text{C})\)**

As previously mentioned (Section 1.4) $t$-$\text{HfO}_2$ is the stable phase above 1750$^\circ$C, though in $\text{Hf}_x\text{Si}_{1-x}\text{O}_2$ samples this is increased to \(\sim1950^\circ\text{C}\)$^{83}$ (see phase diagram in Appendix 1). From the results presented in this chapter, $t$-$\text{HfO}_2$ forms at temperatures between 1000$^\circ$C and 1700$^\circ$C, only occurs in the presence of $\text{SiO}_2$, and then combines with $\text{SiO}_2$ into the $\text{HfSiO}_4$ phase. The $t$-$\text{HfO}_2$ formation in this temperature range is by a different
mechanism, either from that observed at low temperatures (see discussion in Section 3.6.2.2) or that expected at ~1950°C from the phase diagram. At temperatures above ~1750-1950°C, t-HfO$_2$ forms via a martensitic transformation from m-HfO$_2$ (mentioned in Section 3.6.1.4). However the t-HfO$_2$ phase observed in the 1000-1500°C range does not form via this mechanism. The evidence for this is (1) t-HfO$_2$ formation occurs at ~700°C below the expected transformation temperature; (2) the phase disappears on further heating, not transforming to the cubic phase as would be expected from the phase diagram; (3) the t-HfO$_2$ crystallite size is much smaller than that for m-HfO$_2$ at the same temperature. (Crystallite sizes were not calculated for Fig 3.12 because the associated error was too large. However, from the width of the t-HfO$_2$ peak in the scan at 1000°C it is clear that the crystallite size is smaller than that of m-HfO$_2$ at the same temperature). If a martensitic transformation had occurred, the crystallite sizes would be the same.

This implies that the t-HfO$_2$ crystallites have formed directly from the remaining amorphous material, rather than from a martensitic transformation. This means the SiO$_2$ does not cause the m$\rightarrow$t transformation to occur at a lower temperature, but stabilises the formation of t-HfO$_2$ as it forms directly from the remaining amorphous material which is predominantly SiO$_2$ rich.

The key to understanding this crystallisation process is found in Fig 3.13c. This image, typical of many of the particles found in the 1000°C sample and of the majority of the 1400°C sample, shows a large angular particle surrounded by an amorphous layer containing many nano-particles. The nano-particles are evenly dispersed and are ~5nm in size. Based on the XRD results it is likely that the large, angular particles are m-HfO$_2$ and that the small, nano-crystals are t-HfO$_2$. The large angular particles are observed in both the SiO$_2$ free and the lower temperature Hf$_x$Si$_{1-x}$O$_2$ samples where only m-HfO$_2$ is the expected phase, whereas the nanoparticles are only found in SiO$_2$ containing powders. This supports the conclusion that the nanoparticles in Fig 3.13c are t-HfO$_2$. The homogeneity of these nanoparticles in the amorphous matrix and with comparison with images at other temperatures, agrees with the hypothesis that t-HfO$_2$ crystallites have grown directly from within the remaining amorphous SiO$_2$-rich material. In theory it should be possible to determine the phases present by electron diffraction, but in practice, due to the crystallite size (~5nm) and beam damage effects, this is a very difficult experiment to carry out. As well as the small particles
encapsulated in the amorphous material there are also particles of a similar size isolated on the holey-C grid. However, these are sparsely dispersed on the grid and grinding the sample for TEM analysis has probably resulted in these being separated from their original surrounding amorphous material.

The hypothesis is as follows: Most of this sample, assuming heating in an air environment, has formed m-HfO₂ up to ~1000°C. It is known from XRD and TEM that there is still a lot of amorphous material present which mainly consists of SiO₂. However, within this a-SiO₂ matrix a number of Hf “centres” are isolated which have not been consumed to form m-HfO₂. At a temperature of ~1000°C areas that are Hf-rich nucleate into small, spherical particles of t-HfO₂. These t-HfO₂ particles can only remain in this phase because they are surrounded by this SiO₂-rich matrix which has a stabilising effect on the crystals. If no a-SiO₂ is present, the Hf “centres” would continue to be added to the already formed m-HfO₂ crystals and no t-HfO₂ is observed. However, the SiO₂ exerts a strain on the HfO₂ causing t-HfO₂ to form but inhibiting its growth. This is attributed by Maria et al. to the mismatch in thermal expansion coefficient between the SiO₂ and HfO₂. The Si coefficient is ten times smaller than for HfO₂ causing the resultant strain which inhibits phase transformation. Further growth is inhibited partly from the stabilising role of the SiO₂ and partly by the fact that this region of sample is HfO₂ poor, hence once the particles reach a specific size there is no more Hf available for the particles to grow further. Therefore the t-HfO₂ particles are stabilised by the strain induced by the surrounding matrix. As the temperature is increased further, rather than the t-HfO₂ to m-HfO₂ transformation taking place, both particles are consumed, along with any crystalline SiO₂ and remaining amorphous material, to form HfSiO₄. In summary the following scheme is proposed:

\[
\text{amorphous material (SiO₂ rich)} \rightarrow \text{t-HfO₂ + amorphous material} \quad \sim 1000°C \\
\text{amorphous material} \rightarrow \text{c-SiO₂ + amorphous material} \quad \sim 1400°C \\
\text{t-HfO₂ + m-HfO₂ + c-SiO₂ + amorphous material} \rightarrow \text{HfSiO₄} \quad \sim 1700°C
\]

Stabilisation of the tetragonal (or orthorhombic) phases has been observed in both thin films and bulk powder HfO₂ and ZrO₂ samples.
3.6.2.2 Tetragonal hafnia formation in the low temperature regime (400-900°C)

\( t\text{-HfO}_2 \) has been observed after heating the sample in an inert environment to 460-760°C. In air a small \( t\text{-HfO}_2 \)-like feature is observed in the XRD after heating to \( \sim460°C \), but disappears by \( \sim520-540°C \) and is never an intense feature. Unlike at higher temperatures, at lower temperature \( t\text{-HfO}_2 \) is observed both with and without the presence of \( \text{SiO}_2 \), and thus the stabilisation mechanism is not the same as that for the high temperature regime.

**Thermal Analysis**

Firstly the apparent discrepancy between crystallisation temperatures as determined by XRD and thermal analysis will be discussed. The crystallisation temperature as established by HTXRD is \( \sim450°C \) compared with that of \( 550°C \) found by thermal analysis. Hu et al.\(^\text{44} \) discuss, for the case of \( \text{ZrO}_2 \) prepared from an oxychloride precursor, the thermal events occurring giving rise to the single sharp exotherm at about \( 450°C \). They suggest that, despite there only being one peak in the DTA, there are actually two events occurring – the first being crystallisation into small crystallites, and the second being a coalescence of these particles into larger particles. The latter event is known as ‘glow’ or ‘growth’ phenomenon. As defined by Srinivasan and Davis\(^\text{86} \) a ‘glow phenomenon’ occurs when metal oxides undergo a strong exothermic transition and may be determined by the thermal history of the sample. For \( \text{ZrO}_2 \) powders Bondioli et al.\(^\text{87} \) observe a discrepancy between their crystallisation temperature and the exotherm observed in the DTA. They reconcile this by attributing the determination of the crystallisation temperature to the XRD data, and the DTA reveals the temperature at which the ‘glow phenomenon’, or coalescence of particles takes place. Srinivasan and Davis\(^\text{86} \) set out to clarify the distinction between crystallisation and glow/growth phenomenon by considering ‘HfZrO’ oxides. They observe very similar results for \( \text{HfO}_2 \), prepared from an oxychloride precursor, as presented in this chapter. From XRD they observe crystallisation by a temperature of \( 450°C \) but do not see an exotherm in the DTA until \( 585°C \). These temperatures correspond well with the temperature difference between XRD and the main exotherm in the DSC in Figure’s 3.1 and 3.4. The exotherm in the DTA is attributed to coalescence rather than crystallisation.

The question arises as to why no thermal event is found associated with crystallisation. This is most likely due to only a small percentage of the sample initially crystallising
and that percentage increasing gradually as the temperature is increased. Srinivasan and Davis\textsuperscript{86} note that the exotherm cannot be attributed to a rapid increase in crystallite size since the crystallite size remains below 10nm, up to \( \sim 950^\circ C \). Correspondingly, they also observe a large decrease in surface area immediately after the exotherm temperature, implying that the large surface area nanocrystallites have coalesced to become larger particles with lower surface area.

Considering the DSC results in Fig 3.4, one or two small peaks are visible below the main exotherm. The onset of the first peak occurs at roughly the same temperature at which crystallisation is observed in the HTXRD e.g. Fig 3.1. Thermal analysis data by Srinivasan and Davis\textsuperscript{86} as found in reference\textsuperscript{86} are presented in Fig 3.17. On closer inspection of line (b) taken from \( \text{HfO}_2 \) data, a slight increase in intensity is observed at \( \sim 480^\circ C \) (marked by an arrow in Fig 3.17). It is suspected that if the scale was expanded to make this feature larger, this would be very similar to the features observed before the main exotherm in Fig 3.4. This would also be much closer to the crystallisation temperature as reported by XRD.

![Figure 3.17: Srinivasan and Davis thermal analysis data taken from Reference\textsuperscript{86}](image)

The two small features before the main thermal event in Fig 3.4 are present in the samples heated in either air or nitrogen and are therefore independent of heating environment. Either one or two small peaks are resolved in this region – this does not
seem to be associated with the heating environment. The hypothesis therefore is that crystallisation of some of the sample into small crystallites – either m-HfO₂ and/or t-HfO₂ – occurs at about 480°C. On heating to 560°C coalescence of these particles occurs causing the large exotherm (or glow phenomenon) in the DTA/DSC.

**Tetragonal hafnia formation**

As previously noted in ZrO₂, t-ZrO₂ is often the first crystalline phase observed, which then transforms into m-ZrO₂. The temperature and time at temperature required for this transformation varies depending on experimental parameters such as starting materials, pH, heating environment and crystallite size. In contrast to this, for HfO₂ when an oxychloride preparation is used the crystallisation temperature is usually ~450-550°C and the initial crystallisation phase is m-HfO₂ when heated under ambient conditions. However, when heated in an inert environment, t-HfO₂ forms, at roughly the same crystallisation temperature as for m-HfO₂.

As a starting point some of the arguments used to explain t-HfO₂ formation as outlined in section 3.6.1, will be eliminated. Firstly there is Garvie’s theory⁴³ regarding surface stabilisation energy and the crystallite size effect. Following Garvie’s argument through would require that t-HfO₂ could not be stabilised above a crystallite size of 30nm, and that all particles below 11nm had to be of the t-HfO₂ phase. The results presented in this chapter show that both m-HfO₂ and t-HfO₂ crystals exist with crystallite sizes below the 11nm threshold. This is the first reason as to why Garive’s theory does not fit this data. The second reason relates to the formation of both m-HfO₂ and t-HfO₂ phases at the same time and that their initial growth rate is very similar. Garvie’s argument suggests that all the particles would firstly form small t-HfO₂ crystals which, as they grow, would then transform to m-HfO₂. It has been shown with this data that both m-HfO₂ and t-HfO₂ particles grow at a similar rate and with similar particles sizes from ~480-600°C. This strongly indicates that crystallisation from the amorphous starting powder is into both t-HfO₂ and m-HfO₂ simultaneously. Whilst t-HfO₂ does eventually transform into m-HfO₂, at around 540°C, surface stabilisation does not appear to account for the initial nucleation and growth mechanism. Another explanation must be found.

Secondly there is the possibility of contaminants in the structure causing t-HfO₂ formation. XRF results of these samples show that no chlorine or other contaminant
was present in the HfO$_2$ sample and because of the similarity in the results between samples within this temperature range this result can be extrapolated to the SiO$_2$ samples. Whilst the presence of water cannot be entirely ruled out by XRF since O and H are below the detection limit of the technique, however, it is thought from the endotherms in the DTA and from the literature$^{59}$ that nearly all of it has been lost by a temperature of ~450°C.

Whilst there is a lot of potential in the theory regarding local structural similarities between amorphous and crystalline phases, there is neither enough literature available nor the possibility to carry out the required experiments at the moment to verify the theory. For the time being no further speculation can be made and this may be considered in terms of possible future work.

The key experimental observation is that in air m-HfO$_2$ is the first phase to form, while in N$_2$ t-HfO$_2$ forms first. This suggests that in N$_2$ (or Ar or vacuum) the presence of oxygen vacancies stabilising the t-HfO$_2$ phase at 400-900°C is the most plausible explanation. The first major factor indicating that the oxygen partial pressure and hence oxygen vacancies have an important role is that when heated under a reduced oxygen environment t-HfO$_2$ is observed over an extended temperature range. Although not presented in the results, this was originally observed after carrying out HTXRD in vacuum at Imperial College and subsequently in N$_2$ using the CNMS equipment. Also, after heating in Ar in the DTA to ~600°C and carrying out XRD on the sample after cooling to room temperature, t-HfO$_2$ was also observed. The fact that t-HfO$_2$ is observed under all these conditions eliminates the possibility that phase stabilisation may be due to nitrogen incorporation within the lattice. This brings us to the conclusion that the oxygen partial pressure plays a significant role.

Because there is always some m-HfO$_2$ in the sample it is hypothesised that the amorphous material crystallises into both m-HfO$_2$ and t-HfO$_2$ simultaneously. At higher temperatures t-HfO$_2$ transforms to m-HfO$_2$. It is thought that due to the similarity in crystallite sizes and the similar rate of growth between the phases, as estimated from the peak intensities, that both m-HfO$_2$ and t-HfO$_2$ nucleate independently within the amorphous materials. There comes a temperature (540°C for the Hf$_x$Si$_{1-x}$O$_2$ sample) where the t-HfO$_2$ peak intensity starts to decrease while the
m-HfO₂ peaks continue to increase, indicating that the t-HfO₂ particles, once they reach a certain size, transform into m-HfO₂.

To explain why m-HfO₂ and t-HfO₂ phases form simultaneously from the amorphous powder the following hypothesis is presented. In a reducing environment excess oxygen vacancies are formed within the crystal lattice. Because no dopants are present to balance the charge, the lack of oxygen results in a change in Hf oxidation state from IV→III. However, not all the Hf changes oxidation state. As the amorphous material starts to nucleate and grow, areas that have a high concentration of Hf^{III} form t-HfO₂ particles, and areas that have a high concentration of Hf^{IV} form the m-HfO₂ particles. Hence, it is the Hf^{III} that stabilises the t-HfO₂ particles. Simeone et al.⁸⁰, though not attributing the stabilisation as due to Hf^{III} specifically, do comment that only when the oxygen vacancy concentration reaches a certain threshold value does the internal strain field cause the particle to stabilise. As already mentioned, in these samples both the m-HfO₂ and t-HfO₂ particles grow at a similar rate, implying that they grow simultaneously from the amorphous material. Some have suggested⁴³ that all m-HfO₂ first nucleates and grows as t-HfO₂ before transforming into m-HfO₂. The results presented here suggest otherwise. During this growth process the Hf^{IV}:Hf^{III} ratio decreases in the t-HfO₂ particles, since Hf^{IV} is the oxidation state of the majority of the Hf, until there are too few Hf atoms in an oxidation state of III. At this point the t-HfO₂ particle undergoes a martensitic transformation to m-HfO₂ and the particle continues to grow. Considering all the experimental data, this seems to be the most plausible explanation for the formation of t-HfO₂ within the temperature range 400-760°C.

The presence of a small amount of t-HfO₂ in the oxygen containing samples may be due to a small number of oxygen vacancies in the sample. The experiment was carried out in a sealed chamber without flowing air hence it is possible that a small number of oxygen vacancies are present, resulting in a very small amount of t-HfO₂. However, this quickly disappears on heating.

### 3.6.2.3 Effects of Silica

As already mentioned SiO₂ is known to have a stabilising effect on the crystallisation of ZrO₂/HfO₂. It is firstly noted that introducing SiO₂ to the system did not have as large an effect on the low temperature regime as had been anticipated from previous work by Ushakov²³. Although the DSC/DTA results were almost identical for each of the
samples studied, analysis of the crystallisation temperatures obtained from XRD highlights a number of points:

in N\textsubscript{2} environment the crystallisation temperature of both m-HfO\textsubscript{2} and t-HfO\textsubscript{2} phases increased from 420 to 480°C with decreasing SiO\textsubscript{2} content (increasing HfO\textsubscript{2} content)

in air, the temperature for t-HfO\textsubscript{2} crystallisation remained constant at 460°C while the m-HfO\textsubscript{2} crystallisation temperature varied between 420 and 460°C, but not linearly as the SiO\textsubscript{2} content decreased.

the temperature at which t-HfO\textsubscript{2} was no longer detected by XRD from the sample heated in the N\textsubscript{2} environment was 740 to 840°C with decreasing SiO\textsubscript{2} content. However, for the SiO\textsubscript{2} free sample the temperature at which the phase disappeared was at 800°C which did not fit the trend observed for the SiO\textsubscript{2} containing sample.

Assuming SiO\textsubscript{2} has a stabilising role on the crystallisation of the sample, our results follow the opposite trend to that expected in the low temperature region. Instead of crystallisation being delayed to higher temperatures as the SiO\textsubscript{2} content increases, crystallisation occurs at lower temperature with increasing SiO\textsubscript{2} content. This occurred when heated in the nitrogen environment. When heated in air there were fluctuations in crystallisation temperature for m-HfO\textsubscript{2}, but not for t-HfO\textsubscript{2} where the temperature remained constant. Unlike Ushakov \textit{et al.}\textsuperscript{23,27} who observed a complete change in the crystallisation phase and temperature upon addition of SiO\textsubscript{2}, using an oxychloride preparation, such a dramatic change is not observed.

In the high temperature region (1000-1700°C) the crystalline behaviour is quite different. It was not possible to carry out the high temperature experiments under a reducing environment so only the results for air are presented. Here we observe that only in the presence of SiO\textsubscript{2} does t-HfO\textsubscript{2} form above ~1000°C. As the SiO\textsubscript{2} content increases the temperature at which crystallisation occurs is also thought to increase. This is determined from the changes in peak width (and hence crystallite size) and intensity in the 1000 and 1400°C XRD scans (Figs 3.12 and 3.16). It is difficult to determine exactly when crystallisation takes place within this temperature range because only specific temperatures are studied and no large exotherm is observed in the DTA/DSC. However, t-HfO\textsubscript{2} is only able to form in the presence of SiO\textsubscript{2}. This is in agreement with Ushakov \textit{et al.}\textsuperscript{23}, Neumayer and Cartier\textsuperscript{23,52} and Kim and Yong\textsuperscript{88},
however a number of other factors must be considered when comparing these results directly. In light of these results, and those presented in Chapter 4, the starting Hf containing precursor has a significant impact on the results obtained from the starting material – especially when SiO₂ is present. With this in mind only the results by Ushakov²³;²⁷ can be compared directly to those obtained in this chapter since they alone use an oxychloride precursor.

There are two main similarities between our results and those by Ushakov²³;²⁷: in a SiO₂-free environment, crystallisation occurs at about the same temperature as our results with XRD implying crystallisation occurs at a temperature lower than the DSC indicates. When SiO₂ is added to the system it causes stabilisation of t-HfO₂ which crystallises at higher and higher temperature as the percentage of SiO₂ is increased. The major area where results differ is that whilst in Ushakov’s system the initial monoclinic crystalline phase is replaced by t-HfO₂ once SiO₂ is introduced, we observe m-HfO₂ at all stages in the crystallisation process as well as the additional crystallisation of t-HfO₂ at higher temperatures. As far as the author is aware this is the first time this effect has been observed for a HfO₂ - SiO₂ system prepared from a Hf oxychloride precursor. It is also thought that this is the first report of a second t-HfO₂ nucleation directly from the amorphous precursor, as opposed to transforming from the m-HfO₂ phase.

From the ZrO₂/ZrₓSi₁₋ₓO₂ literature there are a number of papers where reported TEM images are similar to those in Figs 3.8 and 3.13. For example the large angular particles in Fig 3.7a,b and 3.13b,c are observed by Tani et al.⁶⁷. The particles in Fig 3.7e,f are observed by Chraska et al.⁴⁶ which they attribute to t-ZrO₂. In our case both t-HfO₂ and m-HfO₂ are present in this sample, both phases being of similar crystallite size. It is therefore reasonable to assume that the large particle in Fig 3.7e is made up of both m-HfO₂ and t-HfO₂ crystallites. Similar particles to those illustrated in Fig 3.13a,b have been attributed to m-ZrO₂ by Srinivasan and Davis⁸⁶ and Noh et al.⁸⁹ (They don’t show images of the particles at high magnification so it is difficult to know what the local structure looked like). There is a lot of similarity between the images in Fig 3.7d and both of these are similar to images presented by Armelao et al.⁹⁰ who try to prepare a homogeneous dispersion of HfO₂ and ZrO₂ particles in a SiO₂ matrix. Their particles are in the 5-10nm range, as are ours. What it has not been possible to find in the literature are either nanoparticles randomly dispersed on the grid (Fig 3.7b) or nanoparticles contained in a SiO₂ matrix surrounding the larger m-HfO₂ grains (Fig
3.13b). Not finding the latter suggests that this may be the first report of a double t-HfO₂ nucleation occurring. From the literature, samples which contain SiO₂ as well as ZrO₂ exhibit effects such as those seen in Fig 3.14c,d. The phase segregation and partial crystallisation was commonly found in the samples, as it is also in thin film samples. From the images it is thought that the light areas are the a-SiO₂ and the darker, generally crystalline areas are the HfO₂ rich regions. Because this effect is found often in thin films the discussion of it will be left until Chapter 8.

3.7 Conclusions/Summary

In conclusion it has been demonstrated that t-HfO₂ can be stabilised both at low (~500°C) and high (~1000°C) temperatures. This stabilisation occurs via two different mechanisms. The first, common to all HfO₂ and HfₓSi₁₋ₓO₂ samples prepared from an oxychloride precursor, at lower temperatures, is due to oxygen vacancies which cause Hf to have an oxidation state of 3. Though no direct evidence has been found for this, once other possibilities have been eliminated, this theory best fits our data.

It has often been reported, for ZrO₂, that the tetragonal phase forms first, transforming into the monoclinic phase as the crystallite size increases. However, it was found for HfO₂ in the low temperature region, that under a reducing atmosphere both monoclinic and tetragonal phases formed simultaneously from the precursor material, and a similar growth rate is observed for the two phases. Whilst the tetragonal phase does eventually transform to monoclinic, m-HfO₂ also forms directly from the amorphous precursor material. It is thought that the m-HfO₂ particles form where there is a higher concentration of Hf⁴⁺, and the tetragonal particles where Hf³⁺ has a higher concentration.

The second stabilisation mechanism, occurs at higher temperatures and is attributed to the strain induced by the surrounding SiO₂ rich amorphous matrix. The Hf atoms which are in the minority in the remaining SiO₂ rich matrix, nucleate forming small crystallites which are stabilised by the surrounding amorphous material. They are eventually consumed to form HfSiO₄. This stabilisation results from the mismatch in thermal expansion coefficients between the two materials.
The stabilising effect of SiO₂ is also observed. By increasing the SiO₂ content crystallisation of t-HfO₂ occurs at higher temperatures above 1000°C. At low temperatures SiO₂ has very little effect on crystallisation, contrary to other reports where the addition of SiO₂ always increases the crystallisation temperature and often phase as well.
4 Powder Synthesis and Characterisation – Butoxide

In this chapter Hf t-butoxide was used as part of a sol-gel preparation method to make HfO₂ and HfₓSi₁₋ₓO₂ powders. These powders are analysed using XRD, thermal analysis and TEM techniques. After discussion of the results comparison will be made with results from the oxychloride route from Chapter 3.

4.1 Sol-gel preparation

HfO₂ and HfₓSi₁₋ₓO₂ powders were prepared using a sol-gel technique following an alkoxide preparation route⁵³. Si(OC₂H₅)₄ (tetraethoxy orthosilane, TEOS, Sigma-Aldrich, 98% solution) was prehydrolysed for 2 hours with water and ethanol (BDH, 96% solution) in a 1:1:1 molar ratio. Alkoxide precursors react more quickly than TEOS and so prehydrolysis was required to ensure the reaction would progress as intended. One drop of HCl (BDH Anal AR 37% solution) was added to act as a catalyst for the reaction⁹¹. The TEOS/water/ethanol mixture was stirred, and the Hf t-butoxide (Hf[OC(CH₃)₃]₄) and remaining water were added drop wise to the solution. The total Hf t-butoxide to water ratio was 1:2. The Hf:Si ratio was 1:1. The mixture was left to gel for 72 hours. The Hf t-butoxide was purchased from both Alfa Aesar (100% purity) and Sigma-Aldrich (99.99% purity). Note that the purity does not include the Zr content of the solution. Since Zr and Hf are very difficult to separate, the expected Zr content is ~2000ppm.

All experiments were the same as those described in Chapter 3 and so specific experimental parameters are not repeated here. The main aims of the experiments were:

1. to prepare HfO₂ bulk samples and investigate the crystallisation process
2. to consider the effect on crystallisation of having SiO₂ present in the preparation

These were investigated using thermal analysis, XRD (high temperature and ambient) and TEM techniques. The main experiments conducted were:
1. thermal analysis to determine crystallisation temperatures and mass loss
2. HTXRD to temperatures of 900°C
3. ambient XRD of samples heated to 800, 1000, 1400 and 1650/1700°C
4. effect of heating environment – air vs. N₂
5. effect of time at temperature on the crystallisation pathway

All results presented here are for the butoxide route. A comparison with the oxychloride results will be made towards the end of the discussion (section 5.4.3).

### 4.2 Hafnia Results

The effect of N₂ and air environments on HTXRD and thermal analysis of HfO₂ (SiO₂-free) samples was investigated. It was found that the heating environment had little effect on results. The thermal analysis results for the HfO₂ powder are shown in Fig 4.1 and have been obtained in an air environment.

The results from thermal analysis using the DSC instrument were of better quality than from the DTA hence the DSC results are shown throughout this chapter. The baseline of the DSC was not flat as was expected and attempts to correct it were unsuccessful. As explained in Chapter 3, this was due to the background/reference scan being collected a number of days apart from some of the experimental data. It was not practical to take a new reference scan for each data set, hence the baseline is not always good. However, all the main features can still be resolved.

