Applications of Hard X-ray Photoelectron Spectroscopy in Semiconductor Materials Characterisation

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A thesis presented for the degree of Doctor of Philosophy



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Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of doctor of Philosophy is entirely my own work, that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

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A combined capacitance-voltage and hard x-ray photoelectron spectroscopy characterisation of metal/ $Al_2O_3/In_{0.53}Ga_{0.47}As$ capacitor structures

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Applications of Hard X-ray Photoelectron Spectroscopy in Semiconductor Materials Characterisation

Lee Walsh

Abstract

The recently developed high energy variant of x-ray photoelectron spectroscopy (XPS), known as hard x-ray photoelectron spectroscopy (HAXPES), has been used to study various semiconductor material systems. Extending the photoemission sampling depth to >10 nm into the material surface by the use of monochromatic x-ray photons in the 2 to 4 keV energy range, enables the acquisition of chemical and electronic information deeper into the bulk than is possible with conventional XPS, and facilitates the investigation of multilayer structures. In this study, combined HAXPES and electrical characterisation studies were performed on Si, GaAs and InGaAs based metal-oxide-semiconductor (MOS) structures in order to cross-correlate the electronic information derived from these different measurement methods. The results obtained indicate that surface potential changes at the semiconductor/dielectric interface due to the presence of different work function metals can be detected using HAXPES measurements. Changes in the semiconductor band bending at zero gate voltage and the flat band voltage values derived from capacitance-voltage (C-V) measurements are in agreement with the semiconductor core level shifts measured from the HAXPES spectra. Experiments have been performed which utilise the increased sampling depth of HAXPES to chemically and structurally characterise Ni-InGaAs and Mo-InGaAs interface formation. These material systems are of interest as possible source drain contacts for use in future high mobility InGaAs based MOS field-effect-transistors due to their extremely low contact resistance and self-aligned formation. Complementary x-ray absorption spectroscopy (XAS) measurements were used in combination with HAXPES data to develop a model of the chemical interactions and compound formation at the Ni-InGaAs and Mo-InGaAs interfaces as a function of anneal temperature.

Chapter 1

Introduction

The focus of this thesis is to investigate the potential applications of the high energy variant of x-ray photoelectron spectroscopy (XPS), known as hard x-ray photoelectron spectroscopy (HAXPES). In this section HAXPES will be discussed in relation to the following: 1) the growth of HAXPES since its initial development and 2) the advantages of HAXPES over conventional XPS in regards to the open questions in III-V metal oxide semiconductor field effect transistor (MOSFET) technologies.

1.1 History

The discovery and subsequent explanation of the photoelectric effect by J.J. Thompson, and ultimately Albert Einstein, led to the theoretical and experimental basis upon which XPS was founded.¹ The first experiments using this basis were performed by Robinson and Rawlin in 1914. They performed simple studies of gold surfaces, using photographic plates, and observed energy spectra.² X-ray Photoelectron Spectroscopy truly began to be used as an analytical technique in its own right in the 1950's, following development by Steinhardt and Serfass.³ Their initial experiments involved using XPS to determine elemental quantities present in a sample by the relative spectral intensities of their peaks.⁴ Further development of the technique was performed by Kai Siegbahn, and his group in Uppsala, Sweden.^{5, 6} In order to use XPS to accurately obtain chemical information of a surface, it was recognised by Siegbahn that the energy resolution needed to improve. He developed an analyser capable of 1 eV resolution, where resolution had been 3 eV up to that time.^{7, 8} Using this analyser and a Cu K α source (8 keV) sufficiently sharp spectra were produced to allow chemical analysis of the surfaces being studied.⁷ It was at this time that ultra high vacuum (UHV) vessels began to be used, as it was appreciated that surface contamination played a large role in the quality and accuracy of the acquired spectra. In addition B.L. Henke's invention of the hemispherical analyser allowed the use of lower energy dedicated XPS sources.⁹

XPS proved to be a powerful technique in the chemical analysis of surfaces. However, almost every physical property changes at the surface due to a break in the material symmetry and this leads to surface reconstruction effects which result in differing surface and bulk characteristics. Looking at the change in the inelastic mean free path (IMFP) of photoemitted electrons with kinetic energy, as seen in figure 1.1, it is clear that in order to increase the sampling depth of XPS there were two options: use very low or very high photon energies and correspondingly drastically increase or decrease the photoelectron kinetic energies.¹⁰ Low photon energy XPS has been achievable at synchrotron sources for a long time, however there are significant drawbacks.¹¹ The very low photon energy means very few core levels are excited and thus valence band measurements are the primary application. Additionally, final state effects have an increased influence, leading to an increase in background signal. The use of increased photon energies was first attempted by Pianetta and Lindau in 1974.¹² It was realised that an increase of the sampling depth from 5-7 nm to 10+ nm would be very useful, especially as thin film deposition techniques had not yet been optimised. At that time, the signal intensity for peaks originating from >5 nm had low counts and poor signal to noise, due to the rapid decrease in sub-shell photoionization cross-sections with an increase in photon energy,¹³ as shown in figure 1.2. Indeed, the early XPS studies by Siegbahn et. al^7 were performed using hard x-ray sources, such as Cu K α (8) keV). However the photon energy was reduced, due to the previously mentioned



Figure 1.1: Diagram shows the increase in IMFP with increasing photon energy¹⁴

signal to noise issue as well as an enhanced interest in the sample surface. In recent times the structures used in conventional MOSFET devices have become increasingly complex so it has become more desirable to characterise samples close to actual devices, as opposed to the model interfaces which have been conventionally measured.

While these experimental issues halted the use of HAXPES in the years following, numerous groups have revived interest in the technique since 2003. The development of purpose-built hard x-ray spectrometers and third generation synchrotron radiation sources has allowed for the re-emergence of HAXPES. Third generation synchrotron sources are optimised for brilliance (photon flux per unit area) through the use of insertion devices. The high photon flux (10¹¹ photons/s) achievable with these third generation sources allows the reduction in photoionisation cross-section to be overcome, while the tunable nature of synchrotron sources allows for the performance of both SXPS (surface sensitive) and HAXPES (bulk sensitive) measurements on the same beamline, such as the I09 beamline currently



Figure 1.2: Dependence of photoionisation cross section on photon energy¹⁵

in development at Diamond Synchrotron. Whereas previous measurements of multilayered structures had been performed by techniques such as secondary ion mass spectrometry or cross-sectional transmission electron microscopy (TEM), where destructive sample preparation is involved, HAXPES measurements have the advantage of being non-destructive. There are currently HAXPES ready beamlines at DESY and BESSY in Germany,^{16, 17} SPring8 in Japan,¹⁸ Brookhaven National Laboratory in the USA,¹⁹ Diamond in the UK, and the ESRF in France where there were two beamlines but only one is still operational.^{15, 20, 21}

1.2 Applications of HAXPES

The increase in, and the tunability of, the sampling depth of HAXPES performed at synchrotron sources has led to an expanded field of application. Figure 1.3 shows the increase in publications containing HAXPES measurements in recent years. The large growth seen in the past five years is primarily due to the increase in HAXPES-ready beamlines. This section will give a brief overview of the areas of research in which HAXPES has been employed. The areas of research have been split into four groups: 1) chemical studies, 2) electronic structure, 3) HAXPES as a complementary technique, and 4) other studies.



Figure 1.3: Number of HAXPES publications in recent years taken from Web of Knowledge,²² as of 30/6/14.

1.2.1 Chemical Studies

Historically, the study of the chemical composition and electronic structure of materials has been the core strength of conventional XPS. The most logical application of HAXPES is, therefore, the chemical characterisation of the surface and bulk of materials, or the interfaces in the case of multi-layered structures. These studies have varied from investigating the chemical bonds present at reactive interfaces to investigating the loss of certain materials during the course of an anneal study. The majority of the work has followed the general trend of materials research in recent years, in that it focusses on applied materials for specific technological purposes.

The depth profiling capability of HAXPES has enabled the non-destructive depth profiling of a number of systems, from the investigation of the chemical composition of passive oxide films on stainless steel,²³ to the study of nitrogen incorporation in HfO₂ and SiO₂ films for use in advanced MOSFET devices.²⁴ The ability to investigate the chemical composition of buried interfaces in multilayer structures has found use in the characterisation of the Fe₃O₄/InAs interface (a prototypical system for spin injection electrodes in spintronic devices²⁵), complex Gebased multilayer devices,²⁶ and thick (>10 nm) Cr-O-Al films on Si substrates.²⁷ HAXPES has also been used to investigate a variety of devices with specific applications including: substrate and oxide materials to replace the conventional SiO₂/Si system for future MOSFETs,^{28, 29} organic and conventional semiconductor-based solar cells,^{30–35} ferromagnetic materials for use in spintronics,^{36–41} exotic oxide materials for use in fuel cells,⁴² materials with superconducting properties,^{43, 44} interface composition and degradation during cycling in batteries,^{45, 46} and material systems for use in non-volatile memory.^{47, 48}

1.2.2 Electronic Structure

Conventional XPS has been previously used to derive some information on the electronic structure of materials. The surface sensitive nature of the technique is one of it's strengths, however, the ability to probe the material bulk would extend it's applications, as the electronic structure at the surface of a material is vastly different to the bulk behaviour, due to the break in symmetry.¹⁴ The bulk sensitive nature of HAXPES adds this functionality.

Investigations have been performed on attempting to evaluate band-bending

in semiconductor based structures, as not only can the Fermi level position in the bulk of the material be evaluated but, due to the tunable nature of synchrotron based HAXPES work, the sampling depth can be varied, allowing for the profile of the band-bending to be measured.^{40, 47} The ability to accurately evaluate the Fermi level position, conduction band minimum, and valence band maximum also allows for the accurate evaluation of electron band line-up and the creation of band offset diagrams,^{30, 32, 43, 49, 50} which are important in determining device performance. Measurement of the valence band edge of a given material or structure also allows for the density of states to be extracted, which can give information on the conductivity and ferromagnetic properties.^{34, 50, 51} HAXPES measurements of magnetized samples have also been performed by *Kozina et. al*⁵² in order to measure circular magnetic dichroism in materials for use in spintronics. This approach involves the use of a phase retarder which the x-ray beam passes through prior to interaction with the sample, and the difference in peak intensity measured at each polarisation allows the circular magnetic dichroism to be evaluated.

1.2.3 Combination of HAXPES and Other Techniques

As the above sections have demonstrated, HAXPES has proven to be very useful in the chemical and electrical characterisation of the material bulk and buried interfaces. Numerous groups realised that it could be even more useful when combined with other techniques in order to gain a more complete understanding of a given sample. This is more than simply performing two techniques on the same sample. It involves choosing an appropriate technique to complement HAXPES for a given sample set.

HAXPES has been combined with x-ray diffraction (XRD) by *Rubio-Zuazo et.* al in order to study the magnetic and transport properties of strongly correlated electron systems.⁵³ XRD is sensitive to atomic structure and the ability to perform both measurements simultaneously on the same sample helps to fully explain the macroscopic behaviour of the studied system. Anniyev et. al combined HAXPES and x-ray absorption spectroscopy (XAS) in order to probe the partial density of states of transition metal based nanoparticle catalysts; the information gained provides useful information as to the reactivity of the catalyst in question.⁵⁴ While HAXPES probes the occupied electronic states, XAS probes the unoccupied valence states. Similar complementary experiments have been performed combining HAXPES with standing wave XPS,⁵⁵ and x-ray reflectivity measurements.²⁶

1.2.4 Other Work

Certain applications of HAXPES, while fitting into either electronic or chemical characterisation, are unique enough to belong in a section of their own. This section discusses such experiments. The ability to non-destructively investigate chemical and electronic properties of materials has positioned HAXPES uniquely in the field of materials science research. As such, it has found applications in the study of the fundamental physical, and electronic properties of various material systems which have been beyond the measurement capabilities of current techniques.

An area which has seen a large publication increase in the last few years is the study of the electron correlation effects present within various exotic oxide materials. Electron correlation simply describes the fact that the behaviour of an individual electron in a material system is not independent of all other electrons, as assumed by the Hartree-Fock approximation. Strongly correlated materials exhibit unusual electronic and magnetic behaviour, some of which is useful in certain applications such as spintronics and Mott insulators. HAXPES has been very useful in the analysis of these correlated materials due to the ability to probe structural, electronic and magnetic properties at a variety of sampling depths into the material. Grebinskij et. al^{56} have investigated the correlation effects present in SrRuO₃, a ferromagnetic metallic oxide which is popular as an electrode material due to its good electrical conductivity and chemical stability. Previous attempts to measure the correlation effects present in this system with techniques such as resonant photoemission spectroscopy have been unsuccessful, however, the application of angularly resolved HAXPES was used to measure the valence bands and identify $SrRuO_3$ as a weakly correlated material. Suga et. al^{57} have used the ability to tune the photon energy, and thus the sampling depth, to characterise both the bulk electronic structure of VO_2 , known to display correlation effects,

and the surface of the material where the electronic structure displays different behaviour.

The Kondo effect was first observed in the 1930's⁵⁸ and fully explained in the 1960's,⁵⁹ however, the fabrication and measurement techniques available did not allow for sufficiently controlled measurement of these systems. Kondo systems are metal compounds in which the conduction electrons are scattered, due to magnetic impurities in the material. Whereas normal metals display a decrease in resistivity with decreasing temperature, these Kondo systems actually show an increase in resistivity at very low temperatures. The bulk sensitivity of HAXPES has allowed researchers to analyse the electronic structure of Kondo systems such as YbNi₃X₉,⁶⁰ YbAl₂,⁶¹ YbCu₂Si₂,⁶² YbB₁₂ and SmB₆.⁶³

1.3 III-V MOSFET Issues

The progress in metal oxide semiconductor (MOS) transistor technology, as shown in figure 1.4, which has continued unhindered since the initial development by Kahng and Atalla for Bell labs in 1959,⁶⁴ is currently reaching a crossroads. The downscaling of the Si channel width, which has increased the number of transistors, as seen in figure 1.5, and thus the power density, on a chip, according to Moore's Law,⁶⁵ is reaching a stage at which quantum tunnelling effects will begin to dominate. Previous issues such as the limit of the dielectric thickness have been addressed by the application of high- κ materials,⁶⁶ which enable higher drive currents and thus increased output power from the device, while also reducing the leakage current, resulting in improved efficiency.