Fig 4.1 shows the DSC and TGA data for HfO₂ heated to 1500°C. There is a total mass loss of ~16%. Each change in slope of the TGA data corresponds to the loss of water and carbonaceous species and coincide with endotherms in the DSC data. There is one sharp exotherm in the DSC data at ~525°C and two broad features at 730-1100°C and 1115-1300°C. Two small ‘bumps’ or peaks are observed at 394 and 456°C (marked 1 and 2 respectively on the graph). These are similar to those observed for the oxychloride prepared sample in Chapter 3 (Fig 3.4) but are less well defined. As with the oxychloride results, the main peak (peak 3) at 525°C does not match the crystallisation temperature as found by XRD, which is between 460-480°C (Fig 4.2a).
The x-ray diffraction results for this sample up to 1700°C are summarised in Fig 4.2. Both ambient and HTXRD confirm that the first phase to form is m-HfO₂. From the ambient XRD results (Fig 4.2b) the crystallite sizes were calculated using the Scherrer equation and were found to vary from about 15-40nm over the 800°C - 1700°C temperature range (Table 4.1).
Figure 4.2: (a) HTXRD carried out at the CNMS and (b) ambient XRD of HfO₂ samples after heating in a furnace between 800-1700°C (m = m-HfO₂)

At 1700°C the particles are smaller than at 1400°C. This may be due to the sample having been heated for less time at this temperature and therefore not allowing the particles to grow sufficiently in size. Also, at high temperatures some of the sample reacted with the alumina crucible hence there was less sample on which to carry out
Hence the large reduction in peak intensity. From HTXRD it is found that crystallisation has occurred by 480°C though there is a hint of the (-111) and (111) peaks at 460°C. Table 4.2 summarises the temperatures at which crystallisation of the m-HfO$_2$ and t-HfO$_2$ phases are observed using the CNMS HTXRD equipment for all samples in this chapter. It also presents the temperature at which there is a hint of the phase appearing in the XRD scan, though it is not clearly visible until higher temperatures. Crystallisation temperatures here relate specifically to the CNMS data and not the Imperial data. Table 4.2 also compares the effect of heating environment on crystallisation temperature for the two samples. Because almost no effect was observed after heating in N$_2$, most samples were analysed in air only. From Fig 4.2a as the temperature increases the m-HfO$_2$ peaks increase in intensity and narrow, indicating that the crystalline proportion of the sample and average crystallite size has increased. m-HfO$_2$ is present up to 1700°C and no t-HfO$_2$ is found in the sample.

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<tr>
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<th>Hint of phase (°C)</th>
<th>Clear (°C)</th>
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<tr>
<td><strong>HfO$_2$</strong></td>
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<tr>
<td>N$_2$</td>
<td>m 460</td>
<td>480</td>
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<td>air</td>
<td>m 440</td>
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<tr>
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<td>880</td>
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<td>t 880</td>
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<tr>
<td>air</td>
<td>m 500</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>t 660</td>
<td>700</td>
</tr>
</tbody>
</table>

Table 4.2: Crystallisation temperatures taken from HTXRD data from the CNMS. Data for HfO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ (x = 0.3, 0.5 and 0.7; m = m-HfO$_2$, t = t-HfO$_2$)
Typical TEM images of the HfO₂ sample after heating to 1000°C are shown in Fig 4.3. There is little indication of any amorphous phase in this sample. Particles are in the form of agglomerates, some of which have broken up leaving individual particles on the holey carbon TEM grid, due to mechanical grinding during sample preparation. From TEM imaging, particles varied in size from ~30-100nm. For comparison, images of the amorphous starting powder before any heating are shown in Fig 4.4. Here ‘particle’ sizes are about 1000nm. These images show uniform morphology leading to the conclusion that the Hf and Si are distributed homogeneously within the precursor. As soon as the amorphous regions were exposed to the beam, they densified. This was visible on the phosphor screen.
4.3 Hafnium silicate results

4.3.1 Hf$_{0.5}$Si$_{0.5}$O$_2$

Introducing SiO$_2$ to the system (Hf$_x$Si$_{1-x}$O$_2$) causes the crystallisation pathway to alter significantly. HTXRD results for the $x = 0.5$ sample are shown in Fig 4.5. The results in Fig 4.5a are from the Imperial HTXRD system because the CNMS HTXRD did not reach high enough temperature to probe the crystalline transitions occurring at $\sim$1000°C. The temperatures indicated on the graph, although calibrated as well as possible, should not be taken as accurate for the reasons described in Chapter 3. t-HfO$_2$ is found to be the first crystalline phase to form between 800-900°C (Fig 4.5a). The crystallite size increases a little as indicated by the narrowing of the tetragonal peak, before transforming into m-HfO$_2$. The scan at 1121°C in Fig 4.5a shows both the t and m phases. Here the peak intensity has decreased at the same time as the m-HfO$_2$ peaks increase, suggesting that a t$\rightarrow$m transformation occurs. To investigate this the HTXRD was used to collect a spectra when the sample reached temperature and after 1 hour of the sample being held at temperature. These scans are overlaid for each temperature in Fig 4.6. From the 1121°C and 1246°C scans (Fig 4.6), the tetragonal to monoclinic transformation is observed over the time held at temperature, and also as the temperature is increased. The t-HfO$_2$ peak decreases in intensity as the m-HfO$_2$ peak increases.
We note from the furnace heated samples (Fig 4.5b) that by 1400°C no t-HfO₂ remains, a little SiO₂ (in the form of cristobalite) has crystallised and HfSiO₄ has started to form. By 1700°C the HfSiO₄ peaks have increased in intensity and the m-HfO₂ peaks have decreased, though not completely disappeared, as was expected by this temperature. This suggests that the reaction is incomplete or there is some sub-stoichiometry in the system. Formation of HfSiO₄/ZrSiO₄ has previously been reported as having slow sluggish kinetics and hence an incomplete reaction at 1700°C is the likely explanation for m-HfO₂ remaining.
Figure 4.6: HTXRD scans from Hf<sub>0.5</sub>Si<sub>0.5</sub>O<sub>2</sub> overlaid from fast scan (blue) and slow scan (pink), taken about an hour apart. The evolution of the phase is observed over time and at each temperature (Pt = peak due to Pt/Rh heater)

The crystallisation temperatures up to 900°C from the CNMS experiments are found in Table 4.2. These vary from the temperatures in Fig 4.5 and 4.6 due to the different experimental conditions used and hence thermal history of the sample. Crystallisation of t-HfO<sub>2</sub> is only a weak feature in the CNMS scans at 880°C and 900°C while in the Imperial data t-HfO<sub>2</sub> has clearly started to form by 875°C. The peak at ~40°2θ in Fig 4.6 is due to the Pt/Rh heater on which the sample is placed for analysis.

The other main difference between the Imperial and CNMS data is that the Imperial data shows no trace of m-HfO<sub>2</sub> until above 1000°C whereas the CNMS data shows two very small ‘bumps’ in the amorphous background (not shown) that correspond in position to the (-111) and (111) m-HfO<sub>2</sub> peaks, at 580°C. This is not observed in the Imperial data due to a much higher noise level because of the experimental set-up and small amount of sample used. From the CNMS data, though m-HfO<sub>2</sub> ‘peaks’ appear at 580°C, there is very little change in intensity as the temperature is increased. Only by 880°C is it possible to distinguish them as clear peaks, but even then the intensity is low with the peaks only just visible above the amorphous background. A small feature, barely visible above the background is also observed at the position where t-HfO<sub>2</sub> is expected. This never forms into a clear peak over the 900°C temperature range investigated.
Thermal analysis results for the Hf$_x$Si$_{1-x}$O$_2$ samples ($x = 0.3$, $0.5$, $0.7$) are presented in Fig 4.7. In the $x = 0.5$ results, a mass loss of about 17% is found (Fig 4.7a). One main exotherm is detected at $\sim$964°C with a possible broader peak spanning 700-1300°C (Fig 4.7b). However, uncertainty about the baseline means it is unclear whether this is a feature or not. The main exotherm is in the temperature range attributed to the crystallisation of the t-HfO$_2$ phase from XRD. At $\sim$1350°C the trace rises steeply indicating that this may be the start of a thermal event that is not completed over the temperature range probed. The baseline of the $x = 0.5$ data is flatter than either the $x = 0.3$ or $x = 0.7$ data. The $x = 0.5$ data was recorded shortly after the instrument calibration was performed suggesting that the baseline changes significantly over time. Unfortunately it was not practical to take more than one calibration data set for these experiments. (The $x = 0.3$ and 0.7 thermal analysis results will be discussed in more detail below).

![Figure 4.7](image)

**Figure 4.7:** (a) Mass loss and (b) DSC results for Hf$_x$Si$_{1-x}$O$_2$ with $x = 0.3$, $0.5$ and $0.7$

### 4.3.2 Hf$_{0.3}$Si$_{0.7}$O$_2$ and Hf$_{0.7}$Si$_{0.3}$O$_2$

The XRD results for the $x = 0.3$ and $x = 0.7$ samples are shown in Fig 4.8. It is known that SiO$_2$ has a stabilising effect on the crystallisation process: the more SiO$_2$ present the higher the crystallisation temperature. The results in Fig 4.8 are consistent with this: the $x = 0.7$ sample (Fig 4.8b), exhibits a lower crystallisation temperature than the $x = 0.3$ sample (Fig 4.8a). From the data presented in Table 4.2 t-HfO$_2$ has crystallised by 640°C for $x = 0.7$. The peak narrows and increases in intensity indicating that a
large percentage of the powder nucleates in the t-HfO$_2$ phase and then the crystallites grow in size. However, at 620°C there is also a very small peak associated with m-HfO$_2$ (Table 4.2). Again this peak is only just visible above the amorphous background and does not increase much in intensity until 800°C where it becomes clearer. Even once the tetragonal peak has formed the intensity is too low to be able to carry out Rietveld refinement to obtain crystallite sizes. Although a kinetics study has not been carried out on this sample, the t-HfO$_2$ peak decreases in intensity and the m-HfO$_2$ peaks increase simultaneously indicating that a process similar to that for the x = 0.5 sample is taking place – i.e. t-HfO$_2$ transforms into m-HfO$_2$. By 1400°C only m-HfO$_2$ remains with the start of both the c-SiO$_2$ and HfSiO$_4$ crystallisation. By 1650°C HfSiO$_4$ has started to crystallise but m-HfO$_2$ remains at this temperature. This is partly because not all of the HfO$_2$ has reacted with the remaining amorphous material to form HfSiO$_4$. However in this sample because it is HfO$_2$ rich we would expect there to be a significant m-HfO$_2$ percentage remaining since not all HfO$_2$ is able to participate in the HfSiO$_4$ formation. From Fig 4.7a a total mass loss of ~10% was observed for x = 0.7. It is unusual that no exotherm in the DSC could be attributed to a crystallisation event is observed, despite the fact that the t-HfO$_2$ phase grows very quickly once it starts to form. The DTA results however did show a broad peak spanning 500-700°C. There is currently no explanation for why this did not appear in the DSC results and may be because of the poor baseline.
The thermal analysis results (Fig 4.7) for the \( x = 0.3 \) sample show that about 13\% of the total mass is lost over the course of heating. In the DSC (Fig 4.7b) two small peaks are observed at \( \sim 998^\circ \text{C} \) and \( 1035^\circ \text{C} \). If these are due to crystallisation within the sample this would confirm that the more SiO\( _2 \) present the higher the crystallisation temperature since the exotherms are at higher temperature than for the \( x = 0.5 \) sample. If the peak is due to the crystallisation of HfO\( _2 \), it is not surprising that the intensity is not as great as for the \( x = 0.5 \) sample, since a much smaller quantity of the sample is crystallising. Though the crystallisation temperature according to the DSC is higher than for the \( x = 0.5 \) sample, there is little difference between the two samples in the XRD when comparing Fig 4.5b with 4.7a. Tetragonal HfO\( _2 \) has formed by \( 1000^\circ \text{C} \), and has completely disappeared by \( 1400^\circ \text{C} \) in favour of m-HfO\( _2 \), c-SiO\( _2 \). There is also a hint of HfSiO\( _4 \) at this temperature. By \( 1650^\circ \text{C} \) HfSiO\( _4 \) is the dominant phase with some c-SiO\( _2 \) and m-HfO\( _2 \) remaining. The peaks at 1650/1700\^\circ \text{C} in all the data sets are quite broad.
The c-SiO₂ peak in Fig 4.8b at 1650°C has broadened compared with that observed at 1400°C. This may imply that after heating for 12 hours at 1650°C the particles have not grown as large as they had at 1400°C after heating for 24 hours. Alternatively this may be expected: since the m-HfO₂ is used to make HfSiO₄ as the monoclinic phase is used up, the crystallite size and number decrease resulting in reduced peak intensity and increased peak widths in the XRD scans. However, since a similar effect was observed for the SiO₂-free environment (Fig 4.5), where no new phases were formed, this is unlikely to be the explanation. This again shows that the time at temperature has an impact on the crystallite size and percentage of the phase that has formed (or transformed).

For cristobalite in the x = 0.3 sample it is interesting that the cristobalite still remains at the highest temperature. This would suggest that HfSiO₄ forms initially from a combination of the remaining amorphous precursor and m-HfO₂ rather than from the crystalline SiO₂ species. The crystalline SiO₂ is used once the amorphous material has been used up.

The behaviour of the sample below about 800°C is puzzling. If the XRD scan at 800°C from Fig 4.8b (Imperial) is magnified sufficiently there is an indication that some m-HfO₂ has started to form though no t-HfO₂ is observed. The data from the CNMS, outlined in Table 4.2, show that there is a hint of m-HfO₂ by 500°C and t-HfO₂ by 660°C which become clearer by 600 and 700°C respectively though it is not until 880°C that there is a larger change in the intensity of the t-HfO₂ peak. A comparison is made in Table 4.1 between the crystallisation temperatures in air or nitrogen. There is little difference between the results confirming that the heating environment has little impact on the crystallisation pathway.

### 4.3.3 TEM images

Figs 4.9 and 4.10 show TEM images of particles typically found in x = 0.5 silicate samples heated to 800 - 1700°C. Many of the particles at 800°C vary in diameter from 20-100nm. Crystalline particles of this size were not expected since the XRD indicates very small crystals for t-HfO₂. There are also large ‘amorphous particles’ (Fig 4.9b) which contains large crystalline particles. It is thought that the crystalline particles are actually sitting above or below the amorphous particle since the amorphous region looks fairly uniform and is similar to the images of the expected amorphous material. It
Figure 4.9: TEM images of Hf$_{0.5}$Si$_{0.5}$O$_2$ samples heated to 800 and 1000°C
Figure 4.10: TEM images of Hf$_{0.5}$Si$_{0.5}$O$_2$ samples heated to 1400 and 1700°C
is unlikely that only one section of it would crystallise without having a similar effect on the surrounding material. The ‘amorphous’ particle actually contains nano-crystals about 2-3nm in size, as seen in Fig 4.9c. It is not clear whether these particles were already present in the sample or whether their formation has been induced by the electron beam.

From the CNMS XRD data there was indication that m-HfO₂ had started to form by 800°C so it is possible that the particles are m-HfO₂. However, the size of the particle in Fig 4.9a is much larger than expected from XRD particle sizing measurements. There is also the possibility of some contaminant species being present on the grid. The sample heated to 1000°C exhibits different morphology. At this temperature only t-HfO₂ is expected. The two most common types of particles are in Fig 4.9d and e (f and g being higher magnification images of e). Considering Fig 4.9e-g first, these ‘particles’ are made up of nanocrystallites of HfO₂, surrounded by remaining SiO₂-rich, predominantly amorphous material. The crystallites are ~5nm in size. Isolated nanocrystals of ~3-5nm were also commonly found dispersed on the grid (Fig 4.9d). These particles were difficult to see in TEM but in STEM mode they are clear (Fig 4.11). Whilst the majority of the particles are likely to be t-HfO₂, once transformed to m-HfO₂ they are still about the same size as the t-HfO₂ particles. In theory electron diffraction is able to distinguish between these phases, but this is difficult experimentally because of the crystallite size and beam damage effects. At 1400°C, as well as particles similar to those in Fig 4.9a, you also get particles such as those in Fig 4.10a, and more commonly large particles such as Fig 4.10b and c. The crystalline particles in Fig 4.10a look as though they are surrounded by an amorphous matrix, but at higher magnification it becomes clear that the whole area is crystalline. Particles at 1700°C look similar to those at 1400°C though larger in size.
4.4 Discussion

The main observations arising from the butoxide results are:

1. the heating environment has little effect on the crystallisation pathway
2. addition of SiO₂ to the system results in a change in initial crystalline phase and temperature
   a. as the percentage of SiO₂ increases, the crystallisation temperature at which a hint of the phase appears, decreases but the temperature at which crystallisation is clear, increases.
   b. m-HfO₂ forms on crystallisation in an SiO₂-free environment compared with t-HfO₂ in the SiO₂ containing sample
   c. in samples where t-HfO₂ forms first, it subsequently transforms to m-HfO₂ as the temperature increases
   d. as the sample is held at temperature the particles continue to grow and/or transform
3. that despite experimental conditions being the same, oxychloride and butoxide prepared samples have different crystallisation pathways.

Sections 4.4.1-4.4.2 deal with the butoxide route before a comparison of the oxychloride and butoxide results is made in section 4.4.3.
4.4.1 Heating Environment

The first key observation is that heating in an inert environment has little effect on the crystallisation pathway of HfO$_2$ either with or without SiO$_2$. Heating in N$_2$ causes no change to the crystalline phase and only minor differences in crystallisation temperature. There is not even a hint of t-HfO$_2$ in the XRD patterns of HfO$_2$ in either air or N$_2$ environments, unlike the oxychloride sample where a hint of a tetragonal peak was present up to ~800°C. In the SiO$_2$-free sample once m-HfO$_2$ forms from the butoxide precursor the crystals grow in size as the temperature increases. There is no indication of any other phase present. In the SiO$_2$-containing sample there is also no t-HfO$_2$ formation at low temperature in N$_2$. Though t-HfO$_2$ crystallises at higher temperatures (>600°C), this is not affected by heating environment as the crystallisation mechanism is the same in air. Because there is no variation in crystalline phase with atmosphere it is concluded that the oxygen partial pressure, and hence oxygen vacancies are not the cause of t-HfO$_2$ stabilisation in the SiO$_2$ containing HfO$_2$ system. This is in contrast to the conclusions reached for oxychloride-derived material where t-HfO$_2$ was observed under low oxygen partial pressure.

4.4.2 Effect of SiO$_2$ on crystallisation

4.4.2.1 Crystallisation Temperature

The second key observation is that addition of SiO$_2$ into the system has a large effect on both the crystallisation temperature and the crystalline phase that forms from the amorphous starting material. For all SiO$_2$ concentrations the initial crystallisation phase changed from m-HfO$_2$ (with no SiO$_2$ present) to t-HfO$_2$, and the temperature at which t-HfO$_2$ had clearly crystallised, increased with increased SiO$_2$ content. The CNMS HTXRD could not be used to investigate the effect of temperatures greater than 900°C. This meant that the specific temperature at which t-HfO$_2$ transforms into m-HfO$_2$ could not be studied as a function of SiO$_2$ content because the transition occurs at ~1000°C for $x = 0.3$ and $x = 0.5$. (This is known from the ambient XRD in Figs 4.5 and 4.8). However, from ambient XRD it was clear that as SiO$_2$ content increased, the crystallisation temperature increased. The increase in crystallisation temperature can be explained as follows. Si is in a glassy-like state forming a network of [SiO$_4$] polyhedra. [HfO$_x$] polyhedra diffuse through the [SiO$_4$] network to start to nucleate and grow. The more SiO$_2$ therefore, the further the [HfO$_x$] have to transverse the material to nucleate hence the higher the temperature required. This in turn requires that more energy be put
into the system to allow the [HfOₙ₋₅] polyhedra to transverse the material and nucleate. This energy is put into the system by increasing the temperature.

The increase in crystallisation temperature resulting from the introduction of SiO₂ may be important to keep the high-κ oxide from crystallising under current device processing conditions. For device applications the high-κ material should remain amorphous to about 1000°C. However, for HfₓSi₁₋ₓO₂ dielectrics it has been observed that, even where a high crystallisation temperature is achieved, the dielectric layer phase segregates into SiO₂ and HfO₂ rich regions resulting in a change in dielectric across the layer and diffusion paths across the layer. This is not wanted in a working device. The phase segregation observed in thin films (See Chapter 8, Figs 8.2 and 8.3) looks very similar to that in Figs 4.9 and 4.10, though clearly the powder samples have been heated for a much longer time than that required for device manufacture and therefore the same degree of segregation would not be observed if the powders had been subjected to a short (~30s) anneal.

4.4.2.2 Crystalline Phase

Results in this chapter show that m-HfO₂ is the stable crystalline phase, but when SiO₂ is present t-HfO₂ forms first from the amorphous precursor. Most reports of t-HfO₂ forming from the amorphous powder (whether in ZrO₂ or in HfO₂ systems) observe t-HfO₂ as the first crystalline phase, with or without the presence of SiO₂ (e.g. references 8,23,39,72,93). Two examples of HfO₂ systems were found where, in the presence of SiO₂, t-HfO₂ forms but in the absence of SiO₂ the m-HfO₂ phase forms23,52. Ushakov and co-workers 23,27 prepared HfO₂ and HfₓSi₁₋ₓO₂ samples from an oxychloride precursor and found that HfO₂ crystallised into m-HfO₂ at 537.9°C or 472.3°C when prepared with N₂H₄ or NH₄OH, respectively. These temperatures are taken from the main exothermic peak in the DTA and in light of the discussion regarding ‘growth phenomenon’ in Chapter 3, should be treated with caution as being the crystallisation temperature itself. However, crystallisation will have certainly occurred by this temperature. When as little as 10% SiO₂ is added to the system the crystallisation temperature, according to the DSC exotherm, goes up to ~740°C and t-HfO₂ is the first phase to form. They also observe that as x decreased the crystallite size, from a sample quenched just after the exotherm in the DSC and analysed by XRD, decreased. This trend in crystallite size is not clear from our data and was not investigated explicitly.
Neumayer and Cartier\textsuperscript{52} also observe a difference in crystalline phase between SiO\textsubscript{2} free and SiO\textsubscript{2} containing samples. Spin coated 100nm HfO\textsubscript{2} and Hf\textsubscript{x}Si\textsubscript{1-x}O\textsubscript{2} films, prepared from an alkoxide precursor, were studied, with $x = 0.25$ and $x = 0.15$. The HfO\textsubscript{2} films crystallised by 500°C into m-HfO\textsubscript{2}, but when SiO\textsubscript{2} was present t-HfO\textsubscript{2} formed. Based on Fourier Transform Infrared (FTIR) analysis it was suggested that even a small amount of HfO\textsubscript{2} perturbs the surrounding SiO\textsubscript{2} network, possibly resulting in t-HfO\textsubscript{2} being favoured above m-HfO\textsubscript{2} as the crystalline phase, whereas in the equivalent ZrO\textsubscript{2} sample no perturbation was detected. This implies that the local co-ordination in the amorphous precursor may have some effect in determining the crystallisation pathway.

Some of the options for t-HfO\textsubscript{2} stabilisation, outlined in more detail in Chapter 3 (Section 3.6.1), are surface energy stabilisation, ion impurities, local ordering and oxygen vacancies. Oxygen vacancies are eliminated from the argument as mentioned above. Local ordering is still a possibility and Neumayer and Cartier’s\textsuperscript{52} work would suggest this has an effect. However, there is not currently enough experimental evidence to come to a conclusion on this issue. The role of impurities within the sample has not been investigated. It is not thought that there is a significant quantity of contaminant species present in the powders. Neumayer and Cartier\textsuperscript{52} note that there is still a lot of carbon in zirconium silicate films after heating to 900 and 1100°C but that there was twelve times more carbon at the lower of the two temperatures hence CH\textsubscript{3}COO\textsuperscript{-} may have a role. However, it is thought that this is unlikely to be the main influence in the tetragonal phase stabilisation since if CH\textsubscript{3}COO\textsuperscript{-} remains in the SiO\textsubscript{2}-free sample it clearly has no effect.

The main contributor to t-HfO\textsubscript{2} stabilisation is the surface energy effect induced by SiO\textsubscript{2}. In these samples strain analysis has not been carried out and so the effect of strain is being incorporated into the term ‘surface energy’ for the sake of this discussion. As discussed previously, in ZrO\textsubscript{2} the t-ZrO\textsubscript{2} particles can be stabilised by having a high surface energy following Garvie’s theory\textsuperscript{43} (see section 3.6.1). The surface energy effect is modified by interfacial effects between touching particles, external pressure that may have been applied to the system as well as a-SiO\textsubscript{2}. From Fig 4.9e-g it is known that many of the particles are in the form of agglomerates. The interfaces between these particles will modify the surface energy. This allows the t-HfO\textsubscript{2} particles to grow to a larger size before transforming, unlike isolated t-HfO\textsubscript{2} particles where the transformation is thought to occur at smaller crystallite sizes because of the lack of the
strain effect. As well as interparticulate interfaces, the interface between the surrounding a-SiO₂ must also be taken into consideration. Maria et al.⁸ attribute the large stabilising effect of SiO₂ to the difference in thermal expansion coefficient between the HfO₂ particles and the SiO₂ i.e. the thermal expansion coefficient of Si is ten times smaller than that for HfO₂. This means that as the sample is heated, because the SiO₂ does not expand as quickly as HfO₂ it imposes a constraining effect on the t-HfO₂ particles, preventing them from transforming into m-HfO₂. Once they gain enough energy, possibly through heating, this transformation can occur. It is also interesting to note that there is no second t-HfO₂ nucleation at ~1400°C as in the oxychloride route.

4.4.2.3 Tetragonal to Monoclinic Phase Transformation

From the kinetic data in Fig 4.6 it is found that t-HfO₂ transforms to m-HfO₂. This occurs both as the temperature is increased and also as the sample is held at temperature. This implies that once the particle reaches an optimum size the constraining effect by the SiO₂ is no longer sufficient to retain the tetragonal phase. To lower its free energy it is more favourable for the t-HfO₂ particle to transform to m-HfO₂. The particles then continue to grow in size. Samples that crystallise at a lower temperature (e.g. x = 0.7) also phase transform at a lower temperature.

The suggested overall mechanism for the reactions occurring in the x = 0.5 sample is:

\[
\begin{align*}
\sim 800°C & \quad \text{amorphous} \rightarrow t\text{-HfO}_2 \\
\sim 1200°C & \quad t\text{-HfO}_2 \rightarrow m\text{-HfO}_2 \\
\sim 1400°C & \quad \text{amorphous} \rightarrow c\text{-SiO}_2 \\
\sim 1700°C & \quad \text{amorphous} + m\text{-HfO}_2 + c\text{-SiO}_2 \rightarrow \text{HfSiO}_4
\end{align*}
\]

The mechanism is the same for all x, though the temperatures at which phase formation and transformation occurs will vary. The only deviation from this is that there is also a hint of an m-HfO₂ phase initially forming from the amorphous precursor. However this does not grow very much. One suggestion is that when HfO₂ nucleates at the edge of the amorphous material, because it is surrounded by less SiO₂ it has less of a constraining effect on the HfO₂, allowing it to form m-HfO₂. In the same volume of material, t-HfO₂ will still nucleate in the bulk because of the constraint of the remaining amorphous material. Because the large ‘amorphous’ particles (i.e. ~1μm) only a small
proportion of the sample is edge material, and so only a small percentage of the sample becomes monoclinic. This in turn suggests that the t→m transformation occurs from the edge of the particle and moves towards the centre as temperature or time increase\(^64\). This also implies that both m-HfO\(_2\) and t-HfO\(_2\) can form simultaneously from the precursor and that not all m-HfO\(_2\) forms by transforming from t-HfO\(_2\). However, the t→m transformation is the dominant mechanism in this sample.