Figure 1.4: Schematic diagram of an n-MOSFET

The continued scaling of MOSFET devices, as described by the International Technology Roadmap for Semiconductors,⁶⁸ beyond the 16 nm node, where 16 nm is the metal 1 half-pitch, necessitates an alternative channel material in order to continue the improvement in performance and efficiency. The prime candidates for replacing Si as the channel material in n-MOS are the III-V family of compound

Microprocessor Transistor Counts 1971-2011 & Moore's Law



Figure 1.5: The evolution of the number of transistors per $chip^{67}$

	Si	GaAs	$In_{0.53}GaAs_{0.47}$	InP
$E_g (eV)$	1.12	1.42	0.75	1.35
$\mu_e \ (\mathrm{cm}^2/\mathrm{Vs})$	800	4000	7000	3200

Table 1.1: Band gap and mobility for Si and III-V materials⁶⁹

semiconductors, in particular GaAs, InP, and InGaAs, while Ge is the likely material for use in p-MOS. As is clear from table 1.1, all three provide significant gains in electron mobility over Si, which in turn should result in faster transistors. In_{0.53}Ga_{0.47}As has recently emerged as the most promising of the III-V materials for integration into n-MOS devices. The 53 % In and 47 % Ga concentrations are used as this particular composition is lattice matched to InP, which is a cheap semiconductor material on which the InGaAs devices can be grown. There are however a number of remaining issues which need to be resolved before InGaAs can be integrated into MOSFET processing:

- 1. The need for a suitable dielectric material.
- 2. A method for lattice matching InGaAs to Si.
- 3. Achieving a suitably low density of defect states for the high- κ /III-V interface.
- 4. The need for a source/drain contact material.

1.3.1 A Suitable Dielectric Material

While Si was a fortuitous material, in that both Si and its native oxide (SiO₂) perform well electrically and have naturally low levels of defect states at the interface, the same cannot be said for InGaAs. The native oxides of InGaAs have very poor electrical characteristics and as such the need for a replacement dielectric is evident.⁷⁰ Intensive research into an appropriate dielectric has highlighted atomic layer deposited (ALD) Al_2O_3 ,^{71, 72} ZrO_2 ^{73, 74} and HfO_2 ^{75, 76}to be the leading candidates.⁷⁰ The ALD is important as it is believed that the chemical pre-cursors

involved lead to a 'self-cleaning' effect which removes the native oxide present at the dielectric/InGaAs interface.^{75, 77, 78}

1.3.2 Lattice Matching to Si

The importance of finding a channel material which is lattice matched to Si stems from the fact that the entire semiconductor industry is designed to produce Si transistors. As such finding a material which can be lattice matched to, and thus grown on, Si substrates requires a much smaller evolution from the current growth facilities in the transition from Si to InGaAs based MOSFETs. While InGaAs itself is not lattice matched to Si, a number of approaches have been developed which involve using buffer layers to gradually alter the lattice properties from those of InGaAs to those of Si as shown in figure 1.6,^{79, 80} however the thickness of the buffer layers required restricts the downscaling of the InGaAs MOSFET. An alternative method involves the direct wafer bonding of III-V and Si substrates, as shown in figure 1.7, which has the advantage of better quality and thinner III-V layers on Si.^{81, 82}







Figure 1.7: Illustration of the direct wafer bonding technique used to produce InGaAs on Si wafers.⁸²

1.3.3 Low D_{it} High- κ /Semiconductor Interface

The greatest issue currently facing InGaAs MOSFET integration is the high density of defect states (D_{it}) at the high- κ /InGaAs interface. The high D_{it} arises due to a multitude of issues including the presence of dangling bonds, dimers and native oxides at the semiconductor surface.^{84–87} High D_{it} results in a restricted, or in extreme cases, pinned Fermi level which hampers MOSFET device operation.⁸⁸ To overcome these issues a number of passivation treatments have been developed; from wet chemical passivation treatments such as $(NH_4)_2S$,^{85, 89, 90} interface control layers,^{91–93} and forming gas (H_2N_2) anneals,⁹⁴ with varying degrees of success. There remains an issue in the evaluation of the electrical characteristics of high D_{it} interfaces, as conventional electrical techniques, such as capacitance-voltage (C-V) profiling, find it difficult to extract definitive information in these cases. The large characteristic response time of the defects involved mean methods such as C-V can only measure small portions of III-V bandgaps.⁹⁵ HAXPES may provide an independent method of evaluating the electrical behaviour of these systems, and may also be able to energy map the interface states across the whole bandgap.

1.3.4 Source/Drain Contact Material

Self-aligned source/drain (S/D) contacts in Si MOSFETs have traditionally been formed by taking, for example, a p-type Si substrate and preferentially doping certain regions with n-type dopants using ion implantation; heavy doping is used to decrease sheet resistivity. These regions act as the S/D in the Si MOSFET as schematically shown in figure 1.8. The self-aligned aspect refers to the manufacturing process. S/D formation involves ion implantation after the formation of the gate stack on the Si substrate; subsequent thermal annealing results in the activation of the Si dopants. The advantage of this process is the formation of the S/D in controlled regions either side of the gate stack, with minimal overlap between the S/D regions and gate contact, and thus a minimal parasitic capacitance.^{96, 97}



Figure 1.8: Illustration of the ion implantation of Si MOSFET to form self-aligned source/drain regions

Unfortunately, unlike Si, ion implantation of S/D regions is not a reasonable solution due to the low dopant solubility of III-V materials.⁹⁸ As a result, an alternative method of forming S/D regions is necessary. A self-aligned silicide-like

(salicide) material is a possible solution. Ni-InGaAs has been the most intensively investigated of these materials, displaying excellent sheet resisitivities and the formation of an abrupt interface with InGaAs.^{99–102} There is, however, still a limited understanding of the formation processes and bonding structures involved. HAXPES could be very useful in addressing this gap in the literature, as the ability to perform depth profiles could help understand both the chemical and structural composition of the Ni-InGaAs layer.
1.4 Thesis Layout and Organisation

Chapter 2 describes the chemical, physical and electrical analysis techniques used in this study, along with the principles behind their operation. The primary technique used in this work is HAXPES, however other techniques such as conventional XPS, XAS, and C-V profiling were also used and are discussed.

Chapter 3 describes the initial HAXPES experiments performed in order to understand the capabilities of the technique and equipment. The extended sampling depth and photon energy tunability are demonstrated along with their application in the study of Al-silicide formation in $Al/SiO_2/Si$ structures. Combined HAX-PES and C-V measurements on $HfO_2/InGaAs$ are detailed along with the photon energy drift issue encountered. Successful application of the combined HAXPES and C-V measurements to the model SiO_2/Si MOS structure using high and low workfunction metals are discussed which demonstrate the ability of HAXPES to measure surface Fermi level movements. Finally, attempts at the characterisation of SiO_2/Si MOS structures following forming gas anneal are discussed.

Chapter 4 focuses on the extension of the combined HAXPES and C-V characterisation method to InGaAs and GaAs based metal oxide semiconductor (MOS) structures. The ability of HAXPES to allow the extraction of Fermi level positions and oxide potential fields is demonstrated on both substrates. C-V measurements of both sample sets are also described and very good agreement between HAXPES and C-V measurements is demonstrated.

Chapter 5 presents an investigation of the Ni-InGaAs and Mo-InGaAs salicide for use as future S/D regions in InGaAs n-MOSFETs. HAXPES, XAS, TEM, and sheet resistivity measurements show the evolution of the chemical, structural, and electrical properties of the salicide throughout the course of an anneal study. The need for the combined application of XAS and HAXPES to fully determine chemical speciation and sample structure is highlighted, and this approach is used to develop a structural and chemical compositional model of the Ni-InGaAs system as it evolves over a thermal annealing range of 250 to 500 °C.

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Chapter 2

Theory and Experimental Techniques

The principal technique used in this report is x-ray photoelectron spectroscopy and its high energy variant, hard x-ray photoelectron spectroscopy (HAXPES). In this section the theoretical and experimental basis of these, and other relevant techniques will be explained. The experimental systems used in this report will also be described.

2.1 X-ray Photoelectron Spectroscopy

2.1.1 Theoretical Basis

XPS is based on the photoelectric effect,¹ which predicts that when a photon strikes an atom one of three outcomes occurs:

- 1. The photon does not interact and passes through undisturbed.
- 2. The photon may interact with an electron and pass all of its energy to that electron causing it to be emitted from the atom, as seen in figure 2.1.



Figure 2.1: Emission of an electron from an atomic orbital due to the photoelectric effect.

3. The photon can be scattered upon interaction with an electron.

The second process is the basis of XPS, as it is these emitted electrons which are measured.

According to the photoelectric effect, no electron emission will occur unless the incident photons are of equal or greater frequency than the threshold frequency specific to the elements being studied. Once this condition is met, the number of emitted electrons is proportional to the intensity of the incident photons. The kinetic energy (KE) of the emitted electrons is directly proportional to the frequency of the photons used. This photoemission process is extremely rapid $(10^{-16} \text{ seconds})$. The relationship is succinctly described by the Einstein equation:²

$$BE = h\nu - KE, \tag{2.1}$$

where BE is the binding energy of the emitted photoelectron in the atom, h is Planck's constant and ν is the frequency of the incident photons. The binding energy of an atom can be explained as follows. An electron (negatively charged) experiences an attraction to the nucleus (positively charged), the closer these are together the stronger the force of attraction. The electron also experiences forces from the other electrons present in the atom. Different atoms have different binding energies due to their different nuclear charges. Any chemical interactions taking place in atoms in compounds, due to covalent or ionic bonds, can also affect the binding energy.

2.1.2 Referencing of Binding Energy

In XPS the binding energy of peaks is an important piece of information. The binding energy is acquired by measurement of the kinetic energy of the photons emitted from the sample. The next issue is how to convert this kinetic energy value into a usable binding energy: While equation 2.1 can give a value for the binding energy, some modifications must be made to account for the experimental setup.

Conducting samples are placed in electrical contact with the spectrometer usually by way of a metal sample holder. This ensures the Fermi level (E_f) of both the sample and spectrometer are at the same energy. The kinetic energy of the emitted electron is then measured according to figure 2.2. A correction to the Einstein equation is therefore needed to fully explain the processes involved in XPS, the work function of the spectrometer (ϕ_{spect}) must be included. So with knowledge of ϕ_{spect} and measurement of the kinetic energy, the binding energy of peaks in the sample can be determined using the following modified Einstein equation:³

$$BE = h\nu - KE - \phi_{spect} \tag{2.2}$$

The software which accompanies modern spectrometers has a built in value of ϕ_{spect} which is used in the calculation of the binding energy. This value can be measured using a clean reference sample such as Ag or Au, and the software parameters can be adjusted until the peak positions match those in the literature.⁴



Figure 2.2: Energy level diagram for sample in electrical contact with spectrometer. 5

When measuring insulating samples, there is an added difficulty in that the Fermi level is not common between the sample and spectrometer. In this case an electron flood gun may be used. Equation 2.1 must once again be altered as the sample's vacuum level is now the same as the energy of the flooding electrons. The equation thus becomes:

$$BE = h\nu - KE + \phi_e, \tag{2.3}$$

where ϕ_e is the energy of the flooding electrons.

2.1.3 Initial and Final State Effects

Binding energy can be explained as the difference in energy between the initial and final states of the electron, described by the equation:⁵

$$BE = E_{final} - E_{initial}, (2.4)$$

where E_{final} is the final state energy and $E_{initial}$ is the initial state energy.

The initial state of the atom is the rest or ground state. Any change in binding energy due to a change in initial state energy is called a chemical shift.³ This may be caused, for example, by the formation of chemical bonds. Any effect on this initial state should affect all core levels for the same element equally, so all core level peaks for that element should undergo the same chemical shift, assuming the same local chemical environment. In most cases any shifts seen in spectra are thought to be due to initial state effects.

Final state effects such as atomic relaxation effects can play a significant role in binding energy. After an electron is emitted from an atom the remaining electrons rearrange. This leads to lowering of the binding energy. This relaxation can take two forms:

- Core hole relaxation
- Relaxation of the surrounding atoms

In core-hole relaxation it is generally the electrons in shells outside that from which the electron was emitted that have greater relaxation effects. The electrons on the inner shells do not contribute to a great extent. Relaxation of surrounding atoms is more complicated. In metals, valence band electrons may be passed from one atom to another to screen the core-hole, while in ionically bonded samples electrons are not free to move between atoms. Instead polarization of the electrons in these materials may occur due to the presence of a core-hole.⁵

Other examples of final state effects include shake-up satellites, where the emitted electron interacts with a valence electron exciting it into a new state while the emitted electron loses some of its own kinetic energy, and multiplet splitting, where the core hole interacts with unpaired electrons in outer orbital, resulting in complex peak splittings, multiplet splitting is most common in transition metals.

2.1.4 Peak Widths

Peak widths are determined by the core hole lifetime, the linewidth of the radiation source and the instrumental resolution of the analyser. The Heisenberg uncertainty relationship allows us to to determine the peak width due to core hole lifetime as:⁵

$$\Gamma = \frac{h}{\tau},\tag{2.5}$$

where Γ is the peak width, h is Planck's constant, and τ is the core hole lifetime in seconds. Γ is generally larger for inner shell orbitals as an inner shell core hole may be filled by any of the outer shell electrons, so the core hole lifetime is shorter. Also Γ increases with atomic number as the valence electron density increases, so there are more electrons to fill the core holes. The contribution due to core hole lifetime is of a Lorentzian line shape.

Instrumental resolution also plays a part, the contribution is of a Gaussian line shape. For XPS spectra in a narrow energy range (<20 eV) the instrumental resolution, and thus the Gaussian peak width, is assumed to be constant. The instrument is expected to have very similar resolution over such a small energy range. Satellite features may also affect peak shape and widths; where this is the

case the peaks tend to have asymmetric line shapes.⁵

2.1.5 Sampling Depth

XPS has a limited sampling depth of approximately 4 to 7 nm,⁶ depending on the material, but why is this so? The advantage of using x-rays is their ability to move almost unimpeded through solids, unfortunately the same cannot be said for the emitted electrons.

As an electron travels through a material it has a certain probability of interacting with any of the atoms present. If it does so it will lose some its energy during this interaction. In XPS however we rely on the kinetic energy of the electrons as the method of determining the atomic orbital from which they were emitted, so any loss in kinetic energy due to collisions renders the electrons useless to XPS. While these electrons are still present in the XPS spectra they form the background signal upon which the core level spectra are seen. The inelastic mean free path is the average distance that an electron can travel in a solid material without interaction. While some electrons will interact in travelling this distance, XPS is a statistics based technique, so the distance where the majority will not interact is of most importance. Beer's law is the equation used to determine the fraction of photoelectrons which suffer no energy loss travelling through a thickness d of a given material. The inelastic mean free path (IMFP) (λ) in the equation is the thickness of material through which 63% of electrons will travel without interaction. Beer's law is:

$$I_k = I_0 (1 - e^{\frac{-d}{\lambda \cos \theta}}), \qquad (2.6)$$

where I_k is the intensity of electrons exiting the material, I_0 is the intensity of incident photons, d is the depth from which the electrons are emitted, and λ is the IMFP. In XPS 95% of the signal comes from a depth of $d = 3\lambda$, and this is known as the sampling depth,⁵ as shown in figure 2.3. The IMFP is kinetic energy dependent and therefore the higher sampling depth of HAXPES is related to increasing the kinetic energy of the photo-emitted electrons, as explained in section 1.1. Figure 2.3 and equation 2.6 also highlight the exponential nature of



Figure 2.3: Exponential dependency of XPS signal with depth into sample.

the XPS signal, which leads to the total signal being weighted towards the sample surface, and thus the surface sensitive nature of XPS.