In the HfO\(_2\) rich sample (x = 0.7) although the HfSiO\(_4\) phase has formed, there is still a lot of cristobalite (c-SiO\(_2\)) remaining at 1700°C. This indicates that HfSiO\(_4\) initially forms from the remaining amorphous material and that the c-SiO\(_2\) is only used to form HfSiO\(_4\) after most of the amorphous material has gone. In this sample (1700°C) there is still some m-HfO\(_2\) present which, if held at temperature for longer, would, along with the c-SiO\(_2\), also form HfSiO\(_4\). It is initially surprising that all of the a-SiO\(_2\) does not crystallise into c-SiO\(_2\). It is thought the reason for this is that two competing mechanisms are occurring: the temperature at which a-SiO\(_2\) crystallises is also the temperature at which SiO\(_2\) (amorphous or crystalline) is used up to form HfSiO\(_4\). Along with sluggish crystallisation kinetics for SiO\(_2\) these competing mechanisms result in little c-SiO\(_2\) forming.

It was noted in the results that at 1700°C the XRD peaks were all broader than at lower temperatures. One possible cause is that at this temperature, because the sample had only been held at temperature for 12 rather than 24 hours, that not all of the sample had yet crystallised. In theory, if held at temperature for longer these peaks may sharpen. The second hypothesis is that this is exactly what would be expected of the sample at this temperature, where both m-HfO\(_2\) and SiO\(_2\) are being consumed to form HfSiO\(_4\). As these two species are being consumed, their crystallite size becomes smaller resulting in peak broadening in the XRD. However, whilst this is plausible it also occurs in the SiO\(_2\)-free sample where there are no phase transformations. Therefore this is not the explanation for the observations.

\subsection*{Comparison of oxychloride and butoxide preparation routes}

It is clear by comparing results from Chapters 3 and 4 that the two different preparation routes result in markedly different crystallisation pathways. The crystallisation behaviour due to heating environment at low temperature in different environments
varies: in the butoxide route one has no effect, for the oxychloride route a different crystalline phase forms. The influence of SiO$_2$ also promotes different crystallisation paths. Two different t-HfO$_2$ stabilisation mechanisms have been hypothesised: the oxychloride sample has stabilisation by oxygen vacancies at lower temperatures and stabilisation by a surface energy/crystallite size effect at higher temperature. For the butoxide route the latter is the mechanism by which t-HfO$_2$ is stabilised. The surface energy/crystallite size effect only occurs in the presence of SiO$_2$. For the first stabilisation route oxygen vacancies are dependent on heating environment.

What is not yet clear is why the two routes should have such large differences in crystallisation pathways; why one contains oxygen vacancies and the other not; why SiO$_2$ prevents crystallisation in one sample and not the other. These questions are outwith the scope of this project, though as already mentioned, it is quite likely that the crystallisation pathway is determined by the local atomic environment within the starting powders. To provide some insight into this theory it was thought that the morphology of the starting materials may hold some answers. Images of the starting powder material from the oxychloride and butoxide preparations are found in Fig’s 3.8 and 4.4 respectively. It is quite obvious that the morphology of the starting powder is different between the two samples. These samples contained no SiO$_2$ so, without equivalent images from the SiO$_2$ containing samples, it is difficult to make a full comparison. However, at first glance it would seem that because of the nature of the butoxide images, they would be conducive to first forming small crystallites. When no SiO$_2$ is present these form directly into m-HfO$_2$ and is not affected by the heating environment. For the oxychloride samples the morphology is completely different. Instead of appearing as individual particles, the ‘particles’ are very large agglomerates which have not separated when suspended in solution. These ‘particles’ are mainly amorphous. This would indicate that the nucleation sites in each sample are different. This is further evidence to promote a fuller investigation into the local atomic structure in the amorphous powders.
4.5 Conclusions

In conclusion, it has been seen, by comparison with samples prepared from an oxychloride precursor (Chapter 3), that the butoxide samples have an entirely different crystallisation pathway on heating from an amorphous precursor powder. In these samples SiO₂ has a large effect on the system. We conclude that SiO₂ has a stabilising role on the formation of t-HfO₂. This stabilisation is due to the large surface energy effect between the amorphous SiO₂ (a-SiO₂) and crystalline HfO₂. The t-HfO₂ transforms into m-HfO₂ before being consumed to form HfSiO₄ at higher temperature. As the SiO₂ content is increased the crystallisation temperature is also increased and the crystallite size on crystallisation reduced. When no SiO₂ is present the crystallisation temperature is much lower and m-HfO₂ forms with no indication of any t-HfO₂ up to high temperatures.

In the SiO₂ containing samples it was also found that the sample continued to crystallise and/or phase transform with time held at temperature. The heating environment had no effect on the crystallisation path.

Tetragonal HfO₂ is stabilised by different mechanisms depending on the starting materials used. At low temperatures in the oxychloride sample stabilisation was attributed to oxygen vacancies, and at high temperatures, surface energy stabilisation. In the butoxide sample the t-HfO₂ phase is also stabilised by the surface energy effect resulting from t-HfO₂ crystals being stabilised in the a-SiO₂. From TEM imaging of the starting powders it is noted that the morphology and hence the local atomic environment within these samples is different providing evidence to support the hypothesis that the local structure of the starting materials is of paramount importance in determining the crystallisation pathway within the sample.
5 Modelling theory and codes

In this chapter, two methods for calculating the electronic structure and hence ELNES, will be described. The theory of band structure calculations as implemented in the multiple scattering and density functional theory codes, FEFF8 and Wien2K, will be considered. Whilst FEFF is based on real-space multiple scattering (RSMS) theory, Wien2K uses density functional theory to calculate the EELS spectra. More space is devoted to describing FEFF code and surrounding issues, than on Wien due to the relative amount of work carried out using each of these packages. Corresponding modelling results are presented in Chapter 6.

5.1 Multiple scattering theory

Multiple scattering (MS) theory treats a solid or molecule as a cluster of atoms. These atoms are represented by atomic potentials from which the excited core electron-wave scatters in real space. The interaction of the outgoing electron-wave with the returning scattered wave produces an interference pattern giving rise to the fine structure on the ionisation edges. There are two main regions of the energy-loss on the ionisation edge: the energy-loss near-edge structure (ELNES), extending to ~30eV above the edge onset, and extended energy-loss fine structure (EXELFS), scattering above ~30eV. The ELNES region is attributed to multiple scattering of the outgoing electron-wave whilst EXELFS is usually attributed to single scattering events (see Fig 5.1). EELS has been described in more detail in Chapter 2.
The multiple scattering method divides the atoms into clusters or shells. For a simple structure such as a cubic structure, each atom within a shell is equidistant from the central atom. Once the structure becomes less symmetric from a calculations point of view it is more difficult to assign specific ‘shells’. For such cases a cluster is defined such that the atoms within the cluster are of a similar, though not identical, distance from the central atom. The inter and then intra-shell scattering is calculated and the results combined. MS theory was originally intended for x-ray absorption spectroscopy (XAS) however, in practice there is little difference between x-ray and EELS spectra – both techniques result in the promotion of an electron to unoccupied electronic states hence both probe the local electronic structure. The theory and resulting model for x-ray absorption spectroscopy can be applied to EELS as well. Hence from the literature the term ELNES is interchangeable with x-ray absorption near-edge structure (XANES) and EXELFS with x-ray absorption fine structure (EXAFS) when theory or results are being considered.

There are many advantages of adopting MS methods compared with DFT (which will be discussed in more detail below). Using multiple scattering techniques, the electronic structure of non-periodic structures such as molecules or biological systems can be calculated with much less computation time as would be required for equivalent DFT calculations which requires a high degree of symmetry for short computation time. Final state contributions such as core-hole effects, inelastic losses and thermal contributions, can also be included, resulting in more accurate calculations.
The starting point for MS theory is Fermi’s Golden Rule. This has been simplified to the one-electron approximation from an equation including many-body effects, and can be represented in the following form:

$$\mu(\omega) \approx \sum_f \left| \langle i | d | f \rangle \right|^2 \delta(\hbar \omega + E_i - E_f)$$  \hspace{1cm} \text{Eqn. 5.1}

where
- $\hbar \omega$ = the x-ray energy or electron energy loss
- $\mu$ = absorption coefficient
- $E_i$ = initial energy of the core-level
- $E_f$ = energy of the final state
- $d = \hat{E} \cdot \vec{r}$ = the dipole approximation
- $\langle f \rangle$ = final state wavefunction
- $\langle i \rangle$ = initial state wavefunction

This describes the standard quasi-particle model.

Implementing this into RSMS codes requires the introduction of the one-electron Green’s function ($G$) so that non-periodic systems can be studied. The structure being considered is not divided into shells as for other MS codes but instead the inter and intra shell contributions are treated separately. The scattering of the electron-wave from the ion cores can be described in terms of phase shifts which are incorporated into the Green’s function. The Green’s function can be described as follows:

$$-\frac{1}{\pi} \text{Im} G = \sum_f \langle f \rangle \delta(E - E_f)$$  \hspace{1cm} \text{Eqn. 5.2}

(symbols are as above). By rewriting Fermi’s Golden rule in this way, a short range order theory is achieved whereby only the few hundred atoms closest to the excited centre need be considered. This reduction in cluster size makes the calculation far more manageable providing a significant reduction in the computation time required for calculations. Addition of self-consistent potentials as implemented in the Feff8.2 code helps to reduce calculation time still further whilst increasing the accuracy of the calculations. (Self-consistency will be discussed further, below).
The Green’s function performs a summation over all one-electron states, using muffin-tin potentials as approximations for the atoms. The muffin-tin (MT) approximation treats each atom as a spherical scattering potential where spheres may touch but not overlap. This is illustrated in Fig 5.2. Each sphere is spherically symmetric and allows the scattering of the electron-wave from the atomic-potential to be treated in terms of phase shifts. The atomic potentials, which are dependent on the charge density, must be calculated well since the strength of the scattering from each site relies on the atomic potential at that site. The area between the spheres, known as the interstitial region, is modelled with a constant potential. Whilst this is a relatively simple model that works well for EXAFS, there are still problems using the MT approximation since it does not account for the more complex nature of the electron density in the atomic and interstitial regions, and hence does not calculate the ELNES or ground state properly. This is due to the MT approximation being good for interactions close to the centre of the atom – the area which most affects the EXAFS region – but not taking into account the weaker interactions and non-spherical like charge distributions that occur towards the edge of the atoms. These edge effects are key to ELNES calculations\cite{96}. Some of this has been overcome by allowing the MT potentials to overlap, however this is only a partial solution. To combat this problem other codes use full potentials\cite{95} and the implementation of self consistent full-potentials in RSMS codes remains a challenge for the future\cite{97}.

![Figure 5.2: Illustration of muffin-tin approximation. Atoms 1 and 2 are surrounded by an interstitial region, I](image)
The next development in multiple scattering theory was made by Durham et al.\textsuperscript{98}. Their theory was that only atoms closest to the absorbing atom made a significant contribution to the calculation. Hence, scattering within a specific shell is carried out to all orders whilst inter-shell scattering is kept to a minimum. Some of the main ideas of this have been incorporated into the FEFF code which will be discussed in more detail below.

### 5.1.1 RSMS as implemented in FEFF8

One feature of particular importance in the Ankudinov et al.\textsuperscript{95} RSMS method as implemented in FEFF is the possibility to calculate both the density of states (DOS) and ELNES simultaneously where most codes calculate only the ground state, or DOS. However whilst DOS is a ground state phenomenon, the ELNES requires the atom to be in its excited state. This means that whilst DOS calculations require the initial state, the ELNES requires the final state including the presence of a core-hole. Although in many cases the DOS and ELNES calculations are analogous, only for systems in which there is a large degree of screening, such as for metals, can this be justified. This is not the case in all systems and so exclusion of a core-hole may significantly effect the ELNES.

High accuracy in XAS/EELS calculations is achieved using self-consistent field (SCF) potentials combined with the full multiple scattering (FMS) approach. This also helps combat some of the poor agreement near-edge calculations with experimental edges that result due to the MT approximation discussed above. Where the acronyms XANES and EXAFS are used in the literature to describe this method, here ELNES and EXELFS will be substituted to reflect the nature of our interest in the code.

As already discussed FEFF implements an RSMS one-electron Green’s function describing the final state as a quasi-particle\textsuperscript{94}. There are two main parts to the multiple scattering calculation which help to increase agreement between calculated and experimental ELNES data. The first part is to include self-consistent field (SCF) potentials. Unlike the MS method, the scattering potentials, are allowed to overlap by as much as 15\% whilst still being approximated by muffin-tin potentials. To carry out self consistent calculations, a cluster is defined within which the SCF will be calculated. This cluster usually contains atoms within the first few shells of atoms from the excited centre. Because the atoms closest to the central atom contribute the most to the near-edge structure it is important these are calculated as accurately as possible. The value of the scattering potentials is used to calculate new densities. These in turn are
fed back into the mixing algorithm and the potentials and densities re-calculated iteratively. This is iterated until the values of the potentials converge, normally taking between 10 and 20 cycles. This calculation allows determination of the Fermi energy as well as calculation of the charge transfer between ions.

The FMS defines the radius of the cluster from the central excited atom, over which multiple scattering is calculated to infinite order. The value of the FMS is determined by the distance from the absorbing atom to where the near-edge structure stops changing significantly. Beyond this radius, the MS path expansion covers a greater energy range but only a small number of low order paths is applied and combined with the FMS. The path expansion should not have much effect on the ELNES but would have greater significance for EXELFS calculations. Ankudinov et al.\textsuperscript{95} refer to this as a combined FMS/high-order MS approach. This approach is adopted so as to reduce the necessary computation time without the loss of any vital information.

### 5.1.2 Core-Hole

A core-hole is formed when the incident electron excites a core electron to an unoccupied energy level. (A core hole refers to both the excitation process and lifetime of the excited state). The lifetime of the core-hole can be much greater than the time for the excitation process itself. This causes the outer electrons to be attracted to the effective potential of the core hole and hence they are bound more strongly. How great this attractive potential is, differs for each system and usually depends on the number of valence electrons. For example, in metallic systems the core hole is effectively screened by the large number of valance electrons which move to lessen the effect of the core-hole potential. Hence, in these cases it is appropriate to describe the ELNES in terms of ground state calculations. However, insulators and semiconducting materials have very little or no core-hole screening and so calculations must take into account the effect of the core-hole. Here a ground state calculation is not sufficient to accurately model the near-edge structure. The effect of the core hole on the ELNES is a red shift to lower energy due to the final state DOS being modified. Inclusion of a core hole in calculations greatly improves agreement with experiment for some systems, but not all. This area is still under active investigation.

A number of different approximations may be used to describe the core hole. FEFF8 adopts the $Z^*$ approximation. Here the electronic configuration of the absorbing atom
is modified such that an electron is moved from a core state (usually 1s) into an available unoccupied orbital. Another, and more widely used approximation is the Z+1 approximation. Here an absorbing C atom would have an extra electron added to it to give the electronic configuration 1s\(^1\)2s\(^2\)2p\(^4\), and therefore be treated as a nitrogen atom. A third model is for the system to contain only half a core-hole. This is described by Slater’s transition-state approximation and takes account of screening of the core-hole by other electrons.

5.1.3 Broadening

Experimentally there are three factors that contribute to broadening of the EELS spectra: instrumental broadening, initial state and final state lifetime broadening. Instrumental broadening results from the limited energy resolution of the spectrometer and the energy spread of the electron source. For example a typical full-width half-maximum (FWHM) of the zero-loss peak (zlp) taken on the Tecnai F20 microscope in STEM under operating conditions used to collect the experimental spectra in Chapter 7, would be about 0.7-0.8eV. Therefore a typical value for instrumental broadening would be 0.7-0.8eV. However, with the introduction of monochromators, energy resolution of 0.12 eV can routinely be obtained, hence in the future better comparison with modelled data will be possible. The effect of instrumental broadening is incorporated into the modelled spectra by convoluting them with a Lorentzian after the calculation has been completed.

Initial state broadening is due to the radiative or Auger decay of the core-hole generated by the excited electron. This results in the spectrum being broadened by the same amount at all energies. The effect of this relative to the instrumental and final state broadening is negligible and often ignored. Final state broadening results from the loss of energy of the final state electron as it falls back to the Fermi level. This energy is lost by the emission of plasmons or creation of electron-hole pairs. The broadening of the spectra is energy dependent resulting in increased dampening of the spectra at higher energies. The degree of broadening will depend on the system being studied, the modelling package being used and the collection conditions of the experimental edge, if an experimental edge is available for comparison. The initial and final state broadening is automatically calculated in FEFF. Instrumental broadening can be added to the spectrum later.
5.1.4 Future development

Although computation time for calculations has been greatly decreased due to some of the approximations discussed above, ELNES calculations in particular still require a large amount of computing time. Recent developments in computing power as well as the introduction of parallel codes have significantly reduced computation time. New algorithms such as the Lanczos algorithm have also helped\(^{94,103}\). However, the area that needs a lot of work is to solve some of the problems associated with using the muffin-tin approximation whilst continuing to reduce the computing time. This will provide much better agreement with experiment for the near-edge structure which is continuing to be a problem. Current work by Joly \textit{et al.}\(^{104}\) looks promising in this area where a real-space approach is being adopted using a finite cartesian grid, however much work still has to be done for it to be implemented for the type of calculations described above.

The developers of the FEFF code are in the process of testing FEFF8.5 which will be optimised for ELNES calculations. This will allow inclusion of collection and convergence angles, orientation effects and the effect of the magic angle amongst other parameters into the input file. These are hoped to give more accurate detail about the fine structure of the ionisation edges.

5.2 FEFF8.2

5.2.1 How the program is used

FEFF8.2 was originally designed to calculate x-ray spectra. However, as already mentioned the theory describing both x-ray and EELS spectra is very similar and so the code can also be used to calculate EELS edges. Some of the differences between experimental EELS spectra and the calculated edges may be attributed to the slight differences between XAS and EELS spectra, however this effect is not thought to be significant. The authors of FEFF8.2 recognise this issue and are currently trying to account for these differences in the distribution 8.5 of the code\(^{105}\). This is currently only available as a trial version whilst remaining issues are resolved. However, it is hoped that this new release will help to resolve some of the outstanding differences between
experimental and modelled spectra. From now on FEFF8.2 will be referred to as FEFF. A feff input file (feff.inp) can be found in Appendix 2. The main cards used are included in the model input file. Further detail will be described for calculations here as is necessary.

FEFF8 works by implementing 6 steps in the form of program modules on the feff.inp file. These are outlined below and are taken from the FEFF8 userguide:

Module 1: the potential energies are calculated self-consistently. The distance from the absorbing atom within which the self consistent field is calculated is specified by the SCF card. This module also calculates the absolute energies and the Fermi level onset.

Module 2: the phase shifts, dipole matrix elements, x-ray cross sections and local density of states (LDOS) is calculated here.

Module 3: here the full multiple scattering (FMS) EELS calculation is implemented. This calculates the FMS for a cluster of a specified size around the central absorbing atom.

Module 4: the PATHS module is used to calculate the multiple scattering paths for the specified cluster.

Module 5: for the paths calculated in module 4, the effective scattering amplitude is calculated.

Module 6: the EELS spectra are calculated from one or more paths.

For crystal structures the feff.inp file can be generated using a program called ATOMS2.5106. This simply requires the space group, unit cell lattice parameters and specific atomic co-ordinates to generate the feff.inp file. A typical atoms input file is illustrated in Fig 5.3.
5.2.2 Determination of FMS and SCF

The atomic potentials, Fermi level and charge transfer are calculated self-consistently. It is firstly important to establish the distance from the absorbing atom required for the SCF loop since this is the rate determining step for the calculation. It is suggested by the authors of the code that a distance from the centre including about 30 atoms is required for accurate potentials calculations, however it is important to check that the SCF converges. Convergence is achieved at different cluster sizes for different systems. To determine convergence, the SCF is increased while the FMS is kept at some constant value, higher than the value of the SCF.
Figure 5.4: Example of spectra in which varying the SCF causes the edge to (a) change (b) not change. (a) N K edge of HfN and (b) O K edge of t-HfO₂.

Figure 5.4a shows an example for HfN where varying the number of atoms included in the SCF cluster changes the shape of the edge. By increasing the cluster size from 27 to 33 atoms the detail between peaks 1 and 2 disappears and peak 2 increases in intensity. Whilst including 57 atoms in the calculation the detail on peak 1 reappears, peak 2 is still far more intense than peak 1. For this structure the edge shape at 81 atoms is very similar to that observed for 27 atoms and therefore an SCF of 27 atoms was chosen for this calculation. In the case of t-HfO₂ in Fig 5.4b the edge only has very minor changes with an increase in number of atoms which would not make any difference to the edge shape, especially after broadening has been applied. The lowest value for the SCF was chosen so as to reduce computation time.

Once the SCF has been determined it is kept constant and the same process is repeated to establish convergence for the FMS. For a highly ordered structure the effect incurred on the edge shape by adding successive shells of atoms to the calculation are observed in the edge shape as additional features are added or removed. For example Scott et al.⁹⁹ consider the effect of adding different shells to the FMS cluster and assign peaks in their spectra to specific scattering events. As the FMS is increased a point will be reached where only minor changes in the edge shape will continue to occur. These
changes will not be significant once instrumental broadening has been applied to match experiment.

Figure 5.5:  Convergence of FMS for the O K edge of HfSiO₄

Figure 5.5 shows the FMS convergence graph for the O K edge of HfSiO₄. The edge shape continues to have significant changes in the detail of the peaks as the FMS is increased until about 148 atoms. As the number of atoms is increased further only minor differences are observed in the peak shape which will make no difference to the broadened structure. In this example the FMS has converged by ~171 atoms. For some structures such as TiN and HfN, it is much more difficult to determine the FMS value. In the case of TiN, if the FMS continues to be increased to a value of 437 atoms, the edge shape is similar to that at 147 atoms, whilst the edge shapes in between are quite different. In that case the lower number of atoms was chosen for calculations. The authors of the code suggest a cluster size of between 50 and 150 atoms should be suitable depending on the material and core-hole lifetime. Most calculations for this thesis use an FMS of about 150 atoms but some calculations require a higher number.
### 5.2.3 Potentials and angular momentum

In the POTENTIALS card the angular momentum for each atom is specified. This determines the cut-off for the basis set which is used to calculate the potentials and the FMS. A value of 0 = s electrons, 1 = s, p electrons, 2 = s, p, d electrons, 3 = s, p, d, f electrons etc. Due to hybridisation in some systems, some higher states may have partial occupancy so it is always a good idea to set the angular momentum to one value higher than would be suggested by the atomic configuration. Alternatively, setting the angular momentum to the default of -1 will automatically account for hybridisation and the need for further atomic states. If the angular momentum is not set correctly the Fermi level may be misplaced resulting in a wrong calculation of the EELS spectra. The example in Fig 5.6 is of a broadened AlN N Kedge spectra with the angular momentum varied. Although the overall edge shape is the same, the peak positions have changed and the energy range condensed with the higher angular momentum value. This significantly affects the results.

![Energy Loss vs Intensity](image)

**Figure 5.6:** Comparison of N K edges of AlN with varying Al angular momentum values. (broadening = 0.4eV)

### 5.2.4 Misplacement of Fermi energy

Even with the correct SCF and angular momentum, the Fermi level may still be in error. This can be compensated for by using either the EXCHANGE or the CORRECTIONS
cards. Using the EXCHANGE card requires that the whole calculation be re-run with an energy shift added. A typical energy shift would be 1-2eV. The alternative and quicker method is to use the CORRECTIONS card which allows small changes in the Fermi energy to be made after the calculation is complete. This is particularly important for systems containing f electrons where the Fermi level placement is often incorrect. Fig 5.7 illustrates this with HfSiO₄, where the Hf includes f states. By shifting the Fermi level 2eV much better agreement with experiment is obtained for the edge as the first peak becomes visible.

![Graph](image)

**Figure 5.7:** Comparison of experimental HfSiO₄ O K edge with FEFF calculations before and after applying a Fermi level shift of 2eV using the CORRECTIONS card

### 5.2.5 Core-Hole

For EELS modelling, whether a calculation is carried out in the ground or excited state can have a large effect on the edge shape. FEFF automatically incorporates a core-hole into the calculation unless it is removed, so the calculation is always carried out in the final state. To remove the core hole, which would be necessary for local DOS (LDOS) calculations, the NOHOLE card is used. Whilst physically a core-hole is always present, it is still debated as to whether inclusion of a core-hole for electron-loss near-edge structure (ELNES) calculations always gives the best modelled result. This may be dependent on the material, the core-hole screening and the lifetime of the core-hole. Using the NOHOLE card also simulates complete core-hole screening in metal systems, for example. Inclusion of a core-hole causes a red-shift in the energy-loss spectra which
is illustrated in Fig 5.8 for TiN where inclusion of a core-hole causes the whole spectra to shift to lower energy. A change in the relative heights of the first two peaks is also noted. For this compound, the height of those two peaks is very important; only with a core hole included is a good match with the experimental edge shape obtained. The example of TiN highlights additional problems with the FEFF code. Only peaks 1 and 4 match the peak positions in the experimental edge when the core hole is included. However, with no core-hole, peak 3 matches the position and peak shape of the experimental edge much better. FEFF seems, for some systems, to expand the edge shape over the first 10eV of the edge, relative to the experimental, and contract the peaks at higher energy. Although the edge shape is modelled quite well, the peak positions are not always a good match. It is not clear why this is observed in some systems but not in others.

![Comparison of inclusion and exclusion of a core-hole on the N K edge of TiN with experimental data](image)

5.2.6 Broadening

In FEFF initial and final state broadening are automatically accounted for as discussed in section 5.1.4. Instrumental broadening, like the Fermi level shift, can be set by the user using either the EXCHANGE or CORRECTIONS cards. Both of these broaden the spectrum using a Lorentzian function. Similarly, as with the Fermi level position, using the EXCHANGE card requires the whole calculation to be repeated however, better convergence may be obtained this way. The CORRECTIONS card adds the broadening to the edge after the calculation has completed. Fig 5.9a shows a
comparison for the N K edge of TiN with 0.6 eV broadening added using both methods. There is very little difference between the two methods so for all calculations the CORRECTIONS card was used to add broadening. This reduced computation time.

![Graphs showing N K edge comparison and O K edge broadening](image)

**Figure 5.9:** (a) TiN N Kedge, comparison between EXCHANGE card and CORRECTIONS card for applying broadening. (b) HfSiO$_4$ O Kedge showing the effects of broadening applied using the CORRECTIONS card (2 eV Fermi level shift; HfSiO$_4$ experimental data taken from ref. 107)

Determining how much broadening is required is not clear. A rough guideline is to broaden the spectrum by the full width half maximum (FWHM) of the experimental zero loss peak. However, in practice broadening can be anything from 0.2 eV – 1 eV depending on the calculation. In Fig 5.9b HfSiO$_4$ has been broadened by different amounts. The edge shape that best fits the experimental data is chosen.