2.1.6 Element Identification

XPS can identify all elements in a sample, except for H and He, and has the ability to detect the presence of elements at concentrations of 0.1-1%. Once a survey scan, as seen in figure 2.4, has been recorded, each peak can be identified to determine the elements present in the sample. A number of reference texts are available^{4, 7} which list the correct binding energy of, and the orbital attributed to, each peak. Usually the most intense spectral feature in an element's spectra is used to identify it (for example the Ag 3*d* in the Ag spectrum). However, sometimes peaks from different elements can overlap (for example the Hf 4*f* and Ga 3*d*) and in that case a different peak may be used.³



Figure 2.4: Survey of an Al sample, with the Al 2s, Al 2p, C 1s, and O 1s core levels identified.

2.1.7 Chemical Shift

Once the elements present have been identified, the next step is to distinguish between the different chemical environments of the same element. As explained earlier changes in the initial state effects, such as chemical environment, alter the binding energy of the electron within the atom, and thus the binding energy of the photoemitted electron. This process is described in greater detail with relation to the silicon/silicon dioxide system, using the Si 1s spectrum shown in figure 2.5.

Figure 2.5 shows a Si 1s spectrum for an 8 nm SiO₂ layer which was thermally grown on a Si (100) substrate. The Si substrate electrons are seen at a binding energy of 1839.2 eV, while those from the SiO₂ appear at a higher binding energy position, chemically shifted by approximately 5 eV. This is due to their different bonding environments. The covalently bonded Si-Si system allows the valence electrons to be shared equally among each of the Si atoms. However, the incorporation of O atoms, which have considerably greater electronegativity than



Figure 2.5: Chemical shift between bulk and oxidised Si (SiO_2) in the Si 1s peak.

Si, results in the transfer of electron density towards the O atoms. As such, the Si-O bonds are more ionic and electrons excited from these Si atoms are leaving an atom with greater positive charge than those within the Si bulk. The effect of this positive charge is to reduce the kinetic energy of the photoemitted electrons, and thus increase their binding energy. The magnitude of the electronegativity difference between two chemically bonded elements will alter the magnitude of the shift seen in the core level spectra, and as such the respective electronegativites of the elements present can be used to identify chemical interactions, as will be shown in Chapter 5 of this study.

2.1.8 Peak Fitting

In XPS different chemical species within the same core level can be found in a narrow energy range (<5 eV), and thus are often unresolved in the spectrum. To fully understand the sample being studied, these peaks must be de-convoluted in

order to ascertain the chemical species present, and also the area of each peak, as this provides information on the relative concentration of each species present.

Specialist peak fitting software is generally used in order to de-convolute the spectra.⁸ The user enters a variety of parameters such as background (most commonly used is the Shirley background), peak widths (Lorentzian and Gaussian), and the approximate binding energy positions of each sub peak. The software then uses a least squares fitting procedure to determine the areas and positions of the sub-peaks present. Peak fitting also allows the determination of accurate values of the peak full width half maximum (FWHM), which can be used to determine a variety of effects on a sample such as band-bending.⁹ The FWHM is a composite measurement of the Lorentzian and Gaussian line widths. The formula for the FWHM is:

$$FWHM = \sqrt{Gaussian^2 + Lorentzian^2}, \qquad (2.7)$$

where the Gaussian and the Lorentzian are the peak widths of each line shape.

2.1.9 Apparatus

Ultra High Vacuum Systems

In order to measure the kinetic energy of the photoemitted electrons from a chemically stable surface, as well as ensuring the detection of a significant number of the photoemitted electrons, experiments are performed under ultra high vacuum (UHV) environments, where UHV is defined as pressures lower than 10^{-9} mbar. At these pressures the inelastic mean free path of an electron is kilometres, meaning that a large percentage of photoemitted electrons reach the detector without interacting with any gaseous molecules in the vacuum system. Another reason for the importance of UHV is to minimise sample contamination. As XPS is limited to an approximate sampling depth of 4 to 7 nm, depending on material,¹⁰ it is important to ensure the sample being measured has a minimum of environmental contamination, such as oxidation or the presence of environmental carbon on the surface. As the surfaces are the prime region of investigation by XPS, the surface reconstruction can be altered by the adsorption of contaminants. Surface contamination also complicates controlled systematic investigations such as anneal or deposition studies. Therefore a UHV environment ensures that the surface under investigation remains chemically stable during the photoemission experiment.

XPS Systems

Most modern XPS systems use a twin anode X-ray source which allows the use of two different anode materials, and thus two x-ray energies, as seen in figure 2.6. The source consists of a Cu anode coated with two metals, Al (1486.6 eV) on one side and Mg (1256.6 eV) on the other. Other anode materials such as Na and Si are also used although Mg and Al are favoured due to their low chemical reactivity. A high energy cathode (10 to 15 kV) is used to bombard the anode with electrons. This bombardment generates a continuous Bremsstrahlung energy distribution emission with characteristic x-ray emission, due to the $K\alpha$ transition for Al or Mg which results from the electron transition between the 2p and 1s core hole created by the incident electron bombardment. The anode is water cooled during operation to prevent heating damage to the Al and Mg films. In order to decrease the background noise due to the Brehmsstrahlung an Al foil (2 μ m thick) is placed at the exit aperture of the dual anode source, removing some of the Brehmsstrahlung, and decreasing the background signal in the XPS spectra.

These x-rays are then incident onto the sample, causing the emission of photoelectrons in the near surface region. The electrons are emitted at all angles from the surface and some are collected by the electron energy analyser. Many analysers have lenses with a specific acceptance angles, which are chosen by the manufacturer so as to keep the total sampling area small enough that only electrons with take-off angles within a narrow range are measured. This is important as it allows the user to know the depth from which all electrons are emitted, also allowing angular resolved XPS to be performed. An electrostatic lens is used, which applies an electric field across the lens in order to focus the collected electrons on the analyser entrance slit.

Hemispherical analysers consist of two concentric hemispherical plates of dif-



Figure 2.6: Diagram showing the operation of a dual anode X-ray source.¹¹

ferent radii, as shown in figure 2.7. A retarding voltage (V_0) is applied across the entrance slit of the analyser, so that the kinetic energy of the electrons are restricted to within the energy range known as the "pass energy", as chosen by the user. The entire XPS spectrum is acquired by varying the retarding voltage in order to ensure that all electron have the same "pass energy". In the hemispherical analyser a voltage is applied to each of the hemispherical plates, and is adjusted to ensure that only electrons with the correct "pass energy" pass through the analyser in order to be detected by the channel plate. If the electrons have kinetic energy outside of the "pass energy" range they will strike one of the hemispherical plates before reaching the channel plate. The electrons are separated according to their kinetic energy while they pass through the analyser, as electrons with lower kinetic energy, but still high enough not to strike the inner plate, will end up closer to the inner plate at the end of the analyser, while the opposite will be true for those of higher kinetic energy.