### 5.3 Reciprocal space calculations

#### 5.3.1 Density functional theory

Using density functional theory (DFT) the electronic structure is calculated using a matrix and either solving for the eigenfunctions or performing a matrix inversion of the appropriate multiple-scattering equations. This is adopted into methods such as the augmented plane-wave (APW) method and full linear augmented plane-wave (APW-FLAPW) method, the linear muffin tin orbital (LMTO) and pseudopotentials methods. Some advantages of using DFT over multiple scattering methods are that accurate self-consistent calculations are obtained, that multiple scattering is achieved to high orders and that the Fermi energy is placed accurately. However some
disadvantages, which are particularly important in the calculation of the ELNES are that neither final-state lifetime broadening or core-hole effects can easily be included and the computational time required is great. There are solutions to the first two of these problems. The final-state lifetime broadening can be included at a later stage using a Lorentzian convolved with the spectrum. Core-hole effects can be incorporated into the calculation by constructing a supercell. The supercell is then translated periodically with sufficient space between the core-holes such that they do not interact. This method, whilst used regularly, only adds to the already high computation time because a large basis set is constructed. The more complicated the structure the larger the basis set and hence the more computing time is required.

DFT attempts to solve the many-body problem of the free electron gas. By introducing the Born-Oppenheimer approximation the many-body problem can be simplified. This approximation fixes the atomic nuclei at specific sites whilst the electrons are allowed to form an electron cloud such that the electron can travel freely within the system. The freezing of the nuclei results in the nuclei having no kinetic energy. The simplified expression becomes:

\[
H = T + V + V_{\text{ext}} \quad \text{Eqn. 5.3}
\]

where \( H \) is the hamiltonian, \( T \) the kinetic energy of the electron gas, \( V \) the potential energy of the electron-electron interactions and \( V_{\text{ext}} \) the potential energy of the external electrons from the nuclei.

This is still difficult to solve, hence density functional theory (DFT) was invented. DFT was formalised by Hohenberg and Kohn in 1964\(^{109}\) which describes the ground state energy in terms of the ground state electron density. After some evolution of the theory, DFT codes involve solving of the Kohn-Sham equations which were first published in 1965\(^{110}\). The Kohn-Sham Hamiltonian is:

\[
H_{\text{KS}} = T_0 + V_H + V_{\text{xc}} + V_{\text{ext}} \quad \text{Eqn. 5.4}
\]

and the equations for which a solution must be found are:

\[
\rho(\vec{r}) = \sum_{i=1}^{N} \phi_i(\vec{r})^* \phi_i(\vec{r}) \quad \text{Eqn. 5.5}
\]
\[ \hat{H}_{KS} \phi_i = \varepsilon_i \phi_i \]  

Eqn. 5.6

\( H_{KS} \) is the Kohn-Sham Hamiltonian, \( T_0 \) is the functional for the kinetic energy of the non-interacting gas, \( V_H \) is the potential of the Hartree contribution and \( V_{xc} \) is the exchange-correlation potential. Equations 5.6 and 5.7 describe the exact ground-state density \( \rho(\vec{r}) \) of the system and the single-particle wave functions, \( \phi_i(\vec{r}) \), which have the lowest-energy solutions. This means a Schrödinger like equation has to be solved for non-interacting single particles.\textsuperscript{111}

Now that there is a solution to these equations the exchange-correlation potential, \( V_{xc} \) has still to be found. To calculate the potential approximations have to be introduced to the calculation. The local density approximation (LDA) can be used where the exchange correlation potential is treated as local to the electrons. This however, does not account for any inhomogeneities in the electron density, which is unphysical. It is therefore important to use an approximation that accounts for the shape of the orbitals hence better representing the electron density. The generalised gradient approximation (GGA) takes this into account and provides a more accurate description than the LDA method. Both approximations can be implemented in the Wien2k code but the GGA method is the one that is recommended.

The next problem is to find a suitable basis set so that the Kohn-Sham equations can be solved. It was found that the crystal structure can be described in terms of plane waves. Ideally this would be an infinite basis set but that is not possible to calculate. Therefore the number of plane waves is determined by considering a sphere in reciprocal space with a radius \( K_{\text{max}} \). Hence all the reciprocal lattice vectors within the sphere are incorporated into the basis set.

The Augmented Plane Wave (APW) method uses plane waves for the regions far away from the nucleus, but closer to the nucleus where the electrons behave as they would in an atom, the basis set is treated in terms of spherical harmonics, or atomic-like wavefunctions. This is represented by plane waves in the interstitial region and the atomic-like wave functions in the atoms.

There are conditions attached to the use of plane waves and atomic like wave functions. Boundary conditions must apply such that the plane waves are continuous in value and
in gradient at the boundary of the atom with the interstitial region. The atoms are approximated using the muffin tin sphere. The muffin tin radii for the different atoms cannot be too different from each other otherwise the boundary conditions cannot be met. In terms of calculation time, this is quite a slow method.

The Linearised APW (LAPW) were introduced to deal with valence and core states. Inclusion of local orbitals (LAPW+LO) accounts for semi-core states which are neither confined to the atomic core nor completely delocalised states. Local orbitals are defined for each angular momentum value. They are zero in the interstitial regions and in any of the MT spheres of the other atoms in the system, and the local orbitals are not allowed to leak out of the muffin tin sphere. The convergence of this constructed basis set is determined by \( R_{\text{mt}} K_{\text{max}} \) (\( R_{\text{mt}} \) is the radius of the smallest atomic sphere in the structure and \( K_{\text{max}} \) is the magnitude of the largest \( K \) vector used to solve the Kohn-Sham equations). This method slightly increases the computation time, however, it provides a much more accurate calculation due to incorporation of local orbitals so the increased computation time is worth the extra computing cost.

APW+lo has also been introduced which also uses local orbitals but different to those used in the LAPW+LO method (hence denoted with lower case). Unlike LAPW+LO, the basis set here is constructed with an energy dependent term. It is found that APW+lo provides the most accurate description for d and f states which are difficult to handle using LAPW and also works better for systems where the muffin tin spheres may be very different in size. Wien uses both LAPW and APW+lo to provide the best description of the systems being studied. LAPW is used for most states in most calculations except in the case of d and f electrons where APW+lo is used to describe the d and f states.

### 5.3.2 DFT as implemented in Wien2K

To begin a Wien calculation, a structure file is constructed containing crystallographic information such as the space group and lattice parameters. The size of the muffin tin radius is also specified. Alternatively, Wien can be left to calculate the muffin tin radii, however, the estimate made by Wien is not always good and the value may have to be changed manually a number of times before the calculation proceeds without errors. A series of initialisation steps and checks are carried out. Firstly the nearest neighbour distances are calculated and the atomic sphere radii determined. The space group and
symmetry of the system is then checked before generation of the atomic densities. Here the method for calculating the exchange-correlation potential (LDA or GGA) can be specified as well as the separation energy which defines which states are core, semi-core and valence states. The method for calculating the electron densities (LAPW or APL+lo) is specified as well as the RK_{max} value. The number of k-points (i.e. the number of reciprocal lattice vectors) is also included, which is often key to the length of time required for a calculation. For calculations it is best to run a quick test to determine the effect of changing the number of k-points. After specifying these parameters the starting density for the SCF cycle is then calculated.

The SCF runs through five modules before determining whether the convergence criterion has been reached. If the convergence criterion has not been reached, these modules will run again with a new starting potential. A description of the five modules is below as described in the Wien2K manual^{112}:

- **LAPW0** this generates a potential from the starting density
- **LAPW1** calculation of eigenvalues and eigenvectors for valence bands
- **LAPW2** calculates valence densities from eigenvectors
- **LCORE** calculates core-states and densities
- **MIXER** mixes the input and output densities

Wien can then calculate electron density plots, density of states, x-ray spectra, optical data and bandstructure among other things. We are interested particularly in the ELNES which is implemented in the TELNES2 module. Firstly the density of states is calculated after specifying whether any higher atomic states must be considered. This is then transformed into the ELNES bearing in mind that, unless put in by hand, no core-hole is present. The edge being considered, the energy range being probed, the microscope parameters such as energy of incident electrons and collection and convergence angles are specified.
6 Modelling Results

6.1 Establishing Standards

It is important to be able to model EELS spectra. This is especially true when investigating unknown compounds and interfaces where accurate modelling is required to aid interpretation. It is therefore important to establish at the outset the usefulness of modelling software by comparing modelled edges with experimental edges from well characterised compounds. It is also useful to compare different modelling software as the different methods implemented have value in different areas. This may highlight where models provide good or bad fits with data and in which aspects of the fit they can be trusted. This also helps developers of the software optimise the codes for future use.

Here we are interested in modelling for two purposes: One is to further understand the crystallisation process involved in the sol-gel materials outlined in chapters 3 and 4. We particularly want to establish a standard for the O K edge of t-HfO₂ which is very difficult to obtain experimentally. To the author’s knowledge there are no publications containing this data. The second reason for modelling is to understand both the crystallisation within the high-κ layer in the thin film samples and the interfacial reaction products at the interface. Both of these effects are accentuated after samples are subjected to a high-temperature anneal. The establishment of a t-HfO₂ standard is of particular importance for understanding the crystallisation within gate stacks containing HfO₂ or HfₓSi₁₋ₓO₂ as it is not clear that crystallisation is always into m-HfO₂. By being able to model possible interface products as well as ideal interfaces themselves, and then compare the models with experimental data, a much greater understanding of the processes occurring at interfaces will be formed. This in turn will help device manufacturers to improve devices. Materials that are of particular interest in the systems studied in this thesis that already have well documented EELS spectra include m-HfO₂, HfSiO₄, TiN and HfN^{32;35;99;108;113;114}. HfO₂ and HfSiO₄ may form within the high-κ layer of the gate stack after a high temperature anneal, TiN is being investigated as a metal gate electrode material and HfN is a product that may form at the interface between the dielectric and gate electrode materials. All the structural parameters used
for calculations have been taken from the ICSD\textsuperscript{1} database. A summary of them can be found in Table 6.1.

The TiN, m-HfO\textsubscript{2} and HfSiO\textsubscript{4} experimental edges have been reported in the literature by a number of groups and so are taken as reliable and reproducible\textsuperscript{32,35,99,108-116}. The HfN, TiN and HfSiO\textsubscript{4}\textsuperscript{32,36,108} experimental edges used in Fig 6.1 are used with permission from M MacKenzie. The m-HfO\textsubscript{2} O K edge was collected on the FEI Titan at Imperial College London and also agrees with the literature\textsuperscript{32,35}. Fig 6.1 shows results from two different modelling codes overlaid with the corresponding experimental spectra. As a first approximation (possibly with the exception of the HfSiO\textsubscript{4} edge modelled using Wien (Fig 6.1b)), reasonable agreement is obtained between the modelled and experimental K edges. The spectra are aligned such that the edge onsets align at 5eV. In general from Fig 6.1 FEFF, provides a good match for peak shape and relative peak intensities whilst Wien provides a better match with experimental in terms of peak positions. There are exceptions to this generalisation.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.1.png}
\caption{Comparison of experimental O and N K edges with modelled data using (a) FEFF8 and (b) Wien2k. The line in bold is the experimental edge, the thinner line is the modelled edge. Experimental edges are from refs\textsuperscript{32,36,108}}
\end{figure}

\textsuperscript{1} Inorganic Crystal Structure Database http://cds.dl.ac.uk/icsd
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Table 6.1: Structural parameters used for FEFF and Wien calculations
In the case of HfN, whilst peaks 1, 2, 3 and 5 are modelled equally well by both Wien and FEFF, peak 4 is only modelled by Wien and is completely missing in the FEFF calculation. The broad shoulder at point 4 on the experimental edge, and the good match with the Wien model, indicates that inclusion of this peak in the model is appropriate. It should be noted that peak 1 only gave a good match with experiment after the Fermi level had been shifted by 2eV to lower energy. The good match of peak 1 in HfSiO₄ is also for this reason. A shift of 2eV was also applied. Without this shift only peak 2 was visible. In many ways it is surprising that such a good fit is achieved between model and experimental for both HfN and HfSiO₄. The Hf in these systems contain f electrons which FEFF in particular does not model well. FEFF automatically freezes the f electron density so that the SCF converges well. It is possible to use the UNFREEZE card to include the f electrons in the SCF cycle and this has been further modified in more recent updates of the code (FEFF8.4 and the trial FEFF8.5 version). In some cases this will cause the SCF cycle to converge and give more accurate EELS edges. For our system the default settings were used.

For HfSiO₄ the poor fit of peaks 1 and 2 in the Wien calculation (Fig 6.1b) is due to the incorrect origin being chosen by the software for the space group. The Hf atom is located at (0,3/4,1/4) and Si at (0,1/4,3/4). These positions are interchangeably crystallographically and depending on which position is specified, the fine structure of the O K edge will vary. A simple shift in the atomic positioning should solve this problem. However, it has not been possible to carry out this calculation due to technical problems with the installation and running of the code. It is hoped this will be fixed in the future. If the correct atomic configuration were in place, peak 1 would become evident which is currently not correct in the displayed result. Apart from that, the shape and relative intensities of peaks 2-5 match the experimental results very well. Comparison with the FEFF results reveal that FEFF does not model peaks 4 and 5 well. Whilst there is a hint of the presence of peak 4, peak 5 is not there at all. This illustrates a problem that occurs due to broadening the spectra. The FEFF spectra have instrumental broadening applied to them. Deciding the degree of broadening is often not an easy task. By including broadening many of the features with less intensity are broadened out. An example of how this affects HfSiO₄ directly is illustrated in Chapter 5 Fig 5.9b where it is observed that as the broadening is increased, what is initially two peaks at ~10eV (graph above) is broadened into one peak. The peak at about 15eV merges completely into the background. However, by including broadening, it is
clearer that the model is similar to the experimental edge – without the broadening this match would not be particularly good.

For TiN, FEFF models the peak shapes and relative peak heights very well. The peak positioning however is not very good. There is an expansion of the peak to peak distance of peaks 1 and 2 and a contraction between peaks 2 and 3 (5-15eV) compared with experimental data. The contraction or expansion of the peaks relative to each other is discussed in Chapter 5 and is a known problem with FEFF.

For m-HfO₂ both models fit the experimental data well with the Wien calculation modelling peaks 3 and 4 better. The intensity of the first peak is lower than that observed experimentally. While our experimental data agrees with that of Agustin et al.³⁵, there is published data available where the relative heights of peaks 1 and 2 differ with differing degrees of ‘filling in’ between the two peaks¹¹⁶. Some of this data would fit the modelled data better than that in Fig 6.1. A clear example of this is discussed by Wilk and Muller¹¹⁶ where HfO₂ films were annealed for 30s at different temperatures in a nitrogen environment. As the temperature is increased peaks 1 and 2 sharpen and the relative intensity changes as the degree of crystallinity is also increased. Results in Chapter 7 also reflect this discrepancy.

Both modelling packages provide sufficient agreement with experimental data and with each other that they can be used to model edge shapes where no experimental data is currently available. Also, it may be possible to model edges where experimental data is available but does not match any of the standard edge shapes. While the problems highlighted here and in Chapter 5 must be taken into consideration, modelling will provide a reasonable description of the main features present in many edge shapes of interest. Because of the ease with which FEFF can be used, the speed with which calculations can be carried out and the possibility of including core-holes and constructing interfaces easily, this was chosen as the modelling package for the following work.
6.2 Hafnia models

HfO₂ exists in four main crystal structures: monoclinic, tetragonal, cubic and orthorhombic. Schematics of these structures are illustrated in Fig 1.3. The crystallographic information for these structures required for modelling is taken from the ICSD database.

m-HfO₂ has a P2₁/C1 space group and its lattice parameters have been obtained both experimentally and theoretically by a number of groups.¹¹⁸;¹³⁴;¹³⁵ There are minor variations in the published data, therefore, for consistency in the calculations the structural parameters presented by Hann et al.¹¹⁸ were used as these were taken at room temperature.

Only one case of the cubic structure is reported in the database and no cases of t-HfO₂ – both of these phases only formed above 1750°C according to the phase diagram (Appendix 1). One dataset for t-HfO₂ was found in the powder diffraction file (ICDD 08-342) but it is labelled as being unreliable. EELS calculations using these structural parameters did not yield good results – the edge onset is too low in energy by ~6eV and important features are missing from the edge shape. Since Zr and Hf are isomorphous the lattice parameters are likely to be very similar to each other and so, by taking the zirconia literature into account, the zirconia lattice parameters can be used to give a model structure. A number of orthorhombic structures are also found in the ICSD database which have also been investigated. The crystallographic information for all structures investigated is found in Table 6.1.

Because m-HfO₂ is the stable room temperature phase it is easy to obtain standards for it and so its near edge structure has been well documented.³²;¹¹⁶;¹³⁶ However, as illustrated in Chapters 3-4, t-HfO₂ can be stabilised by the presence of SiO₂. Obtaining experimental EELS spectra from tetragonal particles which are surrounded by SiO₂ is also difficult. Additional problems such as the overlapping of the SiO₂ O K edge with the O K edge of t-HfO₂ are introduced. It is not usually possible to separate the two edge shapes from each other because the relative composition of material is not known. For both gate stacks and sol-gel powders it is also not clear whether the phase we refer to as t-HfO₂ is actually that at all: it could be cubic or orthorhombic as it is difficult to distinguish between these phases using XRD. Because of beam damage effects and the
small size of the particles or layers being studied, electron diffraction was not possible. Results from the literature report the presence of t-HfO$_2$ in thin film studies$^{6,22,28}$ but as mentioned, due to damage induced by the electron beam in the electron microscope it is likely that crystallisation or phase transformation has occurred during the process of the acquisition. It is therefore necessary to model the different HfO$_2$ edge shapes and to use these as a reference when trying to identify some of the O K edges obtained from what appear to be isolated HfO$_2$ particles, HfO$_2$ encased in SiO$_2$ and from interfaces in gate stacks.

Due to the tetragonal phase being a slightly distorted cubic structure, it is expected that the O K edges for t-HfO$_2$ and c-HfO$_2$ will be similar. From the modelled ELNES in Fig 6.2, this is the case. Only a slight difference in the relative intensity of peaks 1 and 2 is observed. No crystallographic information was available for t-HfO$_2$. Hence, for that particular phase of HfO$_2$ the structural information for t-ZrO$_2$ was used, substituting the Zr sites with Hf. The lattice parameter for zirconia was also used but because of the similar atomic sizes of zirconium and hafnium this should not make a large difference in the calculations. Subtle differences in edge shapes may occur but once the spectra is broadened these should have little effect.

The m-HfO$_2$ structure is more complicated, containing two different oxygen environments. Each of these oxygen environments will cause changes in the fine structure that are different from those in the cubic and tetragonal cases. This is what we observe in Fig 6.2.
Figure 6.2: Modelled O K edges for different HfO₂ structures

There is also similarity between the o-HfO₂ (pbca) edge shape and the m-HfO₂ edges. The separation between the peaks 1 and 2 is about 4.5eV in both cases and the relative intensity of peaks 1 and 2 are similar. From these models the orthorhombic edge shape would fit the m-HfO₂ experimental data better than the edge calculated for m-HfO₂ (see m-HfO₂ experimental data in Fig 6.1).

The three different orthorhombic structures modelled all exhibit quite different edge shapes. The crystal structures of the Pmnb and Pnam phases are similar to each other – this is not surprising as their space group is similar with only a slight difference in atomic positions and lattice parameters. However, some differences remain. Firstly there is a shift in the edge onset by ~1.5eV. All the spectra in Fig 6.2 have been plotted as they came out of the FEFF program and it is thought that the difference in edge onset is related to the structure of the material. In section 6.5.1 the effect of changing lattice parameter on the edge shape is looked at in some detail but there it is observed that as the lattice parameter changes for TiN or HfN structures the edge onset also varies. It is therefore thought that in the case of HfO₂, the difference in edge onset is due to the structural parameters resulting in a misplacement of the edge onset by FEFF. If the two
edge shapes are aligned such that peak 1 overlaps at the maximum in each case, then peak 2 also coincides in energy. With this scenario, the gradient of peak 1 from the edge onset is the same for both structures. However, on the high energy-loss side of peak 1 the gradient of pmnb is less steep and has the effect of filling in the gap between peaks 1 and 2 relative to the gap for the pnam structure.

6.3 Silica

In the 1400-1700°C region in the sol-gel samples, crystalline SiO$_2$ is formed as the cristobalite phase. This is predicted in the HfO$_2$-SiO$_2$ phase diagram$^{83}$ (see Appendix 1). The phase diagram indicates that in all cases where there is a higher percentage of HfO$_2$ to SiO$_2$, SiO$_2$ will crystallise, firstly into the $\alpha$-tridymite phase up to 1450°C and then into the $\alpha$-cristobalite phase between ~1450-1700°C. It is possible for the $\alpha$-cristobalite to exist below this temperature in a metastable state. From XRD results in Chapters 3 and 4 it was found that in all cases the crystalline form of SiO$_2$ was the $\alpha$-cristobalite phase, also known as the ‘low’ phase. There was no evidence of the presence of tridymite. Cristobalite exists in two forms – $\alpha$ and $\beta$. The $\beta$ (or high) phase forms at high temperatures and has a cubic structure. As it cools it transforms to the $\alpha$ (or low) crystalline phase, which is a formed by a displacive, tilting of the SiO$_2$ tetrahedra$^{130}$. The two phases are modelled in Fig 6.3. Because our XRD scans were always taken at low temperatures for samples heated within this temperature range, we always observed the low cristobalite phase.
6.4 Interfaces

One of the problems when interpreting core loss edges taken from the interfaces of gate stacks, is what the edge shape at the interface is caused by. In many cases the interfaces are rough, especially where the high-κ dielectric layer has crystallised. Therefore through the depth of the material being probed, it is likely that edge shapes from a range of environments are being collected. This would result in a spectrum that is a superposition of edges from these different environments. Alternatively, a completely new phase may be forming at the interface. In terms of modelling, some guess work is required to determine which structures may form at these interfaces. The rest of this chapter will be spent considering some of these structures and how best to model them.

Interfacial effects are being investigated at both the substrate/gate-dielectric and gate-dielectric/gate-electrode interfaces. The substrate/gate-dielectric interface between silicon and HfO₂ or HfₓSi₁₋ₓO₂ has been well studied and is fairly well understood (see review by Robertson⁵). The gate-dielectric/gate-electrode interface is much more...
complicated and very little attempt has been made to characterise it. The complication arises from the fact that it comprises of HfO\(_2\) or Hf\(_x\)Si\(_{1-x}\)O\(_2\) in contact with a gate material such as poly-Si or TiN. The structures of the materials on each side of the interface are different and therefore understanding the interface becomes complicated. Even if there was no surface roughness and ‘good’ interfaces were obtained, they are difficult to model as the lattice mismatch between the materials is large and it is not at all obvious which planes would fit together the best. Where ‘good’, relatively straight interfaces form, an interfacial layer also usually forms, which adds the difficulty of guessing what the interfacial product is likely to be. This in turn makes choosing appropriate compounds to model difficult. The gate stacks of interest to us are Si/SiO\(_2\)/HfO\(_2\) or Hf\(_x\)Si\(_{1-x}\)O\(_2\)/TiN/poly-Si and this section focuses particularly on the high-\(\kappa\)/TiN interface.

As a starting point already existing Ti, Hf or Zr nitride, oxide and oxynitride structures were sought from the ICSD database. In the instances where there was a Zr oxynitride structure but no equivalent Hf structure, as in the case of Zr\(_4\)O\(_5\)N\(_2\) (which can also be written as 2ZrO\(_2\)-Zr\(_2\)ON\(_2\)) below, the structural parameters for the zirconium containing structure were used with the Zr atoms replaced with Hf. As an initial investigation HfN, in the rocksalt structure was considered. This is one possible reaction product. The rocksalt form of HfN is conducting\(^{137}\) and the edge shape has been modelled and compared with experimental data in Fig 6.1 and again in Fig 6.4. We have also investigated one Hf\(_3\)N\(_4\) structure with the I-43D space group. This is formed under high temperature and pressure conditions, forming a cubic structure with Hf in eight fold coordination to the nitrogen\(^{133}\).

Two oxynitride structures were found which have been observed experimentally. The Hf\(_4\)O\(_5\)N\(_2\) structure is based on a fluorite structure, containing ordered vacancies. The common vacancy-ordered derivatives of the fluorite structure are the A\(_2\)B\(_2\)O\(_7\) (pychlore) and A\(_2\)O\(_3\) (bixbyite) structures in which there are anion vacancies. Hf\(_6\)O\(_3\)N\(_2\) has the A\(_4\)X\(_7\) structure where Hf has 6, 7 or 8 fold co-ordination with alternating fluorite and bixbyite anion layers. This leads to the 2HfO\(_2\)-Hf\(_2\)ON\(_2\) structural notation with the I4cm (No. 108) space group\(^{127}\). Hf\(_2\)ON\(_2\) is based on the bixbyite A\(_2\)X\(_3\) structure with the IA3- (No.206) space group\(^{126}\).
Both the oxygen and nitrogen K edges, calculated using FEFF for each structure, are shown in Fig 6.4. The edge onsets have all been aligned. We notice that in all cases three main peaks are observed. The overall peak shapes of Hf₄O₅N₂ and Hf₂ON₂ are similar. The N K edge for Hf₄O₅N₂ shows some extra intensity between peak 1 and peak 2 compared with the N K edge of Hf₂ON₂. This may be a real effect or it may be due to the degree of broadening applied. The same degree of broadening (0.5eV) was applied to all spectra. Before broadening all the spectra had extra intensity in this region but after broadening this was no longer observed. Because there is no experimental standard with which to compare the edge shape, the degree of broadening is based on typical broadening requirements of known structures. For both oxynitride structures peaks 1 and 3 are closer together for the O K edge than for the N K edge. Similarly the difference in intensity between peak 3 relative to peaks 1 is greater for the oxygen edge in each case. Where for Hf₂ON₂ the O and N K edges look almost identical, there is a greater difference between the Hf₄O₅N₂ edges, the main feature apart from those discussed being that the dip between peaks 1 and 3 is much less for the oxygen edge compared with the nitrogen.
Figure 6.4: FEFF modelled hafnium nitride and oxynitride structures: O and N K edges

Hf$_2$O$_5$N$_2$ contains five oxygen and three nitrogen environments. As a result each of the spectra requires a superposition of spectra from each of the relevant environments within the crystal structure. The ELNES is calculated for each independent O or N environment and combined with the correct weighting to provide the edge shape displayed in Fig 6.4. The edge shapes for each oxygen and nitrogen site are shown in Fig 6.5. Here we see which atomic environment contributes to the different features observed in the summed, or ‘total’ spectra.

The other complication with this structure is that some of the oxygen sites are only partially filled and so are effectively doped with nitrogen. For example, the O1 site has an occupancy of 19% and the N1 site 81%. To create a structure such as this the O1 sites in the feff.inp file were randomly doped with nitrogen. However, because we know that those atoms closest to the excited atom has the largest effect on the edge shape, the
edge shape for each site will depend on how the structure has been doped. Therefore, the total edge shape will also depend on how the doping has occurred. To properly overcome this problem a large number of calculations would need to be carried out for each site and an average taken. This was impractical. It is assumed that by varying the dopant sites and by combining the different O and N sites that minor effects on the edge shapes for the specific sites, will be accounted for in the final total edge shape (Fig 6.5). However, performing the calculation this way does not account for the ordering of the sites within the structure and further calculations are required to account for this.