An electron detection system is located at the exit of the hemispherical analyser, typically a channeltron or channel plate is used. This is made up of an array



Figure 2.7: Hemispherical analyser design.

of detectors and, depending on where on the plate the electron strikes, the kinetic energy of the electron can be determined. The computer uses these kinetic energy values, the photon energy, and the work-function of the spectrometer, to calculate the binding energy of each electron with respect to the sample's Fermi level, using equation 2.2. This data allows each peak in the spectrum to be attributed to a specific core level of an element, as previously described. The channel plate is essentially made up of an array of electron multipliers. In the multiplier, the incoming electron strikes an initial electrode at the entrance causing secondary emission to occur. This results in the generation of up to three electrons. A voltage applied between the metal plates which make up the tube causes these electrons to strike the next plate once again causing secondary emission, as shown in figure 2.8. This process is repeated along the length of the tube and can transform one initial incoming electron into 10^6 to 10^8 electrons by the end of the multiplier tube, resulting in a measurable signal.

A standard XPS set-up is shown in figure 2.9, this consists of an X-ray source, sample, electron lens, analyser, electron detector, and separate computer set-up. The source, sample, and analyser are held in an ultra-high vacuum (UHV) vessel not shown here.



Figure 2.8: Electron multiplier and channel plate.¹²



Figure 2.9: XPS experimental set-up.¹¹

2.1.10 System Used

The XPS UHV system used in these experiments is shown in figure 2.10 and consists of a three chamber system with in-situ deposition techniques and resistive heating up to 600 °C. There is a load lock maintained at 10^{-2} mbar for the introduction of multiple samples, a preparation chamber at 10^{-7} mbar for in-situ deposition and an analysis chamber at 10^{-10} mbar equipped with a dual anode x-ray source (Mg and Al), and a VG CLAM electron energy analyser with a single channeltron detector. The three chamber set-up allows all deposition to take place outside of the analysis chamber in order to reduce system contamination. It also allows for rapid sample loading, as the analysis chamber does not require venting for sample exchange. The diffusion pumped system attains UHV after a 12 hr bake at 150 °C. The instrumental resolution of this system was measured by the fitting of a Au Fermi edge with a convoluted step function and Gaussian peak, giving an overall energy resolution of 1.1 eV.



Figure 2.10: Dedicated three chamber conventional XPS system.

2.2 Hard X-ray Photoelectron Spectroscopy

HAXPES is a high photon energy based variant of XPS. This section will explain the differences between XPS and HAXPES, and its applications. The history and development of HAXPES was discussed in section 1.1.

2.2.1 Advantages of HAXPES

HAXPES has numerous advantages over conventional XPS. The higher energy of the x-rays used in HAXPES allows the user to extend the sampling depth from 5 to 7 nm at 1.5 keV, for conventional XPS, all the way to 20 to 30 nm at 10 keV.¹⁰ This enables the investigation of samples with thicker overlayers, multi-layered structures, and the bulk chemical structure of the sample.

The sampling depth capabilities of HAXPES are demonstrated in figure 2.11 for spectra acquired at a photon energy of 4150 eV for 8 nm SiO₂ on a silicon substrate, and the same sample following the deposition of either 5 nm of Al or Ni. In this example, a Si(100) substrate had an 8 nm layer of SiO₂ deposited on top, designated as no gate in the figure. The suppression, of the Si 1s signal following the deposition of 5 nm of Al is approximately 92%, of the substrate signal. Deposition of a Ni capping layer on an identical sample almost completely suppresses the Si 1s signal, reducing its intensity by 99%, though these peaks can be measured using narrower scan windows. In these samples a photon energy of 4150 eV can measure a Si substrate signal through a combined 13 nm of metal and SiO₂.

The performance of HAXPES at synchrotron radiation sources enables the photon energy to be tuned, thus allowing the HAXPES measurements to focus on specific buried interfaces at different depths into the sample.¹³ This can be used to complement conventional angular resolved XPS measurements. Lysaght et. al^{14} used this depth profile method to characterise a HfO₂/SiO₂/Si sample, as seen in figure 2.12. In this example a photon energy of 2100 eV is initially used; at this energy only signal from the SiO₂ layer is detected in the Si 1s core level. As the



Figure 2.11: Sampling depth capabilities of HAXPES.

photon energy is increased to 3500 eV, and thus the sampling depth increased, the bulk Si layer which lies below the SiO₂ begins to appear and becomes the dominant peak in the spectrum. Depth profiles can also give a better understanding into how the chemical or electronic structure of a sample changes moving from the surface to the bulk of the material.

2.2.2 Apparatus

The basic HAXPES experimental set-up is similar to XPS, the only differences being in the type of x-ray source and energy analyser used in the measurements.

While some fixed high energy sources are available for laboratory use, such as 8 keV Cu anodes, generally synchrotron sources are used. The important characteristics of synchrotrons are:⁵

• High brightness and high intensity, many orders of magnitude greater than



Figure 2.12: Depth profile of $HfO_2/SiO_2/Si$ sample.¹⁴

that offered by conventional x-ray sources;

- High brilliance, exceeding other natural and artificial light sources by many orders of magnitude: 3^{rd} generation sources typically have brilliance greater than 10^{18} photons/s/ $mm^2/0.1\%$ BW, where 0.1% BW denotes a bandwidth $10^{-3}\omega$ around the frequency ω ;
- High collimation, i.e. small angular divergence of the beam;
- Widely tunable in energy/wavelength by use of a monochromator (sub eV up to MeV range);
- High level of polarization (linear or elliptical);
- Pulsed light emission (pulse duration of one nanosecond or below).

In HAXPES work, the most important aspects of the synchrotron source are the high brilliance of the light, as this is required to overcome the decrease in photoionisation cross section with increasing photon energy. Synchrotrons are generally composed of two connected evacuated rings: an accelerating ring which accelerates the electrons to 99.99% of the speed of light, and a storage ring in which the injected electron beam is stored for experimental purposes, as seen in figure 2.13. The storage ring is not a true ring shape, rather it is shaped like a many sided polygon. This is because as the electrons travel around the corners of the storage ring at almost the speed of light, the change in momentum causes a release of broad spectral radiation which is forward focussed along the direction of electron motion. It is for this reason that the experimental beam-stations are located at these points. This radiation is then used for a wide variety of experiments, including HAXPES, XPS, x-ray standing wave, and x-ray absorption spectroscopy.²



Figure 2.13: Diagram showing layout of storage and accelerating ring which make up a synchrotron, and how wide-spectrum radiation is emitted as the electrons travel around the corners of the storage ring.

Third generation synchrotron sources are generally used for HAXPES measurements due to their high brilliance. This is achieved by the use of insertion devices such as wigglers and undulators in the straight sections of the storage ring. An undulator is a series of vertical dipole magnets with alternating polarity, as shown in figure 2.14. As the electron moves through these magnets its trajectory oscillates causing radiation to be emitted at the trough and peak of these oscillations. The strength and spacing of the magnets is designed so that the emitted radiation undergoes constructive interference at the desired wavelengths, the intensity of the emitted radiation increases with the number of magnets. This results in the production of a narrow energy band of radiation which is highly collimated in the horizontal and vertical directions. Wigglers operate on a similar basis to undulators though higher fields are involved and the radiation emitted is of a broader spectrum.



Figure 2.14: Diagram shows the layout of an undulator and wiggler, where the magnets force the electrons direction of travel to oscillate leading to the emission of radiation.

A number of modifications are necessary to enable an electron analyser to be used for HAXPES. Due to the decrease in the photoionisation cross section in the high energy regime, combined with the fact that HAXPES measurements are generally made on thicker layers and buried interfaces where the signal intensity decreases according to equation 2.6, the acceptance angle of the detector is increased so as to allow a greater proportion of the signal to enter the analyser and thus increase the measured signal. The retarding lens on the analyser also operates at a high spatial magnification, allowing the emitted electrons to be focussed very
accurately onto the entrance slit of the analyser.

X-ray monochromators allow the photon energy at synchrotron sources to be selected by utilising the diffraction of light by crystals, as described by Bragg's law. They also serve as a means of increasing the energy resolution by minimising the influence of background radiation and Brehmsstrahlung. In non-monochromated XPS systems the primary limiter of energy resolution in the experiment is the natural linewidth of the radiation source, usually the $K\alpha$ line. As previously mentioned, Al and Mg are the standard x-ray sources used, and the resolution limit due to the natural linewidth of the $K\alpha$ line is 0.7 eV for Mg and 0.8 eV for Al. A narrow band pass crystal (e.g Si), which transmits light of a narrow wavelength range, and attenuates light outside this range, is typically used in the monochromator. This results in a reduced line width, elimination of Brehmsstrahlung and satellite lines, and a reduction in heat radiation which minimises sample damage. The disadvantages of a monochromator are a reduced x-ray flux, however this can be compensated for by a more efficient collection lens and multichannel detector. A double crystal monochromator is shown in figure 2.15, where the first crystal, which is water cooled in order to remove the heat load caused by the beam, diffracts the x-ray beam, while the second crystal redirects the beam along it's original path.¹⁵



Figure 2.15: Diagram shows the layout of a double crystal monochromator, where the planes of the crystal act as a diffraction grating.

2.2.3 Systems Used

The HAXPES system used in these experiments was the National Institute for Standards and Technology beam-line X24a located at the National Synchrotron Light Source at Brookhaven National Laboratory, and is shown in figure 2.16. A double Si(111) crystal monochromator allowed for photon energy selection in the range of 2.1 to 5.0 keV. A Scienta R4000 electron energy analyser was operated at a pass energy of 50 eV.



Figure 2.16: HAXPES system at the Brookhaven National Laboratory.

2.3 X-ray Absorption Spectroscopy

2.3.1 Theory

The diffraction of electrons from the surface of a sample is inherently surface sensitive due to the strong interaction of the electron with the material, resulting in the small IMFP of the electrons, and thus a very shallow information depth (in the order of nm). This results in techniques which are based on electron diffraction, such as low energy electron diffraction (LEED), yielding information on only the first few nm of the sample. As a result, these techniques are generally used to give information on the surface reconstruction or long range order on the sample surface. Conversely, x-rays interact very weakly with materials, resulting in a very large information depth, yielding bulk sensitive data. X-ray absorption spectroscopy (XAS) uses the bulk sensitive nature of x-rays and measures the change in the absorption coefficient as a function of photon energy to derive information on the chemical structure of the sample. The absorption coefficient α , which describes the absorption of photons by a material, is defined by Beer's law:⁵

$$I = I_0 e^{(-\alpha l)}, \tag{2.8}$$

where I_0 is the incident beam intensity, I is the exiting beam intensity, and l is the distance travelled, usually the sample thickness. However, the amount of radiation absorbed depends strongly on the material being studied and the photon energy, as absorption only occurs if the photon energy is sufficiently high as to cause an electron excitation within a core level of the material. As a result, the XAS measurements are usually performed in a narrow window around the specific core level of interest. In general, the measurements are performed on the K, L, and Medges (corresponding to the n=1, 2, and 3 levels). K-edges are the most commonly measured due to their simpler structure. While the K-edge consists of only a single edge, the L-edge consists of three $(2s, 2p_{1/2}, \text{ and } 2p_{3/2})$, and the M-edge consists of five $(3s, 3p_{1/2}, 3p_{3/2}, 3d_{3/2}, and 3d_{5/2})$. Once the threshold energy, which leads to an excitation of the desired core level, has been reached an optical transition can occur, with the probability of a transition between an initial and final state given by P_{if} . The absorption coefficient begins to drops off above the threshold energy; although absorption does continue, such as in the simplified XAS spectra, as shown in figure 2.17. An XAS spectrum is divided into four regions: 1) pre-edge which is the region up to 10 eV below the absorption edge 2) x-ray absorption near edge structure (XANES) which is $\pm 10 \text{ eV}$ from the absorption edge 3) near edge x-ray absorption fine structure (NEXAFS) which is 10-50 eV above the absorption edge and 4) extended x-ray absorption fine structure (EXAFS) which covers the rest of the XAS spectra from 50 eV to 1000 eV above the absorption edge. The near edge region, XANES and NEXAFS, is more sensitive to the final density of states, and transition probabilities, and as such it is usually used in the identification of the chemical bonds present. The EXAFS region provides information on the coordination number (number of nearest atomic neighbours) of the first shell and further shells in well ordered samples.



Figure 2.17: Spectrum showing the different regions of a typical XAS scan.¹⁶

The structure in the spectrum above the absorption edge is due to interference in the wavefunction of the electron. In an XAS measurement after a core level absorbs a photon, an electron is emitted, leading to a wavefunction which propagates away from the excited atom. This wavefunction is then scattered by the surrounding atoms. Photon absorption for a given core level depends on whether there is an available quantum state of the correct angular momentum and energy for the photoelectron. As a result, the absorption coefficient α measured by XAS also depends on the availability of an appropriate quantum state. This means that if an ejected photoelectron wave scatters off a surrounding atom and returns to the absorbing atom it will alter the likelihood (P_{if}) of another electron being absorbed, and thus alter the measured absorption coefficient. This interference between the outgoing photoelectron wave and the backscattered wave results in the oscillating nature of the XAS signal, as shown schematically in figure 2.18. Depending on both the amplitude of these oscillations, as well as the period, information can be extracted as to the coordination number and distances to the surrounding atoms.

The interference pattern is only seen after the absorption edge because the



Figure 2.18: Schematic diagram showing (a) x-ray absorption for a single atom and the spectrum produced and (b) the interference which occurs between the outgoing photoelectron wave (blue line) and the wave backscattered from a neighbouring atom (red line).¹⁷

excited electron has a kinetic energy of :

$$KE = h\upsilon - h\upsilon_{E_0} \tag{2.9}$$

Where hv is the photon energy, and hv_{E_0} is the threshold energy. hv_{E_0} is usually chosen as being halfway up the absorption edge. So at the threshold energy $hv = hv_{E_0}$ so KE = 0, therefore the electron is excited but has no energy to propagate and thus scatter off the surrounding atoms. It also explains why the further the interference fringes are from the initial peak, the more likely they are due to the second or third shell of surrounding atoms. Due to the very low IMFP of electrons, combined with the fact that the amplitude of the electron wavefunction is inversely proportional to its radius, the scattering which results in the interference pattern seen in the XAS spectra is dominated by the scattering from the atoms in the first shell around the emitting atom.

As mentioned earlier, XAS is fundamentally a bulk sensitive technique due to the large sampling depth of the x-ray photons, so it would be desirable to be able to make XAS more surface sensitive in order to characterise the surface localised effects. By changing the angle of incidence of the x-ray the penetration depth into the sample can be altered, as shown in figure 2.19. While this does not make XAS surface specific, it does act to make it more surface sensitive, so the sampling depth can be altered from millimetres to nanometres. Decreasing the angle of incidence allows more surface sensitive spectra to be acquired to distinguish between chemical species present in the material bulk and the near surface region. The grazing incidence angle chosen is at a critical angle ($<0.2^{\circ}$), where the reflectivity curve of the sample is at a maximum, as seen in figure 2.20.¹⁸ Below the critical angle total external reflection occurs. The XAS signal at a larger angle of incidence (approximately 1°) is entirely bulk sensitive.