![Figure 6.5: Different (a) O K edge and (b) N K edge environments for Hf$_4$O$_5$N$_2$](image)

6.5 Doping

6.5.1 Varying lattice parameters

Before discussing the results of doped structures, it is worth first considering the effect of lattice parameter on the edge shape. An average lattice parameter was used in some cases for FEFF calculations due to two materials with different lattice parameters being combined in a calculation. It was important to first establish the effect of different
lattice parameters on the edge shape. HfN and TiN are two structures where doping and interface structures are modelled (results presented below) so the effect of varying the lattice parameter is investigated for both of these structures (Fig 6.6).

![Figure 6.6: Varying lattice parameter for (a) TiN and (b) HfN](image)

For both materials, as the lattice parameter is increased the edge onset moves to lower energy by 3eV and 2eV for TiN and HfN respectively. Similarly, as the lattice parameter increases the peaks - 1 and 2 for TiN and 2 and 3 for HfN - move closer together in energy. For TiN the relative peak intensities of the first two peaks varies as the lattice parameter is changed and peak 3 increases in intensity. Peak 3 is actually a triplet of peaks as calculated in Feff, however these are not always resolved in the broadened spectra. It is not clear from the experimental data (Fig 6.1) whether there are actually 3 peaks present or not. Either way the resolution of these peaks in the Feff calculation decreases (to be more like the experimental edge) as the lattice parameter is increased. For HfN peak 1 becomes more pronounced and peak 2 narrower as well as peaks 2 and 3 becoming equal in intensity as the lattice parameter is increased. Similarly, peak 4 becomes more intense.
Both TiN and HfN have the cubic rock-salt (NaCl) structure in which each metal atom is coordinated octahedrally to 6 N atoms (and vice versa). This causes splitting of the five d orbitals into higher and lower energy, $e_g$ ($d_{x^2}$ and $d_{x^2}-y^2$) and $t_{2g}$ ($d_{xy}$, $d_{xz}$ and $d_{yz}$) energy levels. In the core-loss spectra peaks 1 and 2 for TiN and peaks 2 and 3 for HfN are due to the $t_{2g}$ and $e_g$ energy levels respectively. As the lattice parameter is increased, the bond length increases, resulting in less overlap of the atomic orbitals and hence a lowering of the overall energy of the system. This is displayed in the EELS spectra by a shift to lower energy as the lattice parameter increases, as observed for both TiN and HfN structures. The $e_g$, $t_{2g}$ splitting is determined by the overlap of the atomic orbitals. As the bond length increases, there is less overlap of the orbitals resulting in a decrease in the splitting between the $e_g$ and $t_{2g}$ states. This manifests itself in the spectra by reducing the energy difference between the first peaks. It was noted that the intensity of the second peak relative to the first (peaks 1 and 2 for TiN and peaks 2 and 3 for HfN) decreased as the lattice parameter was increased. The second of these peaks is due to the $e_g$ orbitals which point along the axes towards the N atoms. Since the intensity of the peak is relative to the degree of overlap of the atomic orbitals, as the lattice parameter is increased and the degree of overlap decreases, the intensity of the peak will decrease. This is particularly noticeable for the peak relating to the $e_g$ energy levels because they are most effected by the increased bond length.

These results should be remembered when trying to interpret data where it has been necessary to use an average lattice parameter. This may affect the interpretation of the edges and especially how they relate to experimental edges.

### 6.5.2 TiN and HfN with O doping of the second co-ordination shell – effect on N K edge

At the interface between HfO$_2$ and TiN the most likely reaction product is some sort of oxynitride compound. Moving away from the HfO$_2$ into the TiN results in changing from a more oxygen-like to nitrogen-like environment since it is the oxygen and the nitrogen atoms that are more mobile. Since it is known that the edge shape is most affected by the first and second shells, as a first approximation calculations were carried out on both TiN and HfN with the second shell (containing N atoms) systematically replaced with oxygen atoms, without any further changes to the atomic list. TiN was chosen since it is the gate material. HfN was chosen to represent a nitride like structure that may form at the interface which had the same structures as TiN thus allowing
calculations to be performed more easily. The lattice parameters for the end member TiN and HfN structures were used for all the calculations. The results of the study are presented in Fig 6.7 as the twelve second neighbour nitrogen atoms are progressively replaced by oxygen.

It must be noted that where there is more than one oxygen atom in the structure there are different atomic environments in which they could be placed. The differing atomic environments will affect the edge shape. In the case of HfN and TiN there were too many permutations of where each of these atoms could be situated to carry out the calculation in a reasonable time frame. It was decided that since this study was just to show the general trend in the changing of the edge shape that covering all the possibilities was not necessary. For TiN (Fig 6.6a) it is noted that as the number of oxygen atoms is increased peaks 1 and 2 become equal in intensity and peak 3 sharpens. During this process the intensity that is present on the low energy side of peak 3 of TiN increases a little and the intensity on the high energy side of peak 2 continues to increase as the number of oxygen atoms increases. All main peak positions remain the same.

Figure 6.7: The effect on the N Kedge of substituting O into the second shell of (a) TiN and (b) HfN structures
Similarly for HfN the main peak positions all remained the same. Peaks 2 and 4 remain the same relative distance from each other. The intensity between peaks 2 and 4 increased close to peak 4 as the number of oxygens increased, and a hint of a peak in this region was observed (peak 3). We also observe the merging of peak 1, which is a distinctive peak in HfN, into peak 2 by 12 O such that it looks more like a shoulder than a separate peak.

Although not useful for giving an accurate edge shape these results indicate that there are significant changes in the edge shape just by having the 2\textsuperscript{nd} nearest neighbour sites varied. Hence, if ideal interfaces were achievable it should be possible to distinguish between anion environments that have more O than N surrounding them.

6.5.3 Randomly doped (Ti,Hf)N structure with ordered inner-shell

Here a nitride structure is considered where the cation site instead of the anion site as above, is doped. In this instance all of the atomic list in the feff.inp file has been randomly doped 50\%Hf and 50\%Ti and the same atomic list is used for all calculations. An average lattice parameter was used to construct the input files. The only difference between the calculations is the Ti:Hf ratio in the first co-ordination shell. Since the first co-ordination shell has the largest impact on the edge shape - more so than the second co-ordination shell - so we would expect significant changes in the edge shape by substituting Ti for Hf. Because both TiN and HfN have the rocksalt structure the central N atom has octahedral co-ordination. With doping of between 2-4 atoms in the first shell there are different positions in which the atoms can sit. The main configurations are illustrated in Fig 6.8. All of these configurations have been investigated in this study. Because it is only the first and second co-ordination shells that significantly affect the edge shape, the positioning and number of dopant atoms in the third shell should not have a large impact on the edge shape. The second shell contains only nitrogen.
The first thing to note is that none of the doped edge shapes in Fig 6.8 are particularly ‘TiN like’. The first two peaks in the doped edge shape are closer together than for TiN. The relative peak intensities are different with peak 1 less intense than peak 2, the opposite to the TiN shape. The gap between peaks 2 and 3 is also filled in more than for TiN. The double front peak disappears by the 3Ti:3Hf configuration looking at the edge shape from the bottom of the graph to the top. Here, only two peaks (2 and 4) of fairly equal intensity are observed. The second of these peaks increases in intensity a little more as the percentage of Hf is increased. As the Hf content increases peak 3 becomes less rounded and sharper, and the gap between peaks 2 and 3, decreases in intensity. Whilst the relative spacing between peaks 2 and 3 is similar to that found in HfN, the decrease in intensity of the gap is contrary to that of the Hf N K edge. In fact, either of the 2Ti:4Hf edge shapes would be a better match for HfN than when the central nitrogen is co-ordinated to 6 Hf atoms in the inner shell. The HfN edge shape here looks different to that displayed in Fig 6.1. This is because here no shift has been applied to the Fermi energy. The reason for this is that if a shift is applied to the Fermi level of TiN, because Feff correctly places the Fermi level in the first instance, unwanted states would be included in the ELNES. The opposite would be true for HfN. This makes calculation of a structure containing both Hf and Ti in it difficult.
case the decision was made not to shift the Fermi level, hence the reason for comparison with an HfN edge that had not had a Fermi correction applied to it.

In summary, we have shown that the atoms closest to the excited atom have a large effect on the edge shape. However, having the inner shell contain all one kind of atom does not give a great match with the end member edge shapes such as TiN or HfN in the case above. Somewhere in the middle gives the best agreement with the end members for a doped structure containing Ti, Hf and N.

**6.5.4 Interpolation of calculated N K edges of TiN and HfN**

Another possibility of what happens at the interface is that due to the roughness of the interface there is actually an overlap of different edges from say the m-HfO$_2$ and the TiN. This can in turn be modelled as a superposition of end member edge shapes. The interface of interest is that between m-HfO$_2$ and TiN. However, because the edge shapes are of nitrogen and oxygen, we cannot model an overlap of these edge shapes because they occur at very different energies. As a starting point the overlap between TiN and HfN has been modelled. In this case both TiN and HfN have been calculated using an average lattice parameter and then superimposed and summed in different ratios. No edge energy offset has been applied to the spectra, the superposition has been applied to the spectra exactly as they came out of the FEFF calculation. In this case a Fermi energy shift was applied for HfN as in Fig 6.1.
From Fig 6.9 we observe a similar trend to the doped inner shell structure in section 1.4.2. With 80%Ti:20%Hf the edge shape remains very TiN-like. It would be difficult to distinguish this edge from TiN if collected experimentally. As the percentage of Hf increases to 40%, changes in the edge become more obvious. Peak 1 starts to form, initially looking like a shoulder on peak 2, which is a feature due to HfN. This increase in intensity as the hafnium percentage increases, until it looks like a proper peak at 20Ti:80Hf. At the same time, the dip between peaks 2 and 4 fills in until peak 3 disappears by 80% hafnium content. By 40% HfN content, the intensity of peak 4 has increased and sharpened with peak 5 decreasing until it disappears altogether by 80% HfN content. As with 80%TiN content, with 80% HfN content it would be difficult to distinguish experimentally between this and the HfN edge shape. One difference from the doping of the inner shell in section 5.4.2 is that whilst in that case the dip between the 2\textsuperscript{nd} and 3\textsuperscript{rd} TiN peaks initially filled in, then decreased in intensity to less than is observed in HfN as the HfN concentration increased. Here the intensity of that region...
remains fairly constant, albeit there is a shift in energy of the area of maximum intensity. The intensity remains fairly similar to that in HfN itself. This technique is therefore another way of modelling the edge shapes that occur at the interface. What becomes clear here is that it is difficult to distinguish an edge shape that is formed due to an overlap of edges with an edge shape that is formed because of intermingling of phases where a new ‘dopant’ phase is formed. Because of the problems remaining with XANES/ELNES calculations, it will be a long time before calculations are accurate enough to be able to distinguish between the mechanism for forming interfaces from the experimental edge shapes.

6.6 TiN-HfN interface calculations

FEFF is a real-space code so it is easy to manipulate the atoms such that interfaces can be constructed. The disadvantage of FEFF over a code such as Wien is that no relaxation of the interface can be carried out. FEFF will therefore only give good results for where a good match in interface structure and lattice parameters is found. On the other hand whilst Wien allows for relaxation, it is more difficult to construct interfaces because of the use of supercells and the computation time greatly increases as the size of the supercell gets larger. As a result FEFF was used here to calculate the interface between TiN and HfN since it was much easier to manipulate and to look at many different effects within a reasonable time frame. Ideally we would want to consider the TiN/HfO₂ interface. This, however, is very complicated because of the different structures of TiN and HfO₂ making it difficult to find matching planes with appropriate atomic spacing where an interface could form. There is also the difficulty of not knowing which phase of HfO₂ forms in the gate stacks. We know that m-HfO₂ often forms but there have also been reports of t-HfO₂ forming

7;22;28. As a result, to a first approximation, an interface between TiN and HfN was constructed and modelled. This was much simpler to calculate since both TiN and HfN have the rocksalt structure. The most obvious interfaces to consider are where the interface occurs at the (111), (100) and (110) terminated planes. The different interfaces and atomic configurations are shown in Fig 6.10.
Figure 6.10: Rendering of the fcc structure for different atomic planes. (a) shows where the plane sits in the atomic structure (b) shows the plan view of the interface (c) the octahedral configuration surrounding the central nitrogen atom for this interface, depending on whether the plane cuts the TiN or HfN side of the TiN/HfN interface.

The interface that is easiest to construct and carry out modelling for is the (111) plane, where all the atoms are nitrogen and each nitrogen sits in an identical octahedral environment with 3Hf and 3Ti atoms in the ‘fac’ configuration. Only one calculation has to be run for this since all the nitrogen atoms are in an identical environment. The calculated edge shape is illustrated in Fig 6.11. The edge shape has something of the character of both TiN and HfN. Peaks 1 and 2 have an energy difference greater than for TiN but this may be an effect due to the structure not being relaxed and a larger lattice parameter being used than would be commonly found for TiN (an average lattice parameter between the HfN and TiN structures was used). Peak 3 resembles, both in
position and shape, the third peak of HfN (Fig 6.1 or 6.5). Hence we have both HfN and TiN like features in the (111) model.

Figure 6.11: N K edges from different interfaces between TiN and HfN (a) shows the different environments at each interfaces plus the interpolation of these different edge shapes (b) shows the interpolated edge shapes for each interface.

The (100) and (110) interfaces are a little more difficult to model since these planes contain both the cation and anion sites. The plane cuts either the Ti or Hf terminated interface. This means that the calculations have to be carried out for a nitrogen atom present for both the TiN and HfN terminated planes of the interface. The nitrogen environments are shown in Fig 6.10c for both of these potential interfaces. For the (110) interface the N atom is always in the ‘cis’ configuration. Modelling was carried out for the different nitrogen environments on both sides of the interface and then summed to provide an average edge shape for the interface with contributions from each environment. The edge shapes for each N environment and the interpolated edge are presented in Fig 6.11. Only subtle differences were found between the K edges taken in the predominantly HfN side of the interface for both (100) and (110) interfaces. This reflects what was observed in Fig 6.8 for the randomly doped structures with ordered inner shell. There also, when only one or two of the innershell Hf atoms were replaced with Ti only subtle differences in the edge shape were observed. The edge shape here is
very HfN like, as one would expect since the atoms closest to the excited atom cause the largest changes in the edge shape. However, the same trend is not seen for the predominantly TiN-like environments. Although the edge shapes look more like TiN than HfN, the features are quite different from those observed for TiN itself, and the N K edges look quite different from each other considering a change of only one atom between the (100) and (110) planes.

Once interpolated, the (100) interface is more HfN like. The main features that distinguish the interfaces from each other are the changing intensity between the first and third peaks, such that a clear peak has formed in this region in for the (111) interface whilst for (100) there is little observed here. The shape and relative intensity of the peaks at ~405 and 413eV also varies at the different interfaces.

The models for each interface have quite distinct features. Although these would look slightly different at an interface as the effects of strain or relaxation have not been taken into account, they are significantly different that they would give different edge shapes after EELS analysis in the (S)TEM. All main features would be present experimentally and so the relevant interface could be determined by comparison with the models.

6.7 Stepping away from interface

Following on from the discussion above regarding the different interfaces possible between TiN and HfN fcc structures, it was decided to study the edge shape as we moved further into the TiN or HfN bulk, either side of the interface. The easiest interface to study is the interface terminating on a (111) plane since all the nitrogens in this plane have the same atomic environment. Fig 6.12 illustrates the changes that occur to the edge shape as the central nitrogen atom for the calculation is moved 1 or 2 successive nitrogen planes away from the interface into both the TiN and HfN sides of the interface. We would expect the K edge to look like that of TiN or of HfN after moving only a few planes into the material since it is mainly the nearest neighbours that have an effect. Fig 6.12 shows that the EELS of the N K edge only two planes away from the interface (4 shells) is almost indistinguishable from TiN or HfN by considering the edges in the appropriate direction away from the interfaces. Whilst excellent
agreement is achieved for TiN in showing a bulk like N K edge, the same is not true for HfN, although reasonable agreement is still achieved. The reason for the poor agreement for HfN may simply be due to the miscalculation of the Fermi level by FEFF for edges where the hafnium has a larger influence. This is the same problem as described in section 5.4.2 regarding shifting the Fermi level when both Ti and Hf are present. This problem is currently irresolvable. Future development of the code will need to take this problem into account. While it is fine to shift the positioning of the Fermi level for known standards, when structures are intermixed or there is doping involved there is not such a straight forward solution.

![Diagram](image)

**Figure 6.12:** Illustration of what happens as you move one or two nitrogen planes away from the HfN/TiN [111] interface. Calculated TiN and HfN edges are displayed in black for reference.

At one plane away from the interface (2\textsuperscript{nd} co-ordination shell), the excited nitrogen atom has octahedral co-ordination to six Hf or Ti atoms respectively. Here, although the edge shape is starting to look more like TiN or HfN, there are still some major differences. In the case of the TiN side of the interface, the intensity of the first two peaks are the reverse of what they should be, and the energy spacing between all the peaks is less than for TiN itself. For HfN, reasonable agreement is achieved but the results are hampered by the incorrect Fermi level placement as discussed above.
Focusing on the TiN-like structure, we see here that not only the first, but also the third co-ordination shell has a large impact on the edge shape. The nitrogen sitting one plane away from the interface on the TiN side, although surrounded by all Ti atoms, the edge shape does not give particularly good agreement with that of TiN. This is because the third co-ordination shell contains Hf atoms. When looking at the 2nd plane, it is the 5th co-ordination shell that contains Hf atoms and here these can be considered as too far away to have a significant impact on the edge shape. However, three coordination shells away from the excited N atom still has a significant contribution to make to the edge shape.

6.8 Conclusions

This chapter has highlighted the necessity of obtaining good models that are in agreement with experiment so as to help with interpretation of experimental edges that are not yet understood. Two modelling programs were investigated – Wien2K and FEFF8.2. Reasonable agreement with experiment was obtained with both programs. FEFF8.2 was chosen for most calculations due to its ease of use, particularly in constructing interfaces. A number of possible HfO$_2$ structures were modelled. These will help determine the crystalline HfO$_2$ phases present in both sol-gel and thin film samples. Possible reaction products of known compounds were also modelled to assist interpretation at interfaces in thin films. It was found that the atoms closest to the absorbing atom had the largest influence on the edge shape with a significant effect extending as far as the third shell. This was observed in various experiments through doping of both the anion and cation sites. Where a randomly doped (Ti,Hf)N structure was investigated with the first co-ordination shell (containing the Ti and Hf atoms) was systematically varied, it was observed that the more Hf atoms in the shell, the more HfN-like the edge shape became. This effect was not so pronounced for increasing the number of Ti atoms closest to the central N.

Because interfaces in the thin films are not generally flat and a lot of roughness is observed after annealing, the edge shape obtained experimentally may result from an overlap of edge shapes collected through the depth of the interface being probed. These can be modelled by overlapping the edge shapes of the materials adjacent to the
interface. In this case that would mean an O and an N K edge therefore the modelling was carried out for a TiN:HfN interface since HfN is a possible interface reaction product. It was found that when about 20% of the other edge shape was included in the fit, the edge still looked like the TiN or HfN end members, but as the percentage increased, the edge shapes started to change such that they would be distinguishable from the end member materials if those edges were collected experimentally. They also looked different enough from the doped structures to be able to distinguish between these effects experimentally. However, problems associated with the Fermi level placement with some calculations make a direct comparison difficult.

The ease of changing atoms within the FEFF program allowed an interface between two rocksalt structures to be conducted and three of the different planes to be considered. The results show that whilst there were a number of features in common between the edge shape obtained at each interface, the edge shapes looked significantly different from each other and could be distinguished in experimental data.

Whilst these models will be very useful for helping interpret EELS spectra, it is recognised that there are a number of issues that will need to be resolved before modelling will ever be able to accurately predict what is observed experimentally.


7 EELS of Powders

7.1 EELS acquisition and processing

Samples were prepared for TEM analysis using the oxychloride and butoxide powders discussed in Chapters 3 and 4. The powders were mixed in isopropanol and dropped onto a holey or lacey carbon film. The isopropanol was then left to evaporate from the grid, leaving the particles of interest.

EELS data was collected both on the Tecnai at the University of Glasgow and on the Titan at Imperial College London. All EELS spectra in this thesis were taken in STEM mode. The method of collection in each instrument is similar. On the Tecnai acquisition is controlled by Digiscan and the data is processed within Digital Micrograph (DM). In the Titan either DM or the FEI software ‘Tecnai Imaging and Analysis’ (TIA) are used to control the spectrometer and carry out data processing. For the Titan the type of experiment being carried out determines the software used to collect and analyse the data. In general, for a single spectrum acquisition, DM was used; for a line spectrum, TIA was used. The TIA line spectra were generally converted to DM format for processing. However, data collected by taking a raster scan over an area were processed within TIA itself.

Line spectra or spectrum images are collected by firstly selecting a line or area of interest. The number of spectra to be collected per region (line or area) are defined, as are the acquisition time and the number of spectra to be acquired per pixel. Once the spectrum has been collected at one point the electron beam is moved to the next point, under computer control, and the process repeated. It is also possible to correct for drift although this facility was not used for any of the results presented here.

Typical acquisition conditions for spectra collected on the Tecnai operating at 200kV are C1 = 2000μm, C2 = 50μm, spot size 9 with a convergence semi-angle of 8.8mrad. Collection conditions were: spectrometer entrance aperture = 2mm; camera length = 30mm for core-loss data; collection semi-angle = 10mrad; dispersion = 0.2eV/ch; integration time = 10s/spectrum with 5 spectra recorded at each
point and summed. The energy resolution from the zero-loss peak (zlp) recorded at a camera length of 150mm was 0.7-0.8eV. Similarly for the Titan operating at 300kV: C1 = 2000μm; C2 = 50 or 70μm with spot size 6 or 9 respectively, depending on experiment; C3 was disabled. This resulted in a convergence semi angle of 10mrad and 14mrad for the different C2 apertures. Low-loss data was collected at a camera length of 196mm, 0.01-0.05eV/pixel and an acquisition time of ~0.08s resulting in an energy resolution of between 0.65-0.75eV for the full-width half-maximum (FWHM) of the zlp. Core-loss data was recorded at a camera length of 48mm or 77mm with collection semi angle of 18.1 and 11.1mrad respectively, an energy dispersion of 0.1-0.3eV/pixel depending the edge collected, and an acquisition time of between 5 and 10s per spectrum. The time per spectrum was dependent on whether single or multiple spectra were collected at each point and whether there was contamination or drift.

Some samples had a lot of contamination in STEM. Plasma cleaning helped reduce this but it was not possible to clean the sample for long due the carbon film also being attacked by the plasma. It was also suspected that the plasma caused damage to the sample itself. Thus plasma cleaning was carried out for a maximum of 12s in an H2/O2 gas mixture as a compromise. Tests are still underway to look at the damage effects caused by the plasma cleaner. For many of the badly contaminated samples, instead of taking point spectra, a window was selected over which a STEM raster scan was taken and EELS spectra collected and summed.

Once the EELS spectra have been collected the energy calibration is checked. Ideally both low and core-loss spectra should be obtained in the same spectrum so that the whole spectrum can be aligned with the zlp at 0eV resulting in accurate edge onsets for the core-loss spectra. However, this is not always practical leading to the low-loss and core-loss spectra being acquired after each other. This introduces errors such as drift of the zlp between acquisitions which must be taken into consideration when interpreting edge onsets of core-loss data. Great care must be taken by the user during data acquisition to minimise these problems.
7.2 Oxygen K edges from powders

The first experiment on the powder samples was to confirm whether the O K edges present in the literature\textsuperscript{138} were reproducible. EELS was carried out on powder samples where a specific phase was known to be present. The experimental edge shapes shown in Fig 7.1 are taken from samples prepared from a butoxide route, heated to 800°C and 1700°C. The m-HfO\textsubscript{2} edge was taken from a SiO\textsubscript{2}-free sample that had been heated to 800°C. The HfSiO\textsubscript{4} and amorphous SiO\textsubscript{2} (a-SiO\textsubscript{2}) were taken from a SiO\textsubscript{2}-containing sample after heating to 1700°C. The standard edges (solid black line in Fig 7.1) were collected previously at the University of Glasgow by Dr M MacKenzie. The standards were obtained from a number of sources: (a) HfSiO\textsubscript{4} was grown by J Hanchar\textsuperscript{2}, (b) HfO\textsubscript{2} powder (monoclinic, Sigma-Aldrich, UK), and (c) SiO\textsubscript{2} (isolating oxide on Sematech Si/SiO\textsubscript{2}/HfO\textsubscript{2}/poly-Si wafer). These spectra have been reported previously\textsuperscript{107,139}.

The edge onsets for HfSiO\textsubscript{4} and m-HfO\textsubscript{2} were aligned at 5eV, and a-SiO\textsubscript{2} was positioned by aligning peak 1 with peak 2 of m-HfO\textsubscript{2} as presented by Agustin \textit{et al.}\textsuperscript{35}. Fig 7.1 compares the experimental spectra (coloured lines) and standard edge shapes (black lines). Good agreement is obtained between experimental and standard edges. The HfSiO\textsubscript{4} edge does not fit the standard edge as well as for m-HfO\textsubscript{2} and a-SiO\textsubscript{2} - the first peak is not resolved, and has lower intensity than the standard. The m-HfO\textsubscript{2} and SiO\textsubscript{2} edges, on the other hand, are a good match with the standard edge. These results also confirm that there is still amorphous material remaining in the powder samples after heating to 1700°C since an O K edge for a-SiO\textsubscript{2} is found in some of these samples. That the sample has not fully crystallised after twelve hours at such a high temperature is indicative of the overall crystallisation process having slow reaction kinetics.

\textsuperscript{2} J Hanchar, George Washington University
Fig 7.2a-c shows O K edges obtained experimentally from SiO₂-free samples heated to 1700°C. Here m-HfO₂ is the only phase expected to form. The experimental edges are also compared with standard m-HfO₂, a-SiO₂ and Al₂O₃ edges. The first thing to note is that edges (a)-(c) are all different from each other and therefore do not all match the edge shape expected for m-HfO₂. This is contrary to results from a sample heated to 800°C where all the O K edges matched the expected m-HfO₂ edge shape (shown in Fig 7.1).

From Fig 7.2 edge (c), within the level of the noise, matches the standard m-HfO₂ edge. However, similar edges have also been collected where the first peak (peak 1) is less intense. It is possible to model such edges as a combination of a-SiO₂ and m-HfO₂ but this should not be the case as there should not be any SiO₂ present in the sample. Similarly (a) matches a-SiO₂ within the level of the noise. Edge (b) does not fit with any of the standard or overlaid HfO₂:SiO₂ edges (see later discussion).
It is thought that the edge shape in Fig 7.2(a) is due to either Al$_2$O$_3$ or a-SiO$_2$ from a contaminated crucible. After heating to 1700°C the HfO$_2$ powder was difficult to remove from the crucible as it bonded with the Al$_2$O$_3$, so in the process of removing it, it is possible that some of the Al$_2$O$_3$ was mixed with the sample. Fig 7.2 shows both crystalline and amorphous Al$_2$O$_3$ (α-Al$_2$O$_3$ and a-Al$_2$O$_3$) for comparison with (a). The experimental Al$_2$O$_3$ edges are too wide to fit edge (a), whereas a-SiO$_2$ fits well. The presence of SiO$_2$ in the sample can be explained as follows: since the crucibles are reused from previous experiments it is possible that a small amount of SiO$_2$ contaminant from previous samples has resulted in these edge shapes. At high temperatures the SiO$_2$ can bond with the alumina crucible. Some of this may remain ingrained in the crucible which may then react with the sample in the crucible when heated to high temperature. Only in samples heated to this high temperature do these un-recognised edge shapes appear. This corresponds with the temperature at which the sample starts to melt or to bond significantly with the crucible in which it is placed. This serves as a warning for interpretation of EELS edges or TEM images of samples heated in this way to high temperature – the edge shape obtained or the image may not actually be due to the crystalline species expected. Where possible this should be verified by other means such as electron diffraction or energy dispersive x-ray (EDX) analysis.
Bearing this in mind, a number of spectra were recorded from both oxychloride and butoxide, SiO₂-containing and SiO₂-free samples heated over the 800-1700°C range. Whilst some of the collected edges match the expected standard edge shapes, many of them could not be assigned to known standards. Some of these edges were recurring and are presented in Fig 7.3. These edges were collected from a butoxide Hf₀.₅Si₀.₅O₂ sample heated to 1000°C and 1400°C (Fig 7.3a-b) and an oxychloride prepared HfO₂ sample heated to 1700°C (Fig 7.3c). The O K edges in Fig 7.3d-e were taken from a SiO₂-free oxychloride sample after heating to 1700°C: Fig 7.3d was a single spectra taken from one particle (particle shown in Fig 7.5) and Fig 7.3e is a sum of 5 spectra from a linescan across the same particle (line 2 on Fig 7.5).

Three of the commonly found O K edge shapes (Fig 7.3a-c) differ from the standard m-HfO₂ and SiO₂ edges. These O K edges are reproducible within each sample. In the 1000°C sample t-HfO₂ is the primary phase expected with a small amount of m-HfO₂ appearing – neither of these edges were found experimentally. The aim of these experiments was to find an experimental edge shape for t-HfO₂. However, comparison of Fig 7.3a with the modelled t-HfO₂ O K edge in Chapter 6 (Fig 6.2) and with the...
experimental t-ZrO$_2$ edge shapes (see McComb), shows that this edge does not resemble the expected two peak ELNES of the O K edge of t-HfO$_2$. At first glance the edge is quite similar to a-SiO$_2$ – the gradient of the edge onset matches that of a-SiO$_2$ but the peak is much broader than for SiO$_2$. A better fit for peak width is found with a-Al$_2$O$_3$, however the peak shape still is not a good match. This particular spectrum is quite noisy and there is a large thickness contribution which may be contributing to the discrepancy, since the features ~10eV above the edge onset cannot be distinguished. However the main near-edge features are still clear.

Edge (b) is taken from a powder heated to 1400°C. According to XRD this sample should contain m-HfO$_2$, c-SiO$_2$ and a little HfSiO$_4$. Again the experimental edge does not fit any of the standard edge shapes. Although it is most like HfSiO$_4$ the ratio of the first two peaks and the energy spacing between them does not fit with HfSiO$_4$. Another possibility is that the edge is an overlap of a-SiO$_2$ with HfSiO$_4$. To test this the HfSiO$_4$ and SiO$_2$ edges were summed in different ratios, the peaks being aligned according to the peak energies set out by Agustin et al. However, the resultant edge shapes (not shown) reveal that the peak separation and the slope of the edge onset do not match Fig 7.3b. An overlap of these two edges therefore does not fit this edge shape.

The third edge (Fig 7.3c) resembles m-HfO$_2$ – the two main peaks have the same energy separation as in m-HfO$_2$ (Fig 7.1), and there is a clear dip in intensity between the two peaks as expected for m-HfO$_2$. What differs is the peak ratio. This sample is expected to contain mainly HfSiO$_4$ and m-HfO$_2$ but as seen from Fig 7.1 that there is still a-SiO$_2$ present at 1700°C.
An investigation was carried out as to whether it is possible to model the edge in Fig 7.3c as a combination of the binary m-HfO$_2$ and a-SiO$_2$ edge shapes. To investigate this further, model EELS spectra were produced by summing the standard experimental O K edges of m-HfO$_2$ and a-SiO$_2$ in different ratios and the changes in edge shape monitored (Fig 7.4). These were then compared with some of the previously unassigned edge shapes such as those in Fig 7.3c. After fitting the spectrum in Fig 7.3c with some of these edge shapes a good fit was achieved with the 70Hf:30Si edge. This indicates that the area of the specimen from which this edge shape was recorded was most likely to be a mixture of the two phases where the m-HfO$_2$ particles are surrounded by a-SiO$_2$ such that the incident electron beam probes both environments. The edge therefore has a contribution from both SiO$_2$ and m-HfO$_2$. Alternatively a new phase may have formed. However, because such a good match is achieved with the overlaid 70Hf:30Si edge it is thought that it most likely occurs from the electron beam probing both environments.

The edges presented in Fig 7.3d and e were particularly surprising as this sample was prepared in an SiO$_2$-free environment and should have contained only m-HfO$_2$. However, once again the sample had been heated to 1700°C so it is possible that the sample has been contaminated by the crucible. Considering Fig 7.3d, whilst there are two peaks in this edge that match the peak positions of m-HfO$_2$, the peak ratio of the
80Hf:20Si edge, the edge onset has a less steep gradient and peak 2 is much broader than would be expected from this ratio of edges. SiO₂ should not be present in this sample at all since none was used in the sample preparation. The edge shape remains unassigned.

The data in Fig 7.3e was acquired from the particle shown in Fig 7.5. The particle in this STEM image is typical of the particles in this sample. The data was collected from the line marked by the number ‘2’. Five spectra were summed to give the edge shape and to help reduce the effects of noise. Each spectrum had the same peak spacing and relative peak intensity so the summed shape is representative of the edge obtained from that part of the sample (which differs from the line spectrum taken from line ‘1’ in Fig 7.5, described in detail below). The energy spacing between peaks 1 and 2 matches that of m-HfO₂ but the peak ratio is different: the first peak has a higher relative intensity and the gap between them filled, in comparison to m-HfO₂. This cannot be modelled by an overlap of SiO₂ and m-HfO₂ edges. Using an m-HfO₂:SiO₂ model, at no point is the first peak more intense than when the sample is fully m-HfO₂. However, that is not to say that the edge is not from m-HfO₂.

Wilk and Muller{116} report a change in the m-HfO₂ edge shape as the annealing temperature of the sample is changed. They start from what appears to be an amorphous, thin film sample and as they heat portions of it to different temperatures the
edge shape changes - in particular the ratio between peaks 1 and 2 and the filling in of the gap between these peaks. All the grains investigated are monoclinic and of sufficient size that grain size should not affect the ELNES. It is interesting to note that the edge Wilk and Muller obtain from the ‘amorphous’ part of the sample has a peak ratio similar to that in Fig 7.3e. It is likely that this ‘amorphous’ area of the sample did not remain so during the course of the spectrum acquisition. Crystallisation on a 1-2nm scale is likely to have been induced by the beam which results in the acquired edge shape. Wilk and Muller conclude that the variation in edge shape is due to local variations in the structure, most likely caused by oxygen vacancies and change in oxygen coordination to the Hf. The peaks increase in intensity as the annealing temperature is increased indicating that the average Hf coordination increases with temperature as there are fewer oxygen vacancies present. Not enough spectra have been collected and analysed to determine if this is true for the samples in this chapter. If oxygen vacancies are the main contributor to the local structure, they should also have a large influence on the t-HfO$_2$ edge shape since it is found that these cause the t-HfO$_2$ stabilisation at lower temperatures in the oxychloride preparation route. Comparison with t-edges stabilised by a crystallite size/surface energy effect, should yield a similar effect. This does bring into question the validity of a ‘standard’ m-HfO$_2$ and whether it is, in fact possible to have such a thing as a standard edge when there is so much local variation between particles that are nominally the same. This has many implications for other structures.

Before proceeding with further results from this particle, it is important to consider how the t-HfO$_2$ edge is modified by the presence of SiO$_2$. Since obtaining an edge for t-HfO$_2$ is the aim of this investigation, a similar analysis as for overlaying m-HfO$_2$ and SiO$_2$ edges (Fig 7.4) is carried out for t-HfO$_2$:SiO$_2$, using the FEFF modelled t-HfO$_2$ edge from Chapter 6. Fig 7.6 gives an idea of the edge shapes resulting from this. The spectra have been overlaid such that the SiO$_2$ peak matches the second peak of the t-HfO$_2$ edge. It must be remembered, this can only be used as a rough guide for interpretation.
7.3 Line Spectra from powders – O K edges

Line spectra were obtained from samples to investigate the change in edge shape across the particle. Unfortunately the spectra were quite noisy however, two of the better spectra are shown in Fig 7.7 and Fig 7.11.

7.3.1 Spectrum 1

The first spectrum (Fig 7.7) is from an oxychloride, SiO$_2$-free sample that has been heated to 1700°C in which only m-HfO$_2$ is expected to be present. A line profile was taken across the sample from the line marked ‘1’ in Fig 7.5 (line = 47nm, 10 points per line). Scan 1 in Fig 7.7 starts where the mark ‘1’ is on the particle in Fig 7.5, and scan 10 is at the opposite end of the line. The results are compared with the standard O K edge for m-HfO$_2$. The sample drifted by about 16nm towards the top left hand corner of the image during acquisition. There may also have been a small amount of contamination during acquisition.
Despite this sample containing only m-HfO$_2$, none of the edges in Fig 7.7 match the standard m-HfO$_2$ edge shape well. Whilst all spectra match in relative peak positions, only spectra 3, 4, 8 and 9 match the peak ratio of the standard m-HfO$_2$ edge. Though the peak ratios match, the dip between the peaks does not. The edge onset for all
experimental edges has a shallower gradient and the two main peaks are wider than for m-HfO$_2$. In all cases the dip between peaks 1 and 2 is significantly shallower than for m-HfO$_2$ though by different degrees in each spectrum. There is a question as to whether the variation in the dip between peaks 1 and 2 is an artefact due to noise. To try to address this some of the spectra that look similar in Fig 7.7 were summed to see if the variation in features became any clearer (Fig 7.8). Only a small difference in edge shape is found between summed spectra 7-10 and 4-6, but the difference in peak shape and the dip between the peaks is much more obvious when comparing with summed spectra 1-3. This indicates that whilst variation between adjacent spectra is minimal, there is a clear difference in edge shape as the beam moves across the sample.

![Figure 7.8: Spectra from Fig 7.7 summed and compared](image)

The peak splitting in the near-edge structure is from the crystal field splitting due to the local atomic environment within the HfO$_2$ particles. The relative peak intensity is proportional to the number of electrons occupying the energy levels and the peak spacing results from the separation between the energy levels. In the simple case of cubic HfO$_2$ (c-HfO$_2$) the Hf d states are affected by the O atoms which are in a tetrahedral environment. This results in splitting of the d states into doubly and triply degenerate energy levels (Fig 7.9).
Figure 7.9: Schematic of crystal field splitting of Hf d orbitals due to O atoms

For cubic HfO₂ (assumed from the example of ZrO₂ Ref 142) the first peak in the EELS spectra is due to the doubly degenerate e₂g states and the second peak to the triply degenerate t₂g states. The separation between the peaks is due to the separation, Δ, between t₂g and e₂g. t-HfO₂ is essentially cubic but with a slight shift in the atomic positions (Fig 7.3). The d orbital splitting remains close to that of c-HfO₂ but will result in broadening of the peaks because of the states - assigned t₂g and e₂g for c-HfO₂ - become slightly nondegenerate. The crystal field splitting for m-HfO₂ is more complicated due to the HfO₇ polyhedra. For m-ZrO₂ it has been suggested that there is a (2+1+2) splitting of the d orbitals 143. This again will result in broadening of the peaks, a reduction in the gap between the peaks and changes in peak separation compared with c-HfO₂. These effects may become even more pronounced with changes in the local coordination environment.

If defects are present - for example vacancies or dopants - the edge shape would be altered. The spectra in Figs 7.7-8 are taken from a sample which should contain only m-HfO₂. The experimental edge shapes, however, differ from the standard m-HfO₂ edge shape as found in Fig 7.1. The main deviations from the standard edge are that the peaks are broader, the relative peak ratios vary and the decrease in intensity between the peaks has lessened or, in some cases, has almost completely disappeared.

There are two main hypotheses to explain the variation in edge shape shown in Fig 7.8. Firstly, the variation may be due to thickness effects. Because this area of the sample is particularly thin the outgoing electron interacts with fewer atoms than in the bulk of the material resulting in a large contribution to the edge coming from the surface. The local atomic environment is altered due to many atoms being situated near the surface and...
therefore not in the ‘bulk’. The surface itself gives rise to defects - commonly vacancies, surface oxidants or contaminants - which will also influence the edge shape and hence may be the cause of some of the differences in the O K edge observed in this sample. The second possible cause of edge shape variation is that there are local atomic variations within the crystal, possibly caused by oxygen vacancies in the structure itself. The EELS measurements are made from a spot of ~0.2nm in diameter so local variations on this scale can be detected.

Neither of these hypotheses adequately explain the observations. For hypothesis 1 the electron beam would have to probe a depth of less than ~2nm for the edge to be altered by the defects near the surface - this was found from modelling calculations in Chapter 6. The region investigated appears to be a single particle (Fig 7.5), the depth being probed is greater than 2nm which means the surface will have minimal effect on the edge shape. However, hypothesis 2 does not adequately explain the results either. Whilst it is likely that local variations may account for the differences in edge shape, it is not thought that there is a high concentration of oxygen vacancies in m-HfO2 as determined from the sol-gel work in Chapters 3-4. Therefore, if there is local variation within the m-HfO2 structure, it is not clear what the cause of it is.

In summary, it is not clear why the edge shape varies. Although the spectra are quite noisy, there is still some variation in the edge shape which is more apparent after summing adjacent spectra and is therefore thought to be a real effect.

### 7.3.2 Spectrum 2

A butoxide silicate sample was heated in a furnace to 940°C for 2 weeks to try to cause all the Hf in the sample to form t-HfO2, so that no isolated Hf remained in the a-SiO2. From this it was hoped that the O K edge of t-HfO2 could be obtained. Particles in these samples were found both as part of agglomerates in the SiO2-rich matrix and as individual nanoparticles (~2-5nm) dispersed on the carbon grid with no evidence of surrounding amorphous material. The particles dispersed on the grid are more suitable for obtaining a t-HfO2 O K edge since there is minimal contribution from a-SiO2. However, these samples contaminated badly in STEM which made imaging of individual particles very difficult and EELS analysis impossible. Instead some of the larger agglomerates of particles were investigated. The result from one of these is displayed in Fig 7.11 with the accompanying image in Fig 7.10.
Figure 7.10: Area of sample from which Line spectra in Fig 7.11 was taken. The point on the line marked ‘1’ relates to scan 20
Figure 7.11: Butoxide (SiO₂ containing) sample heated to 940°C to induce t-HfO₂ formation

The sample drifted during data acquisition towards the top left hand corner of the image. Though the effect of drift was small it means that direct correlation between the scans in Fig 7.11 and the point from which the scan was taken on the line in Fig 7.10
was not possible. Line spectra were taken from two regions on the sample. Both data sets were quite noisy and so the results reported here are from the better of the two data sets. The spectra are related to the image in Fig 7.10 such that ‘spectrum 20’ in Fig 7.11 is at the end of the line marked ‘1’ and ‘spectrum 1’ is at the opposite end of the line. From the STEM image the dark and light, HfO₂ and SiO₂ rich regions are clearly distinguishable in the thinner regions, from which the line spectra was taken. Ideally investigation into how the edge shape changes as the probe is moved from a dark to light region and also as the probe is moved across the HfO₂ rich region is wanted, however since there was some sample drift it is difficult in this instance to correlate the spectra and the image exactly. The spectra are also noisy, due to contamination issues making interpretation of features in the edge shapes difficult.

None of the spectra in Fig 7.11 are an exact match for the m-HfO₂ standard in Fig 7.4, though the spectra taken from the thinner region of the sample (spectrum 19 and 20) bear most resemblance to the standard m-HfO₂ edge Fig 7.1. Due to the quantity of a-SiO₂ in this sample it is quite likely that both HfO₂ and SiO₂ regions are being probed simultaneously within each spectrum and it is therefore important to compare the results with the t-HfO₂:SiO₂ ratios in Fig 7.6 and the m-HfO₂:SiO₂ ratios in Fig 7.4. The two peaks in both the t-HfO₂ and m-HfO₂ edges have the same energy separation. The first peak in the modelled t-HfO₂ edge is much less intense than for m-HfO₂ and so when combined with the SiO₂ edge this first peak becomes weaker in intensity and therefore does not match with the edges in Fig 7.11. However, it is worth remembering that there is no experimental t-HfO₂ edge for comparison, so the t-HfO₂:SiO₂ ratios are not as reliable as the overlaid m-HfO₂:SiO₂ edges. It is also possible that due to beam damage effects during collection of the edges, if the sample started as t-HfO₂, the sample may have damaged and a phase transformation to m-HfO₂ have occurred.
Bearing these issues in mind it is more informative to sum spectra from Fig 7.11 that are similar that fulfil certain pre-determined conditions, and compare those. Two main points of variation between the spectra are the relative ratio between peaks 1 and 2 and the dip between these peaks. Generally, the variation in the dip between the peaks is at the level of the noise and better data sets are required to consider this effect further. The main criterion, therefore, for overlaying and summing spectra was that the peak ratios were the same and the peak separation similar. The spectra were compared with spectra from Fig 7.4 where m-HfO₂ and SiO₂ had been summed in different ratios. The spectra from Fig 7.11 were then separated into categories of different m-HfO₂:SiO₂ ratios and then summed. Spectra 1, 3 and 16 were omitted from the summations due to noise and poor peak fits.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Spectra summed</th>
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<tr>
<td>1</td>
<td>1-20</td>
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<tr>
<td>2</td>
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<td>3</td>
<td>4, 6, 8, 12, 17, 19, 20</td>
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<td>4</td>
<td>2, 9-11, 13, 18</td>
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<td>5</td>
<td>5, 14-15</td>
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Table 7.1: Spectra summed from Fig 7.11 to give edge shape (spectrum) in Fig 7.12
It should be noted that due to the inhomogeneity of the sample the spectra that were summed were not necessarily adjacent to each other. From these results most of the spectra can be modelled as a linear combination of the binary m-HfO$_2$ and SiO$_2$ spectra which suggest that the electron beam is probing both of these atomic environments. However, comparison with m-HfO$_2$ is not entirely consistent with the sample since the sample should contain t-HfO$_2$ rather than m-HfO$_2$. Since it is not yet clear how these two edges differ, it is also possible that the edge shapes are of t-HfO$_2$ and not m-HfO$_2$. Without a more reliable t-HfO$_2$ edge, this cannot be determined. Whilst most of the spectra can be assigned to a particular HfO$_2$:SiO$_2$ ratio, there are still some discrepancies between the ideal and experimental edge shapes such as peak widths, dip between peaks and the gradient of the edge onset. To verify these details requires further data collection to determine whether these effects are real or due to noise, but they may provide key information on the tetragonal particles, or on how the edge varies as the probe is moved across the nanoparticle.

As well as an overlap of binary edges, there are other possible explanations for the edge shapes that occur. Firstly, the interface between two materials – t-HfO$_2$ and a-SiO$_2$ - may be probed. At the interfaces the local atomic environment is modified from that of the bulk material either side of it. Secondly, since the particles are about 2-5nm in size little of the material will reflect a bulk-like ionisation edge. This may result in variations to the edge shape as the local environment across the particle is probed. Due to the crystallite size they may have undergone structural relaxation which again can cause changes in the edge shape. It may be possible in future to investigate this effect combining Wien2k simulations with experiment. Thirdly, the variation in the ionisation edges may be due to defects within the structure. These may be either bulk or surface effects such as oxygen ion vacancies which may result in broadening of the peaks and change in intensity between the two main peaks. In this sample it is not believed that the stabilisation of the t-HfO$_2$ particles is due to oxygen vacancies, it is thought to be more likely due to the critical crystallite size effect and stabilisation by the surrounding amorphous matrix. The variation in edge shape is therefore not likely to be due to vacancies within the particle itself but more likely due to thickness and surface effects. It would be interesting to compare the edges for t-HfO$_2$ formed from an oxychloride preparation with a butoxide preparation. Before this analysis can be done it must first be possible to separate the particles from the SiO$_2$ otherwise there will always be doubt over the validity of the results.
7.4 Conclusions

In conclusion it has been possible to reproduce O K edges of m-HfO$_2$, HfSiO$_4$ and a-SiO$_2$ that match standards from the literature. However, alongside these a number of edges that do not fit the standard edge shapes were found. Some of these it was not possible to assign at all. Others were modelled using an overlap of m-HfO$_2$ and SiO$_2$ edge shapes in different ratios. This is to be expected for samples that contained SiO$_2$, but some of these samples as prepared did not have any SiO$_2$ present. This may have resulted from contamination from the crucible used during the heating experiment, though nothing appeared in the XRD. In the samples that were meant to contain only m-HfO$_2$, edges were collected that were not the standard edge, the first peak of which were generally more intense than that of m-HfO$_2$. The changes in edge shape within a sample must be due to local atomic variations, the most likely cause of which is oxygen vacancies which change the average Hf coordination number. If there is so much variation in edge shape from particles that are known to be m-HfO$_2$, it brings into question the validity of the edge used as a standard. This also relates to the discrepancy between modelled and experimental edges in Chapter 6. If oxygen vacancies cause such a change in O K edge then the modelled edge may in fact be closer to a perfect m-HfO$_2$ crystal than first thought.
8 TEM of Thin Films

In this chapter results from electron microscopy of ‘Hf$_x$Si$_{1-x}$O$_2$’ thin films are presented. In particular, the effects of damage, sample thickness, Hf$_x$Si$_{1-x}$O$_2$ composition and annealing conditions as well as the effect of processing on Si/SiO$_2$/Hf$_x$Si$_{1-x}$O$_2$ and Si/SiO$_2$/Hf$_x$Si$_{1-x}$O$_2$/poly-Si gate stacks have been studied using TEM.

8.1 Experimental set-up

Thin films prepared by IMEC (Leuven, Belgium) were investigated to further develop understanding of the crystallisation process occurring in the films. Metal-oxide chemical vapour deposition (MOCVD) was used to grow Hf$_x$Si$_{1-x}$O$_2$ films on Si (100) wafers. The Hf$_x$Si$_{1-x}$O$_2$ layer was grown at 650°C using precursors TDEAH (tetrakis diethyl amino Hf) and TDMAS (tetrakis dimethyl amino Si), on a ~1nm chemical oxide (SiO$_2$) layer. The target Hf$_x$Si$_{1-x}$O$_2$ layer width of 20nm was deposited with varying Hf$_x$Si$_{1-x}$O$_2$ compositions of $x = 0.3$, 0.5 or 0.7. Fully processed films had a further 100nm of amorphous Si deposited at 610°C which was then exposed to a 1000°C thermal anneal for 10s. This resulted in crystallisation of the gate into poly-Si. Six films were prepared in total: three as-deposited and three fully processed with $x = 0.3$, 0.5 and 0.7, respectively. Though these films are much thicker than would be used in devices, they were chosen as a better comparison with the bulk powder samples studied in Chapters 3 and 4. Thin films of 1-2nm exhibit different characteristics than thicker films. Since a better understanding of the chemistry and crystallisation in the bulk material is required, before trying to interpret results from 1-2nm films, it is best to consider the wider films to gain a more detailed understanding, then relate this to thinner layers.

TEM cross-sections were prepared by standard grinding, polishing, dimpling and ion milling techniques. TEM was carried out at the University of Glasgow on an FEI Tecnai F20 TEM/STEM equipped with a field emission gun, with an accelerating voltage of 200kV. Following the initial beam damage experiment (Section 8.2.1), a set
of standard operating conditions were used such that results between experiments were consistent and so as not to expose the sample to more of the electron beam than was necessary. The standard operating conditions for parallel illumination of the sample were an extraction voltage of 3.8kV, C1 aperture of 2000μm, C2 aperture of 70μm, objective aperture 100μm and a magnification of 450kx on the phosphour screen.

Experiments were carried out to investigate a number of factors:

1. damage induced by the electron beam;
2. the effect of sample thickness on TEM images;
3. the influence of a poly silicon capping layer and annealing temperature;
4. the influence of Hf$_x$Si$_{1-x}$O$_2$ composition on the crystallisation path;
5. the effect of heating environment.

The main parameters investigated were the SiO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ layer widths and the degree of crystallisation within the high-κ layer.

8.2 Experimentation and Results

The first set of experiments were conducted to determine the experimental conditions to be used for all following experiments.

8.2.1 Beam damage

Firstly, any damage effects due to the electron beam on a sample were investigated\textsuperscript{107}. From this analysis a set of imaging conditions were established in which a sample receives a minimal electron dose whilst still being able to distinguish features in the images. From preliminary investigations it was anticipated that fully processed samples which remained amorphous would be more greatly affected by beam damage than as-deposited samples, since they had already been heat treated to high temperature. This prior heat treatment results in some samples remaining amorphous, though phase segregation may be induced. Under the electron beam this process is driven further and may result in crystallisation. Also, because SiO$_2$ is thought to increase the crystallisation temperature\textsuperscript{8} (see later results), a sample of high SiO$_2$ content was chosen for the experiment since it was thought that samples with high HfO$_2$ concentration are
likely to have already crystallised due to the high temperature anneal – hence the beam damage effect would not be as clear.

With these considerations a fully processed Hf$_{0.3}$Si$_{0.7}$O$_2$ wafer was used to investigate electron beam damage effects. An area of sample was exposed to the electron beam and images taken at different time intervals. Whilst the electron dose, rather than time the sample is exposed to the beam, is of greater interest, the correct acquisition conditions were not recorded for this sample to allow the dose to be calculated. These conditions that were determined were then implemented in all the following experiments and the electron dose calculated using the following equation:

\[
\text{Electron Dose} = \frac{(\text{exposure time} \times \text{beam area})}{(\text{beam current} \times 1 \times 10^{-9}/e)} \quad \text{Eqn. 8.1}
\]

where electron dose is measured in e/nm$^2$, beam area in nm$^2$, exposure time in s, beam current in nA and electron charge in C.

An area of the Hf$_{0.3}$Si$_{0.7}$O$_2$ sample was exposed to the electron beam and images taken every few minutes. Some of these images, after exposure to the electron beam for 0, 454 and 909s are shown in Fig 8.1a-c. At $t = 0$s a clear SiO$_2$ layer, ~1.3nm wide, is visible (Fig 8.1a). The Hf$_x$Si$_{1-x}$O$_2$ layer above is about 14.7nm wide, much less than the expected 20nm. As the time under the beam is increased the SiO$_2$ layer disappears completely, reducing the total layer width (SiO$_2$ + Hf$_x$Si$_{1-x}$O$_2$) to ~14.4nm and 12.5nm at time 454s and 909s respectively. With the reduction in layer width comes roughening of the interfaces resulting in an error of 1.5nm in the layer width estimation at $t = 909$s. Whilst after 454s there is still a clear interface between the Hf$_x$Si$_{1-x}$O$_2$ layer and the silicon substrate, by 909s this has also disappeared.

At $t = 0$s the Hf$_x$Si$_{1-x}$O$_2$ layer had separated into light and dark areas. In TEM mode diffraction and mass-thickness contrast results in thicker regions, heavier elements and crystalline regions appearing darker. For cross-section TEM samples such as those presented here, the thickness across the width of the layer is taken as uniform. Any contrast observed in the images is predominantly due to the difference in elemental distribution, with some effect due to crystallinity. Therefore the separation of the Hf$_x$Si$_{1-x}$O$_2$ layer into light and dark regions is interpreted as being due to SiO$_2$ and HfO$_2$-rich regions respectively. This will be referred to as ‘phase separation’. No lattice fringes were observed in the high-κ layer at $t = 0$s. The dark, HfO$_2$-rich regions
were easier to distinguish and were about 1nm in diameter. As the time was increased to $t = 454s$ the light and dark regions increased in size to ~2-4nm and lattice fringes in some of the dark areas are visible, indicating crystallisation. By $t = 909s$ the HfO$_2$-rich areas all appeared crystalline with the SiO$_2$-rich areas remaining amorphous. The crystals were 4-6nm in diameter. With the forming of HfO$_2$ crystals (i.e. with long-range order) in an amorphous, SiO$_2$-rich matrix (i.e. with only short range order), an HfO$_2$-rich layer forms at the Si/SiO$_2$ interface and an SiO$_2$-rich layer forms at the poly-Si interface. This becomes clearer in the images as time increases. Because of the damaging effect of the electron beam, the electron dose was kept to a minimum for all further experiments. No damage to the sample was observed after exposure to the electron beam of 10s, corresponding to an electron dose of $\sim 1x10^6$ e/nm$^2$. To ensure that there is no damage contributing to the TEM images, each of the samples had been exposed to the electron beam for half of this time ($\sim 5s$, $0.5x10^6$ e/nm$^2$) unless otherwise indicated.

### 8.2.2 Sample Thickness

The specimen thickness can significantly contribute to the features observed in the TEM micrographs. For example, the thicker the area being investigated the more contribution this will have to the contrast, hence obscuring contrast due to mass and crystallinity. Hence an optimum thickness must be established at which to carry out experiments. This may be dependent on the features being considered. To investigate thickness effects, an as-deposited Hf$_{0.3}$Si$_{0.7}$O$_2$ sample which was then heated in a tube furnace to 600°C in flowing air for 24hr was used. (This treatment was for the purpose of the experiment outlined in section 8.2.5). The standard sample preparation results in a hole in the sample with thin regions of the layers of the gate stack at each end of the hole. The thickness of the sample increases as you move along the layer in a direction away from the hole. Hence to carry out this experiment, images of areas of sample were recorded moving further from the hole, and the sample thickness measured.
Figure 8.1: Sample $\text{Hf}_{0.3}\text{Si}_{0.7}\text{O}_2$  (a)-(c) Damage experiment on fully processed film: variation of dose (i.e. time) received by an area of sample;  (d)-(f) Thickness experiment on as-deposited film: variation of sample thickness at low dose
In contrast to the sample used for the damage experiment (Section 8.2.1), the total layer width was found to be between 18.3 and 19.3nm for all sample thicknesses (Fig 8.1d-f). This is closer to the target value of 20nm than for the capped sample (Fig 8.1a). The SiO₂ layer width is 1.7-2nm and the HfₓSi₁₋ₓO₂ width is approximately 16.6-17.3nm. As the sample thickness increases it becomes more difficult to distinguish the Si/SiO₂ and SiO₂/HfₓSi₁₋ₓO₂ interfaces due to the roughness of the interfaces through the sample and so it is easier to quote the total HfₓSi₁₋ₓO₂ + SiO₂ layer thickness instead of each layer individually. Some have commented that as the sample thickness increases the SiO₂ layer width decreases³³. However, it is not evident that increasing the sample thickness has a large effect in these samples other than the difficulty in distinguishing interfaces.

Sample of thickness t/λ = 0.25, 0.61 and 1.05 were investigated using an x = 0.3 as-deposited wafer. At t/λ = 0.25 (Fig 8.1d) phase separation on a scale of ~1nm is observed. As the thickness increases this becomes more difficult to see, until at t/λ = 1.05 the HfₓSi₁₋ₓO₂ layer looks homogeneous as it is too thick to see the small scale phase segregation in the sample. Therefore a sample with t/λ = 0.2-0.5 is suitable for carrying out further experiments relating to the degree of crystallinity in the layer. However, at t/λ = 0.61 the SiO₂ layer is more easily distinguished. Hence for measurement of layer widths a sample with t/λ = 0.5-0.7 is sometimes more appropriate. This is implemented in Section 8.2.5.

### 8.2.3 Composition Effects

Different HfₓSi₁₋ₓO₂ compositions of high-κ layer result in different behaviour under processing conditions and hence differences in device performance. For example alloying HfO₂ with SiO₂ is known to increase the crystallisation temperature of HfO₂⁸. The effect of composition in both as-deposited and fully processed wafers was investigated. Fig 8.2 shows TEM images of the as-deposited (Fig 8.2a-c) and fully processed (Fig 8.2d-f) samples with compositions of x = 0.3, 0.5, 0.7. Images were taken with the lowest possible electron dose. A sample thickness with t/λ = 0.1-0.3 was chosen, with an average value of ~0.2. The t/λ is displayed on each image in Fig 8.2. As described already, this thickness is most suitable for observing features in the HfₓSi₁₋ₓO₂ layer.
Composition has little effect on the as-deposited samples - slight mottling of the Hf$_x$Si$_{1-x}$O$_2$ layer is seen for each composition indicating the start of phase separation, but there is little to distinguish between the samples. The fully processed samples are therefore of more benefit for investigation of composition effects. An SiO$_2$ layer is present in all three of the fully processed samples (Fig 8.2d-f). The SiO$_2$ layer width decreases as x increases, (~1.4nm at x = 0.3 to 1.0nm at x = 0.7 - Table 1). In contrast the Hf$_x$Si$_{1-x}$O$_2$ width increases with increased x.

As x increases the degree of crystallisation in the layer also increases. When x = 0.3 the layer is amorphous though it has separated into dark and light, HfO$_2$ and SiO$_2$ rich regions. At both x = 0.5 and x = 0.7 the Hf$_x$Si$_{1-x}$O$_2$ layer shows a significant degree of crystallinity. The x = 0.7 composition has a higher degree of crystallinity but this is to be expected due to the higher HfO$_2$ content in the sample.

The other main observation is that as the HfO$_2$ content increases the interface between the Hf$_x$Si$_{1-x}$O$_2$ and poly-Si increases in roughness. Because of this it becomes difficult to determine the Hf$_x$Si$_{1-x}$O$_2$ layer width and hence a range of widths are given for the last sample in Table 8.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hf$<em>x$Si$</em>{1-x}$O$_2$</th>
<th>SiO$_2$ width</th>
<th>Hf$<em>x$Si$</em>{1-x}$O$_2$ width</th>
<th>Total width</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.3</td>
<td>as-deposited</td>
<td>1.8 nm</td>
<td>16.5 nm</td>
<td>18.3 nm</td>
</tr>
<tr>
<td></td>
<td>fully-processed</td>
<td>1.4 nm</td>
<td>14.7 nm</td>
<td>16.1 nm</td>
</tr>
<tr>
<td>x = 0.5</td>
<td>as-deposited</td>
<td>2.1 nm</td>
<td>18.0 nm</td>
<td>20.1 nm</td>
</tr>
<tr>
<td></td>
<td>fully-processed</td>
<td>1.1 nm</td>
<td>16.8 nm</td>
<td>17.9 nm</td>
</tr>
<tr>
<td>x = 0.7</td>
<td>as-deposited</td>
<td>undetermined</td>
<td>17.6 nm</td>
<td>19.0 nm</td>
</tr>
<tr>
<td></td>
<td>fully-processed</td>
<td>1.0 nm</td>
<td>14.8-17.9 nm</td>
<td>15.8 – 18.8 nm</td>
</tr>
</tbody>
</table>

Table 8.1: Effect of composition and processing on SiO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ layer widths with x = 0.3, 0.5, 0.7.
Figure 8.2: Influence of composition and processing on Hf$_x$Si$_{1-x}$O$_2$ thin films with $x = 0.3$, 0.5 or 0.7
8.2.4 As-deposited vs. processed wafers

Figure 8.2 also compares as-deposited and fully-processed wafers for each composition, x = 0.3, 0.5, 0.7. The as-deposited samples all have a similar Hf$_x$Si$_{1-x}$O$_2$ layer morphology. The total layer width (SiO$_2$ plus Hf$_x$Si$_{1-x}$O$_2$) is 18-20nm in each case with no clear trend relating SiO$_2$ or Hf$_x$Si$_{1-x}$O$_2$ layer widths to composition - only a hint of phase separation is apparent in the images (Fig 8.2 a-c). For all compositions once a capping layer has been added the Hf$_x$Si$_{1-x}$O$_2$ layer phase separates and/or crystallises, the degree of crystallinity increasing with x. Phase segregation and crystallisation occurs after a high temperature anneal at 1000°C. At x = 0.3 the Hf$_x$Si$_{1-x}$O$_2$ layer separates and a darker HfO$_2$-rich layer forms at both the SiO$_2$/Hf$_x$Si$_{1-x}$O$_2$ and the Hf$_x$Si$_{1-x}$O$_2$/poly-Si interfaces. Though not as clear, there is also a dark band present at the SiO$_2$/Hf$_x$Si$_{1-x}$O$_2$ interface for x = 0.5 and 0.7 but not at the upper interface. Table 8.1 shows that as the Hf$_x$Si$_{1-x}$O$_2$ width increases as x increases. Correspondingly, the SiO$_2$ layer decreases in width. The total layer width therefore increases as the HfO$_2$ content increases as does the degree of crystallisation.

The SiO$_2$ layer is narrower in the fully processed compared with as-deposited samples. The Hf$_x$Si$_{1-x}$O$_2$ layer width also decreased with processing.

8.2.5 Effect of annealing conditions – air vs. N$_2$

An attempt was made to relate the crystallisation pathway in the bulk, sol-gel work with that found in the thin film samples. In bulk samples (Chapter 3 and 4) crystallisation started to occur after heating to ~450°C using the oxychloride route, and at ~600°C (depending on composition) for the butoxide route. Whether the heating environment was oxidising or reducing, had a large effect on the crystalline phase formed. To try to better understand the effect of heating environment and to give an indication of which bulk preparation route the MOCVD chemistry most resembled, as-deposited, uncapped wafers with compositions x = 0.3, 0.5, 0.7, were heated to 600°C in a tube furnace in either flowing air or nitrogen. A heating rate of 10°C/min was used and the samples held at temperature for 24 hours before being cooled to room temperature. A sample thickness of t/λ = 0.5-0.7 was used to investigate layer widths (Fig 8.3), and images where t/λ = 0.2-0.3 were used to investigate crystallisation of the Hf$_x$Si$_{1-x}$O$_2$ layer (Fig 8.4). Two thickness regions are used because layer widths were difficult to distinguish.
in the thinner samples, but there was not enough contrast in the Hf$_x$Si$_{1-x}$O$_2$ layer in the thicker samples to look at phase segregation and crystallisation.

<table>
<thead>
<tr>
<th>Sample Hf$<em>x$Si$</em>{1-x}$O$_2$</th>
<th>SiO$_2$ width</th>
<th>Hf$<em>x$Si$</em>{1-x}$O$_2$ width</th>
<th>Total width</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>1.8 nm</td>
<td>17.0 nm</td>
<td>18.8 nm</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.0 nm</td>
<td>17.1 nm</td>
<td>19.1 nm</td>
</tr>
<tr>
<td>x = 0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>3.6 nm</td>
<td>18.5 nm</td>
<td>22.1 nm</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.3 nm</td>
<td>17.2 nm</td>
<td>19.5 nm</td>
</tr>
<tr>
<td>x = 0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>air</td>
<td>3.5 nm</td>
<td>18.1-19.5 nm</td>
<td>21.6-23.0 nm</td>
</tr>
<tr>
<td>N$_2$</td>
<td>2.1 nm</td>
<td>17.7-19.3 nm</td>
<td>19.8-21.4 nm</td>
</tr>
</tbody>
</table>

Table 8.2: Effect of annealing for 24 hours at 600°C on SiO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ layer widths ($\lambda/\lambda = 0.5$-0.7)

8.2.5.1 Layer widths

For $x = 0.3$ there is very little difference in SiO$_2$ or Hf$_x$Si$_{1-x}$O$_2$ widths due to heating environment (Table 8.2). This result is not reflected at the other compositions where the heating environment has a large effect on the layer widths with the SiO$_2$ layer increasing by ~1.3nm when heated in air rather than N$_2$. There is a similar increase in the Hf$_x$Si$_{1-x}$O$_2$ width. For $x = 0.7$ the Hf$_x$Si$_{1-x}$O$_2$ width was difficult to determine due to roughness on the top surface. As a result a range of widths are quoted for this composition in Table 8.2. The total layer width of SiO$_2$ + Hf$_x$Si$_{1-x}$O$_2$ increased by 2-3nm after heating in air compared with N$_2$. Relating this back to Table 8.1 where layer widths were measured for the as-deposited samples, we note that the SiO$_2$ layer width after heating in N$_2$ (Table 8.2) is close to that of the uncapped samples in Table 8.1. The Hf$_x$Si$_{1-x}$O$_2$ layer width is slightly less in the N$_2$ samples than for air.

8.2.5.2 Phase segregation in the Hf$_x$Si$_{1-x}$O$_2$ layer

Phase segregation and crystallisation has commenced in all samples after heating at 600°C (Fig 8.4), whereas little phase segregation was observed in the as-deposited samples. All of the images show light and dark areas in the Hf$_x$Si$_{1-x}$O$_2$ layer due to separation into SiO$_2$ and HfO$_2$-rich areas. The separation is on a <1nm scale. For $x = 0.3$ and 0.7 more phase segregation has occurred in the N$_2$ than air samples. Fig 8.4a,b and d show a darker band next to the SiO$_2$ layer indicating a Hf rich region, with this effect probably also present in Fig 8.4c. Figs 8.4a-c also show a darker region at the top surface. This is clearest on the $x = 0.3$ image. However an intensity profile across the $x = 0.5$ and 0.7 layers indicates the same occurs here, though not as pronounced due to less clear phase segregation. This banding at the edges of the layer
is mainly present in the air heated samples. In Fig 8.4a particularly, it looks as though there is a HfO$_2$-rich layer at the top and bottom interface with chemical separation in between.

In contrast to this the sample in Fig 8.4e has a more gradual change in intensity from darker at the SiO$_2$ interface to lighter at the top surface. Again, though not as clear, this effect may also be present for x = 0.3 (N$_2$). Both x = 0.7 samples have started to crystallise – one crystalline grain is observed in each image. Comparing this back to Fig 8.2c it is clear that the additional heating to which this sample has been subjected relative to the as-deposited sample, has resulted in some phase segregation and crystallisation within the high-$\kappa$ layer.
Figure 8.3: Effect of annealing for 24 hours at 600°C on Hf$_{x}$Si$_{1-x}$O$_{2}$ as-deposited samples with $x = 0.3, 0.5, 0.7 \hspace{1cm} \lambda = 0.51 - 0.65$

Figure 8.3: Effect of annealing for 24 hours at 600°C on Hf$_{x}$Si$_{1-x}$O$_{2}$ as-deposited samples with $x = 0.3, 0.5, 0.7 \hspace{1cm} \lambda = 0.51 - 0.65$
Figure 8.4: Effect of annealing on Hf$_{x}$Si$_{1-x}$O$_{2}$ as-deposited samples with $x = 0.3, 0.5, 0.7$ $t/\lambda = 0.2 - 0.3$
8.3 Discussion

The key observations from the results presented in this chapter are summarised below:

1. Amorphous to crystalline transition:
   a. as the HfO$_2$ content increases, the extent of crystallisation increases in fully processed samples (Fig 8.2);
   b. the extent of phase segregation decreases as HfO$_2$ content increases in as-deposited samples, after heat treatment at 600°C for 24 hours.
   c. roughening of interfaces increases as the degree of crystallisation increases
2. Phase segregation to interfaces:
   a. a HfO$_2$-rich layer often forms at the SiO$_2$/Hf$_x$Si$_{1-x}$O$_2$ interface once phase segregation begins;
   b. a dark band sometimes forms at the top surface as well as the bottom;
   c. a continuous change in intensity from dark at the bottom interface to light at the top interface occurs in some samples.
3. Layer widths:
   a. the presence of a capping layer causes a decrease in both SiO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ layer widths;
   b. heating uncapped samples to 600°C for 24 hours in N$_2$ has little effect on the SiO$_2$ layer but causes a decrease in width in Hf$_x$Si$_{1-x}$O$_2$;
   c. heating in air greatly increases the total layer width for $x = 0.5$ and 0.7 but has little effect on $x = 0.3$.

8.3.1 Amorphous to crystalline transition

After it was established that the electron beam could induce phase segregation and crystallisation, great care was taken to expose the sample to a minimal electron dose so that any features observed may be attributed directly to the behaviour of the sample (unless otherwise indicated).

8.3.1.1 Extent of crystallisation and phase segregation

It is not surprising that as the HfO$_2$ content increases, the extent of crystallisation would increase since it is well documented that SiO$_2$ suppresses crystallisation in thin films as
well as in bulk samples\(^8,23\). HfO\(_2\) films, containing no SiO\(_2\) have been found to crystallise after being subjected to thermal anneals of 1000°C (e.g. References \(^{35,144}\)). Since SiO\(_2\) suppresses crystallisation, it is expected that as the HfO\(_2\) concentration increases, more of the sample will appear crystalline.

This was observed experimentally in the fully processed samples (Fig 8.2d-f) by varying composition - at \(x = 0.3\) where there is no crystallinity, whereas at \(x = 0.7\) the sample looks fully crystalline. Hence, the higher the HfO\(_2\) content the more crystalline the sample. For \(x = 0.3\), though no lattice fringes are visible, the layer has separated into HfO\(_2\) and SiO\(_2\) rich regions. The HfO\(_2\)-rich regions are \(~1\text{nm}\) in diameter and are within a glassy-like, SiO\(_2\)-rich matrix. Phase segregation is also observed in the samples heated to 600°C for 24 hours (Fig 8.4). It is apparent for heating in both air and nitrogen environments that phase segregation has occurred, though only for \(x = 0.7\) is there any hint of crystallisation. The degree of phase segregation decreased as the HfO\(_2\) content increased which is to be expected since the dark HfO\(_2\)-rich regions, which are more visible, become a much higher percentage of the sample. This resulted in light and dark patches rather than a homogeneous dispersion of \(~1\text{nm}\) light and dark regions, as for Fig 8.2d where the patches are 2-3nm in size.

By comparing the different stages of processing – as deposited, heating at 600°C and fully processed (1000°C) - it appears that all the samples initially undergo phase segregation before crystallising. However, the mechanism by which this occurs is unclear. The two main possibilities are (1) spinodal decomposition and (2) nucleation and growth. The first involves a homogeneous separation of the whole layer into distinct regions of SiO\(_2\) and HfO\(_2\) concentrations. Phase segregation via a nucleation and growth mechanism differs in that it only occurs around specific nucleation sites. It may therefore be inhomogeneous. According to Stemmer et al.\(^{28}\) the compositions of the Hf\(_x\)Si\(_{1-x}\)O\(_2\) films in this chapter would all fall within the extension of the miscibility gap of the phase diagram and therefore spinodal decomposition would be the cause of phase segregation. Experimentally it is difficult to distinguish between these two mechanisms. However this actually occurs, a simplistic model to explain our results which covers both options, is that the [HfO\(_3\)] polyhedra diffuse through the amorphous SiO\(_2\) matrix to form HfO\(_2\)-rich centres. These centres then continue to grow until it is thermodynamically favourable for crystallisation to take place. For Hf\(_x\)Si\(_{1-x}\)O\(_2\), when \(x\) is low the Hf has to travel quite a large distance through the silica to ‘find’ other Hf
atoms. This results in small SiO$_2$ and HfO$_2$-rich regions, ~1-2nm in diameter, which are constrained by the surrounding amorphous SiO$_2$-rich material. As the concentration of Hf increases the Hf atoms are not required to travel as great a distance through the sample before finding other Hf regions resulting in a less homogeneously segregated layer. The SiO$_2$ forms a physical barrier through which the HfO$_2$ cannot easily diffuse. If there is a high concentration of SiO$_2$ present the physical barrier will be larger and hence the Hf regions will be smaller.

The second effect of SiO$_2$ is to suppress crystallisation of the Hf-rich regions by applying a constraint. Where there is a high percentage of SiO$_2$ this effect will be large and may be sufficient to inhibit crystallisation altogether. Maria et al.\textsuperscript{8} account for the suppression of crystallisation by considering the large difference in thermal expansion coefficients between HfO$_2$ and Si – the thermal expansion coefficient of HfO$_2$ being ten times larger than for Si. This causes a thermal expansion mismatch, resulting in tension between the HfO$_2$ and SiO$_2$-rich areas hence constraining the size of the amorphous HfO$_2$ regions. The amorphous, Hf-rich regions may subsequently crystallise if supplied with sufficient energy. Alternatively, if the SiO$_2$ content is reduced there will be a point at which the thermal mismatch will no longer be sufficient to prevent crystallisation - hence why crystallisation observed in the $x = 0.5$ and 0.7 fully processed films and a hint is observed in the as-deposited 600°C films at $x = 0.7$.

In reality it is not clear by what mechanism crystallisation occurs. As discussed above, because of the high Hf content there is a high probability that the Hf will be distributed in such a way that nucleation and growth occurs in some areas with spinodal decomposition in others. There may be two different crystallisation mechanisms occurring in this sample: areas that already contain high Hf content will nucleate and grow; in areas where there is a lower Hf content the Hf may first diffuse out of the silica rich regions (phase segregation) and then crystallise. Alternatively, the Hf that diffuses away from the SiO$_2$ regions may be incorporated directly into areas where nucleation and growth has already commenced. It is not clear which mechanism is used for crystallisation with this concentration of HfO$_2$. However, it is expected that there is little difference in the resulting layer morphology.
8.3.1.2 Roughening of interfaces

The increase in roughness at the top of the Hf$_x$Si$_{1-x}$O$_2$ layer or the Hf$_x$Si$_{1-x}$O$_2$/poly-Si interface has been noted by other groups for HfO$_2$ as being due to the crystallinity of the sample. The HfO$_2$ grains grow in random orientations and ‘push up’ above the layer or into the gate layer as they form. Triyoso et al. studied this effect in HfO$_2$ by looking at TiN capped samples relative to uncapped. The simple use of TiN as a capping layer constrains the crystallisation but also prevents the roughening of the top layer due to mechanical constraint of the crystals. It is therefore not surprising that the samples with the largest degree of crystallisation should result in a rough top layer, as the m-HfO$_2$ crystals grow out of the layer. It is in the crystalline samples (e.g. fully processed with $x = 0.7$) that the most roughening is observed.

8.3.2 HfO$_2$ and SiO$_2$ segregation to interfaces

8.3.2.1 HfO$_2$ layer at bottom interface

The results show that with phase segregation an HfO$_2$-rich layer forms at the SiO$_2$/Hf$_x$Si$_{1-x}$O$_2$ interface in the majority of samples. This effect is particularly noticeable in Figs 8.1, 8.2 d-f, 8.4.

Little data has been reported for either HfO$_2$ or Hf$_x$Si$_{1-x}$O$_2$ regarding segregation of phases resulting in a higher concentration of HfO$_2$ at the SiO$_2$/Hf$_x$Si$_{1-x}$O$_2$ interface. From modelling studies it was found that if the Si/HfO$_2$ interface was sub-stoichiometric then Hf would diffuse towards the silicon surface to satisfy its dangling bonds. At the same time oxygen diffuses into the Si surface. For a stoichiometric interface there is little displacement of Hf towards the interface, though oxygen still diffuses into the Si layer. In this case the interface is more uniform because the Hf and O diffusion processes are not competing. The Hf remains in a 4 or 5 coordination environment. However, only when the interface is passivated with oxygen is the Hf fully saturated. Van Benthem et al. confirmed that isolated Hf atoms diffuse into the SiO$_2$ layer by reconstructing a through-focus series on an aberration corrected S/TEM microscope, while Agustin et al. found Hf clusters protruding into the SiO$_2$ layer. These seem to support our results in terms of a Hf-rich region forming at, or protruding into, the SiO$_2$ layer. The mechanism by which this occurs is not clear. Modelling work by Hakala et al. would suggest that these Hf clusters form by satisfying dangling bonds due to substoichiometry at the interface.
8.3.2.2 Other contrast variations

Whilst most samples which had started to phase segregate resulted in a HfO₂-rich region at the SiO₂/HfO₂ interface, and a mixture of HfO₂ and SiO₂ regions were observed in the rest of high-κ layer, a few of the images show different behaviour in the layer. In some cases, as well as a HfO₂-rich layer at the bottom interface, one also formed at the top surface independent of the presence of a capping layer e.g. Figs 8.1a,d-f, 8.2d, 8.4a-c. This, combined with the discussion above may suggest that the interfaces contain possible sites at which it is favourable for nucleation and growth of the HfO₂ phase. This may be due to substoichiometry at these interfaces, as previously discussed.

In contrast the sample in Fig 8.1b-c, that has undergone beam damage, results in a SiO₂-rich region at the top interface. This is accompanied by an increase in size and crystallisation of the HfO₂ regions. This may suggest that during the process of HfO₂ regions forming and crystallising, they expel the SiO₂ from them, hence an SiO₂ rich region forms at the top interface²⁸.

In other samples whilst a darker, HfO₂-rich layer forms at the lower interface the contrast gradually changes over the width of the high-κ layer (Fig 8.3c and 8.4e). The dark layer does not form distinctive ‘particles’ or nuclei, and whilst there is some indication of segregation within the layer, the total intensity decreases across the width. Wiemer et al.²⁵ observe something similar for 5, 10 and 20nm HfO₂ films where investigation using x-ray reflectivity led to the conclusion that there was a decreased density at the top surface due to the migration of SiO₂ to this surface during annealing. If this diffusion occurs in HfO₂ and SiO₂ films, it is much easier for the Si to migrate to the top surface in an HfₓSi₁₋ₓO₂ film. This therefore will result in a greater percentage of HfO₂ at the SiO₂/HfₓSi₁₋ₓO₂ interface. It is also possible that the change of contrast is due to a sample preparation effect whereby the area near the hole is thinner than that at the SiO₂/HfₓSi₁₋ₓO₂ interface.

The discussion above relating to Hf and O diffusion may also explain why a gradual change in contrast is observed across the layer - HfO₂-rich layer at the bottom and SiO₂-rich layer at the top surface – though it remains unclear whether in HfₓSi₁₋ₓO₂ samples it is the SiO₂ that migrates to the top surface/interface, the Hf migrating to the bottom interface or O diffusion which results in Si or Hf rich regions. From the HfO₂
and ZrO$_2$ films some of these options are suggested$^{22,24,147}$ but because Si is incorporated into the high-$\kappa$ layer itself, the system becomes a little more complicated.

### 8.3.3 Layer widths

It was noted that the total layer widths were always narrower than the layer width specified by IMEC. In particular the layer with Hf$_{0.3}$Si$_{0.7}$O$_2$ composition was consistently narrower than for other compositions. This is thought to be due to how the layer widths are calculated and subsequently deposited in the MOCVD process.

For all compositions, samples with a poly-Si gate resulted in narrower SiO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ layer widths. This was always accompanied by crystallisation or phase segregation of the layer (Fig 8.2). This decrease in layer width is due to densification of the layer during chemical separation or crystallisation$^{35}$. This fits with sol-gel work where it was noted that samples after being subjected to HTXRD analysis had densified in the alumina holder. Triyoso et al.$^{20}$ investigated both ALD and MOCVD HfO$_2$ layers deposited or grown at 300 and 370$^\circ$C by ALD and at 550 and 650$^\circ$C by MOCVD, with a Pt gates. After a rapid thermal anneal they observed a decrease in layer width – the deviation from as-deposited width decreased with increased HfO$_2$ deposition temperature. For example, the layer width changed by 6.8% for the 300$^\circ$C sample, 2.4% for the 370$^\circ$C sample and 1.6% for the 550$^\circ$C sample, as determined by elipsometry. This indicates that densification of the layer occurs since at 370$^\circ$C and above the film is partially or fully crystalline at deposition. The samples deposited at higher temperatures because they are already partially crystalline, will not undergo as much densification on annealing as the samples with lower deposition temperature. Their work also reported the effect of exposure to atmosphere on the widths of the films. They found that the layer width increased after one months exposure to atmosphere, by $\sim$2% for a 5nm MOCVD film. The ALD films, by comparison, only increased by $\sim$0.1%. This serves as a warning about sample storage, and also for industry regarding effects to their processors resulting from their lifetime exposed to air.

Bohra et al.$^{22}$ also claim, from glancing incidence x-ray diffraction, that the HfO$_2$ layer decreases, but that the SiO$_2$ layer increases with annealing temperature. Their explanation is that O diffuses from the HfO$_2$ towards the SiO$_2$/HfO$_2$ interface, resulting in the SiO$_2$ layer widening and the HfO$_2$ narrowing, keeping the overall layer width the same. However, our results indicate that the Hf$_x$Si$_{1-x}$O$_2$ layer is actually decreasing in
size due to densification of the layer during crystallisation. This is supported by the total layer width varying for each composition, indicating that the decrease in Hf$_x$Si$_{1-x}$O$_2$ layer is due to more than just the diffusion of O into the SiO$_2$ layer.

The formation of wide silica layers due to electron beam damage has been investigated by Docherty et al.$^{33}$ for Si/SiO$_2$/HfO$_2$ (4nm)/poly-Si gate stacks. They found that as-deposited samples (i.e. no poly-Si gate or high temperature anneal) resulted in a widening of the SiO$_2$ layer after exposure to the electron beam but having a poly-Si cap had little effect. The widening is ascribed to consumption of the Si layer by the oxygen. A fuller description of this can be found in reference $^{33}$. Even though great care has been taken to limit beam damage effects in the experiments in this chapter, there may still be beam induced changes as discussed here. Docherty et al.$^{33}$ observe two growth rates for SiO$_2$ formation. They try to account for the oxygen source and conclude that one cause of the widening of the SiO$_2$ layer is a consequence of oxygen migration across the surface. The first source of oxygen was suggested to come from excess oxygen or water trapped in the high-κ layer. The second source of oxygen is from the glue required for sample preparation. It was found this could be prevented by using a physical gold barrier layer. The initial rate of growth of the SiO$_2$ layer from the high-κ layer due to the glue, is faster than the second. No growth was observed in the fully processed stacks at the doses investigated. Both sources of oxygen migration and diffusion must be taken into consideration when investigating the SiO$_2$ layer width in the Hf$_x$Si$_{1-x}$O$_2$ gate stacks.

There have been a number of reports that nitrogen in the interface layer e.g. SiON, stops the growth of the layer in both HfO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ films$^{24,37,148-150}$. The growth of the layer is attributed to diffusion of either O from the high-κ layer or Si from the substrate (though for Hf$_x$Si$_{1-x}$O$_2$ samples, the Si may also originate from the high-κ layer), which is inhibited by the presence of N$^{24,147}$. Others have shown that O diffusion is from the HfO$_2$ layer by depositing a Hf layer between the Si and HfO$_2$ layers, which acts as a barrier to O diffusion$^{147}$. The barrier layer becomes a silicate layer but stops diffusion of Si into the HfO$_2$ and O into the Si layer if thick enough. Hence diffusion is attributed to both Si and O, but O was calculated to have a diffusion rate 50 times that of Si. Similarly a comparison between Hf$_x$Si$_{1-x}$O$_2$ and HfSiON films reveals that almost no interface layer forms in the HfSiON sample but that the Hf$_x$Si$_{1-x}$O$_2$ film results in ~2nm SiO$_2$ layer$^{37}$. It is also noted by these authors that N suppresses crystallisation$^{37,148-150}$.
This leads onto the heating in air vs nitrogen experiment on the as-deposited wafers. Heating in air relative to N₂ results in a large increase in both HfₓSi₁₋ₓO₂ and SiO₂ layer widths. In this case it is clear that the excess oxygen in the heating environment has a large effect on the layer widths. SiO₂ forms and the HfₓSi₁₋ₓO₂ layer widens. Though not directly investigated here, this must result in a change in composition of the HfₓSi₁₋ₓO₂ layer to accommodate the excess oxygen. As discussed already, once the HfₓSi₁₋ₓO₂ layer crystallises it is not clear whether there are oxygen vacancies present. If there are, and these result in crystallisation of HfO₂ into the orthorhombic or tetragonal phases, the excess oxygen is filling up vacant oxygen sites. This in turn would result in crystallisation into the monoclinic rather than orthorhombic or tetragonal phases. Alternatively, there may now be an excess of oxygen in the layer which causes it to expand and when crystallisation occurs the oxygen sits at an interstitial position in the lattice. This is an area which requires further investigation. It is however clear that oxygen is one of the causes of SiO₂ formation. It remains unclear as to why heating in air has little effect on the layer widths for x = 0.3.

As already mentioned for the HfₓSi₁₋ₓO₂ layers above, modelling of different interfaces indicates that SiO₂ forms, partially due to O diffusion into Si, whether the SiO₂/HfO₂ interface is stoichiometric or not, only that in the latter case the SiO₂ layer is wider³¹.

The majority of studies indicate that the main cause of widening of the SiO₂ layer is due to diffusion of oxygen from the high-κ layer. However, a number of questions remain unanswered as to whether the oxygen is in excess in the HfₓSi₁₋ₓO₂ layer, or whether it diffuses from its lattice position forming a substoichiometric HfₓSi₁₋ₓO₂ layer. If the latter, does this have any bearing on the phase forming on crystallisation of the sample, keeping in mind that O vacancies have been proposed to explain the crystallisation behaviour in some bulk samples (see Chapters 3 and 4). This may in turn explain why the t-HfO₂ (or orthorhombic) phase is found in HfₓSi₁₋ₓO₂ films in the literature⁷,²²,²⁶,²⁸.
8.4 Conclusions

The electron beam induces both growth of the SiO$_2$ layer and phase segregation and crystallisation of the Hf$_x$Si$_{1-x}$O$_2$ layer. Growth of the SiO$_2$ layer occurs by two mechanisms: (1) oxygen diffusion from the Hf$_x$Si$_{1-x}$O$_2$ layer towards the Si/Hf$_x$Si$_{1-x}$O$_2$ interface occurs and (2) oxygen migration from the glue which can be prevented by using a barrier layer or gate. The latter process occurs in both as-deposited and fully processed samples. It is not clear whether in the first case it is excess oxygen within the layer or oxygen that, once diffused, leaves the Hf$_x$Si$_{1-x}$O$_2$ layer oxygen deficient. When heated explicitly in an air environment, oxygen penetrates both the SiO$_2$ and Hf$_x$Si$_{1-x}$O$_2$ layers, widening the layers in both cases. Hf$_x$Si$_{1-x}$O$_2$ layer widths also decreased as annealing temperature was increased, and also with increased HfO$_2$ content due to densification of the layers with increased crystallinity in the layer.

On heating, and with increased HfO$_2$ composition, the Hf$_x$Si$_{1-x}$O$_2$ layer narrows due to densification upon phase segregation and crystallisation. Phase segregation may occur via spinodal decomposition or by a nucleation and growth mechanism. It is not possible from these results to know which of these is the correct mechanism since the morphology of the film in both cases looks similar. The formation of a HfO$_2$-rich region at the Si/SiO$_2$/Hf$_x$Si$_{1-x}$O$_2$ interface may suggest that nucleation sites exist at the interface, hence it would be deduced that phase segregation occurs via a nucleation and growth mechanism. The HfO$_2$ rich region at the interface is suggested to form due to Hf dangling bonds forming during O diffusion into the Si. These are then satisfied at the Si interface. In some samples a similar HfO$_2$-rich region forms at the top interface. Other samples have a gradual change in intensity across the width of the layer.

When trying to compare the MOCVD process to one of the sol-gel routes, the crystallisation behaviour and tendency for the film to phase segregate into small crystallites is most like the morphology of the butoxide Hf$_x$Si$_{1-x}$O$_2$ samples.
Chapter 9 Conclusions and Further Work

9 Conclusions and Further Work

9.1 Summary of Conclusions

In this project a number of techniques have been employed to better understand the chemistry and local atomic structure of HfO\textsubscript{2} and Hf\textsubscript{x}Si\textsubscript{1-x}O\textsubscript{2} in both bulk and thin film samples. Use of analytical techniques such as thermal analysis, XRD, HTXRD, TEM and STEM-EELS, combined with EELS modelling, have resulted in a greater understanding of these materials for CMOS device applications.

9.1.1 Sol-gel work

Two different sol-gel preparation routes were used to make HfO\textsubscript{2} and Hf\textsubscript{x}Si\textsubscript{1-x}O\textsubscript{2} precursor powders. The resulting amorphous powders displayed very different crystallisation pathways when subsequently heated clearly indicating that the starting materials play a huge role in the crystallisation process.

9.1.1.1 Tetragonal hafnia formation

The expected phase to form below ~ 1750°C is m-HfO\textsubscript{2}, however it was found that t-HfO\textsubscript{2} formed in many of the samples prepared from both oxychloride and butoxide preparation routes. Three different crystallisation mechanisms were identified:

At low temperatures (∼400-800°C) the t-HfO\textsubscript{2} phase is thought to be stabilised by oxygen vacancies. The t-HfO\textsubscript{2} phase was only observed in this temperature range in the oxychloride samples and only in an inert (i.e. nitrogen or argon) environment. The presence or absence of SiO\textsubscript{2} had no effect on the results. Having discussed possible causes of t-HfO\textsubscript{2} formation in Chapter 3, it was concluded that in this temperature range, because t-HfO\textsubscript{2} only formed where there was low oxygen partial pressure, that oxygen vacancies were responsible for the stabilisation. It was shown that there was no dopant species in the powder and so it was suggested that an Hf\textsuperscript{III} species exists to maintain charge neutrality within the crystal structure. These t-HfO\textsubscript{2} crystals transform into m-HfO\textsubscript{2} on further heating such that by 900°C only m-HfO\textsubscript{2} is observed. t-HfO\textsubscript{2}
formation at ~450°C in bulk HfO₂ or HfₓSi₁₋ₓO₂ bulk samples has not been observed before.

It was also noted in this temperature range that both m-HfO₂ and t-HfO₂ form simultaneously from the amorphous precursor. Whilst a t→m transformation occurs as the crystallite size increases, m-HfO₂ also grows directly from the amorphous powder. The suggested reason for this occurring is as follows: areas where Hf³⁺ is in the majority t-HfO₂ particles crystallise, where Hf⁴⁺ is in the majority, m-HfO₂ crystallises. In an air heated sample this means m-HfO₂ is the main phase with only a very small amount of t-HfO₂ forming. The converse is true in a reducing environment.

The second method of t-HfO₂ stabilisation is due to the surface energy/critical crystallite size effect first commented on by Garvie in 1965⁴³. In the oxychloride samples containing SiO₂, at higher temperature (~1000-1600°C) t-HfO₂ again nucleates and remains until it is used to form HfSiO₄. From TEM micrographs these particles are found to be ~5nm diameter on average and are surrounded by the remaining amorphous material (mainly SiO₂). This leads to the hypothesis that the particles are stabilised by a surface energy/strain effect resulting from the surrounding amorphous matrix. At these high temperatures most of the HfO₂ has crystallised into m-HfO₂. This means that only a small amount of Hf is left in this SiO₂-rich amorphous matrix such that when t-HfO₂ crystallises, the particles remain small since there is little Hf remaining to cause them to increase further in size. Because the particles are constrained by the surrounding SiO₂-rich matrix, phase transformation to the m-HfO₂ phase is inhibited.

The third case of t-HfO₂ stabilisation is found in the butoxide preparation and only occurs in the presence of SiO₂. Stabilisation is also due to surface energy stabilisation and the critical crystallite size effect, but the mechanism by which this occurs is different from above. In this case crystallisation of the amorphous powder is directly into the t-HfO₂ phase at ~1000°C for an Hf₀.₅Si₀.₅O₂ sample. The t-HfO₂ then transforms into m-HfO₂ as heating continues. The formation of t-HfO₂ is again thought to be due to a surface energy effect. The HfO₂ particles nucleate and grow but due to the constraining effect of the surrounding amorphous SiO₂ matrix they are kept in the tetragonal phase. Unlike the example above, because there is plenty of Hf available, the particles continue to grow until a critical crystallite size is reached, at which point it is more thermodynamically favourable for the particle to transform to m-HfO₂ than remain
as t-HfO$_2$. No second nucleation of a tetragonal phase at higher temperatures has been observed for this sample.

### 9.1.1.2 Effect of silica

The effect of the presence of SiO$_2$ in the system was investigated. It was found in the case of the oxychloride preparation that SiO$_2$ had little influence on the crystallisation temperature or on the phase formed on crystallisation. Where it had an effect was in the high temperature range. In the absence of SiO$_2$ m-HfO$_2$ was the only crystalline phase observed up to 1700°C. However, in the presence of SiO$_2$, t-HfO$_2$ crystallises at temperatures of ~1000°C for $x = 0.5$. Also, with increasing SiO$_2$ content the crystallisation temperature of this high-temperature t-HfO$_2$ phase increases.

In the butoxide sample the crystallisation pathway from the amorphous powder is significantly altered by the addition of SiO$_2$. The phase on crystallisation changes from m-HfO$_2$ in an SiO$_2$-free environment to t-HfO$_2$ when SiO$_2$ is present, and the crystallisation temperature increased by 120-400°C depending on SiO$_2$ percentage. As with the oxychloride sample, as the SiO$_2$ content increases the crystallisation temperature increases.

Whilst the increased crystallisation temperature and change of crystal phase associated with addition of SiO$_2$ (e.g. Ref 23) has been widely reported, where SiO$_2$ effects crystallisation only in the high temperature region with very little effect in the low temperature region has not been reported before.

### 9.1.2 Modelling

To better understand experimental EELS spectra it is necessary to model the edge shapes – first to ascertain a good match with experiment and once achieved to have a degree of confidence in structures that are modelled where either no experimental data exists or doped/interface structures are considered. It was of interest to this thesis and to the wider project collaboration, to model EELS spectra of both bulk materials used in devices and of possible interfacial materials that form during device manufacturing.

Firstly, reasonable agreement was achieved between standard experimental and modelled spectra for bulk TiN, HfN, HfSiO$_4$ and m-HfO$_2$ materials. The main features were modelled well so it is expected that the main features in models of unknown
materials can also be used to aid interpretation of experimental EELS spectra. A number of other HfO$_2$ structures were modelled, none of which had any experimental EELS spectra available for comparison, though spectra for ZrO$_2$ could be found. These models are useful for observing the change in edge features as the structure is varied. Some possible reaction products that may form at the TiN/HfO$_2$ interface were then modelled and the different oxygen and nitrogen environments within them considered. By separating out the EELS edges from different atomic environments, the contribution of each atomic position to the features on the combined edge shape can be studied.

An area of particular interest was in the effect on the edge shape of doping the structure. Experimentally this may take place in the form of nitrogen or excess oxygen incorporation into the interface either due to diffusion from the high-k layer or during gas purges as the gate stacks are moved between processing tools. Alternatively, intermixing of Hf and Ti may occur at the upper interface. Of interest was how the edge shape varied as the level of doping changed, and also how far the dopant species could be from the atom being probed to stop affecting the edge shape. For doped structures it was found that the first and second shell (1$^{st}$ and 2$^{nd}$ nearest neighbour atoms) had the largest influence on the edge shape. Even varying the atomic configuration by one or two atoms in these shells resulted in a large change in the features on the edge shape. However, the extent of this effect also varied depending on the dopant species used. In a randomly doped (Ti,Hf)N structure the more Hf in the first shell resulted in the edge looking more HfN like, however, when Ti was in the majority the edge shape, though containing many TiN-like features, did not resemble TiN as well.

When the electron beam probes the interface it is possible that the electrons pass through areas where materials overlap. To try to simulate this, linear combinations of end-member spectra (e.g. HfN and TiN) were combined in different percentages. It was found that only when more than 20-40% of the other material was included in the model was the spectra distinguishable from the end member spectra.

An area of particular interest was in modelling the interface between m-HfO$_2$ and TiN. Because of the difference in structures it was decided that the simpler HfN/TiN interface would be investigated since HfN is a potential interfacial reaction product. Three interfaces were constructed: [111], [100] and [110]. The EELS spectra from these interfaces were different showing that different interface structures can be
distinguished between. It was also found for the [111] interface that by moving two nitrogen planes away from the interface into the TiN bulk, the edge shape was almost indistinguishable from the bulk signal. Moving into the HfN bulk by the same distance, all the features of HfN were present but the edge was still distinguishable from the bulk edge shape. However, with this it was noted that there were a number of calculation issues remaining unresolved such as lattice parameters used and Fermi level placement.

Whilst modelling is a very useful tool to help gain understanding in the area of EELS analysis, there are still many issues that must be resolved before modelling can ever predict what is expected experimentally.

**9.1.3 EELS of powders**

A good match was obtained between standard O K edges and those collected from the oxychloride and butoxide powder samples, m-HfO$_2$, a-SiO$_2$ and HfSiO$_4$. However, some samples gave spectra which did not fit any of the standard edges where it was not possible to assign the features of the edge to any particular compound. In some cases it is thought that the sample had been contaminated by the crucible during heating hence giving O K edge shapes that cannot be accounted for. This would also fit with the possibility of contaminant species observed in the asymmetry of the peaks in the 1700°C XRD scans in Chapters 3 and 4. Many of the edges taken from samples containing SiO$_2$ are due to the electron beam probing both m-HfO$_2$ and SiO$_2$ environments and can therefore be modelled by an overlap of a-SiO$_2$ and m-HfO$_2$ edges. However, in samples where there is no SiO$_2$ the m-HfO$_2$ edge varies significantly from particle to particle, and even across the one particle. This must be due to local variations in the structure which have been suggested to be due to oxygen vacancies. This brings into question whether any edge can be classed as a ‘standard’ for this structure if the variation in edge shape between crystalline particles is so great. It also suggests that the models in Chapter 6 may not be as inaccurate as first thought if this large variation in edge shapes exists.

**9.1.4 TEM of thin films**

Si/SiO$_2$/Hf$_x$Si$_{1-x}$O$_2$ films were studied before and after activation ($x = 0.3$, 0.5, 0.7). Activated samples also had a poly-Si cap on top of the HfSiO layer. It was found that the electron beam induced widening of the SiO$_2$ layer and phase segregation and crystallisation within the high-κ layer. Growth of the SiO$_2$ layer is thought to come
from two mechanisms: (1) migration of O across the surface of the sample due to the glue used during sample preparation (2) diffusion of O from the high-\(\kappa\) layer. The first mechanism can be prevented using a barrier or capping layer. This means that the increased SiO\(_2\) width in the fully processed samples is likely via diffusion of oxygen from the Hf\(_x\)Si\(_{1-x}\)O\(_2\) layer. It is not yet clear whether the oxygen diffusion is from the lattice sites or whether there is excess oxygen in the system. This diffusion occurs under the electron beam, however, it was also found that when heated in an air environment oxygen caused widening of both the SiO\(_2\) and HfSiO layers.

On heating the Hf\(_x\)Si\(_{1-x}\)O\(_2\) layer narrows and densifies by phase segregation and/or crystallisation. As \(x\) increases the layer width decreases since there is more HfO\(_2\) present to crystallise. It was also noted that in many of the samples a dark, HfO\(_2\)-rich layer formed at the SiO\(_2\)/HfSiO interface, and in some cases also at the HfSiO/poly-Si interface. At the lower interface this is suggested to be due to Hf dangling bonds which form when oxygen diffuses into the SiO\(_2\) layer. To satisfy the dangling bonds the Hf atoms diffuse towards the interface and are satisfied by the Si. This tendency to form HfO\(_2\)-rich regions at the interfaces suggests a nucleation and growth, rather than spinodal decomposition mechanism, leading to crystallisation within the layers.

### 9.2 Further Work

The research conducted in this thesis has greatly helped further the understanding of the HfO\(_2\) and HfSiO systems. However, as with all research, many more questions have been raised that remain to be answered.

#### 9.2.1 Sol-gel work

From the sol-gel work many questions remain as to the mechanism of formation of t-HfO\(_2\), especially in the low temperature region as found from the oxychloride preparation. Oxygen vacancies are the obvious answer but how they occur remains unclear. It has been proposed that Hf\(^{III}\) is formed which allows the t-HfO\(_2\) stabilisation and further investigation into this is required. X-ray photoelectron spectroscopy (XPS) involves the promotion of an inner shell electron to the vacuum region caused by the influence of an incident x-ray photon. This can be used to determine the elemental
composition of a sample and, of importance to the results here, the electronic state of an element present in the sample. Hence XPS analysis may be used to determine whether any Hf$^{III}$ is present in the relevant sol-gel powders.

It has been suggested by others$^{53,60,77,78}$ that the local structure within the ‘amorphous’ starting material has a large influence on the resultant crystallisation pathway, and results comparing the oxychloride and butoxide routes here would also suggest this. Comparison of the interatomic distances in the amorphous starting material compared with those in m-HfO$_2$ and t-HfO$_2$ would be useful in this regard. This work has reportedly been carried out for ZrO$_2$ using neutron diffraction$^{60}$, raman spectroscopy$^{77}$, and wide angle x-ray scattering$^{78}$. Access in the UK to the ISIS neutron source would allow experiments to be carried out to provide information on the local environment of the materials, and in particular the amorphous materials, under investigation.

One aim of the sol-gel work was to produce a standard t-HfO$_2$ powder from which an O K edge could be obtained to assist interpretation of EELS spectra from thin film samples. Unfortunately, this was not achieved in the duration of this experimental work. Though a sample was prepared from which an O K edge could be obtained, it was not possible experimentally because of contamination problems. In the future a new sample should be prepared in which t-HfO$_2$ forms and where the t-HfO$_2$ particles can be isolated on the holey carbon grid, away from any SiO$_2$ material. The utmost care must be taken to avoid contamination which was prohibitive in carrying out this experiment previously.

Once a standard t-HfO$_2$ O K edge is obtained EELS will also be useful to verify some of the features assumed from TEM micrographs and have been used to make some of the hypotheses in the current work. For example, it would be very useful to confirm that the small particles observed in the amorphous matrix in the 1400°C sample, are in fact t-HfO$_2$ as hypothesised. Similarly, for samples where phase segregation is observed, such as those in Fig 7.10, EELS can be used to probe the structure of the different environments across a sample. Correlating edge shapes to specific areas in the sample is of great importance and may provide further clues as to how the crystallisation process occurs. For these experiments contamination and drift problems need to firstly be resolved.
9.2.2 Modelling

The combination of modelling work with experimental EELS may provide significant understanding to the source of the changing edge shapes from crystalline m-HfO₂ particles. The suggestion of oxygen vacancies being the cause of this can be investigated using FEFF or WIEN2k. This can be combined with a systematic investigation of edge shapes within crystalline particles, within and between samples heated to different temperatures.

Until now most of the modelling work has been carried out using FEFF however, it is hoped that Wien2K can be used further to understand and model interface structures. Wien has the advantage over FEFF in that a degree of relaxation of the structure can be included, allowing better lattice matching for interface construction. This is particularly important if any headway is to be made in modelling the m-HfO₂/TiN interface that is of particular interest. However, FEFF has proven to be very useful in establishing trends observed in systematically varying or doping structures, and in constructing some simple interface models. An area that remains to be investigated is to construct an interface whereby the bulk material is on one side and vacuum is on the other. This will allow changes in the edge to be observed as the electron beam probes the material at points moving away from the interface.

An area of key importance to the discussion of t-HfO₂ stabilisation is whether or not oxygen vacancies have a role. This is a key question that modelling will be able to help address. Instead of investigating the effect of dopants in the structure, the dopants can be replaced by vacancies and similar analysis carried out. Comparison with experimental spectra will aid interpretation of experimental results.

9.2.3 Thin films

From planar thin film samples electron diffraction studies should be possible to help determine the crystalline species present in the high-κ layer. Great care must be taken when carrying out these experiments however as the electron beam can induce crystallisation and phase transformation which would result in errors in the electron diffraction pattern from the ideal situation. In thin film samples where phase segregation has taken place it is not always clear whether crystallisation has also occurred. Using annular dark field imaging of planar samples it may be possible to determine which areas are or are not crystalline by selecting specific spots in the
electron diffraction pattern (if there is one). This may also help with determining the size of these particles.

Whilst thick, 20nm samples, were used for this study so that better comparison could be made with bulk material, in reality devices will be using much narrower high-κ layers. The behaviour at interfaces, for example, may be different where only a narrow metal-oxide layer is present. A study into how properties such as layer widths, diffusion and crystallisation are affected in HfSiO layers of different widths would be an interesting continuation of the current work.

As this project was originally meant to entail analysis of interfaces using EELS, a study into the effect on the EELS spectra at interfaces would be a natural continuation of the work carried out so far. This would combine the experimental work carried out on the powders with the modelling work done on possible interface products and on the interfaces themselves. From TEM imaging an Hf rich layer was observed at the bottom interface which can be investigated further using EELS.
Appendix 1 - Phase Diagrams

(a) HfO$_2$-SiO$_2$, (b) ZrO$_2$-SiO$_2$, (c) HfO$_2$ temperature-pressure and (d) metastable HfO$_2$-SiO$_2$ phase diagrams$^{8,28,83,151}$
Appendix 2: Feff Input file (feff.inp)

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END

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**Title of calculation** – defined by user

**Edge to be calculated and amplitude reduction factor**

**Determines which modules are run and printed by the program**

**Specifies the cluster size over which the potentials are calculated self-consistently**

**The XANES card tells FEFF to calculate the near edge structure**

**The FMS card determines the cluster size around the absorbing atom for which the full multiple scattering is calculated**

**The Fermi level displacement and instrumental broadening can be added after the main calculation has finished**

**The potentials card assigns a potential to each unique atom in the structure. The angular momentum for each atom and the stoichiometry are also specified.**

**The atoms card specifies the atomic positions for each atom in the cluster.**