Figure 2.19: Normal and grazing incidence XAS.



Figure 2.20: Reflectivity curve of an XAS sample highlighting the critical angle of $0.15^{\circ}.^{18}$

2.3.2 Data Analysis

It is helpful to plot the absorption coefficient α as a function of the wavevector k instead of the photon energy where:

$$k = \frac{2\pi}{\lambda} \tag{2.10}$$

By plotting the XAS spectra in this manner the oscillations have a constant, instead of an increasing, period. The amplitude of the oscillations depends on the number of nearest neighbours, while the period of the oscillations is related to the bond lengths between the emitting atom and the surrounding neighbours. By choosing a specific element in a bond, say Ni in NiAs, you can probe the atoms surrounding that Ni atom. The presence of NiAs can be confirmed by acquiring the XAS spectra of the As edge. However due to the fact that the XAS spectra is a sum of the interference of a large number of electron wavefunctions, there is likely to be more than one bond type present in an amorphous system, so evidence of numerous bonds may be evident in a single spectra. It is for this reason that the spectra for pure reference materials are usually acquired for the materials likely to be present in a given system. The spectra for the unknown sample can then be compared to the reference spectra of the pure reference samples. The reference spectra then act as XAS 'fingerprints'.

2.3.3 Apparatus

XAS measurements are generally performed at synchrotron radiation sources due to the variable photon energy requirement, which allows the user to choose a photon energy specific to the absorption edge being studied. Synchrotron sources are also important for XAS due to their high brilliance, which means that despite the weak interaction between the x-ray and the sample, the relatively small contribution made by surface atoms is still measurable.

XAS can be performed by a transmission measurement, where the sample, usually a powder, is very thin. In this case the beam intensity is measured by an



Figure 2.21: Experimental setup for XAS.

ion chamber before the sample (I_0) , and the beam is measured again by the same method after it has passed through the sample (I_t) . In this work, however, the preferred method was fluorescence detection. In this case the x-ray fluorescence is measured. This is produced when the core hole created by the initial electron excitation is filled by another electron decaying from a higher filled level. The energy of the emitted photon is dependent on the energy difference between the two levels, and is thus characteristic of the emitting element. A fluorescence ionisation detector is used to measure the fluorescence (I_f) , with the appropriate filters in order to keep out the scattered background.

The XAS apparatus is shown in figure 2.21. A crystal monochromator is used to tune the x-ray energy to the desired absorption edge, while slits are used to alter the intensity of the incident x-rays. The ion chambers are essentially gas filled capacitors. They are filled with an inert gas, such as N_2 , the atoms of which absorb the incident x-ray, ejecting an electron, which then ionises the surrounding gas. A voltage is applied across the chamber which sweeps any electrons produced to a detector, where a current is measured. The x-ray intensity is then measured from this current. Typically an ion chamber absorbs 10% of the incident x-rays.



Figure 2.22: Experimental XAS system.

2.3.4 Systems Used

The XAS system used in these studies is located on beamline X23b at the national synchrotron light source in Brookhaven National Laboratory, as shown in figure 2.22. The experimental apparatus is located within an x-ray hutch for operator safety. A Cowan double crystal monochromator with an energy range of 3.5 to 10.5 keV is used for photon energy selection. The hutch contains ion chambers for transmission measurements and a Stern-Heald detector¹⁹ for fluorescence measurements.

As there are slight changes in the incident photon energy with time, due to variations in the synchrotron source, a number of XAS scans are taken. These are then corrected for energy, and summed to improve the signal to noise. The sample is positioned on a three axis sample table which can be computer controlled. This enables accurate sample alignment as well as glancing incidence XAS, as described in section 2.3.1.

2.4 Capacitance-Voltage Profiling

2.4.1 Theory

Variable frequency capacitance-voltage (C-V) measurements allow information on the dielectric constant of the oxide layer, the density of states at the interface, the effects of trapped charge, and the presence of any Fermi level pinning to be deduced. C-V measurements are performed by applying a DC bias voltage to the sample, and using an AC signal to measure the capacitance at each bias voltage. This bias voltage sweep acts to drive the MOS into accumulation, depletion and inversion. The capacitance value (C) can be determined using the following equation:

$$C = \frac{Q\epsilon}{\sigma d} \tag{2.11}$$

Where Q is the charge on the plates, ϵ is the dielectric constant of the material, σ is the charge per unit area, and d is the capacitor plate separation.

This behaviour can be clearly understood using energy band diagrams. The energy band diagram of an ideal p-type substrate at zero bias voltage in contact with a metal of workfunction ϕ_m is shown in figure 2.23 In these diagrams a modified work function, $q\Phi_m$, measured as the energy separation from the metal Fermi level E_{FM} to the conduction band of the oxide, is used. In this ideal case, the metal and semiconductor work functions are equal $(q\Phi_m = q\Phi_s)$. As the energy band diagram shown is for a p-type sample, the Fermi level resides below the intrinsic level (E_{Fi}) , close to the valence band edge. This is important as the position of the Fermi level relative to the intrinsic level determines the conduction properties of the device.



Figure 2.23: Energy band diagram for an ideal p-type MOS capacitor.²⁰

The application of a negative bias voltage on the metal acts to raise the Fermi level of the metal by an amount qV above the semiconductor Fermi level as shown schematically in figure 2.24, however, the work function values do not change due to the applied voltage, rather an electric field is generated across the oxide layer, as shown by the slope in the oxide bands. The bands of the semiconductor bend reflecting the drop in potential across the depletion region generated by the applied bias. The band-bending can be understood as being due to the accumulation of holes at the semiconductor/dielectric interface, so if for p-type in accumulation there is a large density of holes at the interface, then the charge at the interface increases leading to the conduction and valence bands bending upward. The concentration of holes (p) can be calculated using a combination of the density of states function (giving the number of available energy states in the band structure) and the Fermi-Dirac equation (giving the probability that each state will be occupied by an electron). This gives us:

$$p = n_i e^{\left(\frac{E_i - E_f}{\kappa T}\right)},\tag{2.12}$$

where κ is the Boltzmann constant, T is the temperature in Kelvin and n_i is the



Figure 2.24: Energy band diagram showing accumulation in a p-type MOS.²⁰

electron concentration.

The Fermi level can only 'move'by bending of the conduction and valence bands, and thus the position of the Fermi level within the band gap is altered, as seen in figure 2.24. Accumulation causes a p-type sample to become 'strongly' p-type, where the Fermi level resides closer to the valence band edge. In this situation, the gate metal acts as one capacitor plate and the region of majority carriers acts as the other. In equation 2.11 the plate separation d is at a minimum when it is equal to the oxide width, so the maximum capacitance value (C_{max}) is recorded.

Conversely if the polarity of the bias voltage is reversed, the metal Fermi level is lowered by an amount qV, resulting in a voltage rise across the dielectric. The majority carriers are forced away from the semiconductor/dielectric interface, causing the conduction and valence bands to bend downwards, resulting in the semiconductor Fermi level residing closer to the conduction band, as seen in figure 2.25. The device is now in depletion mode, leading to a lower capacitance value, as d is increasing. As this bias voltage is increased the bands continue to bend downwards as seen in figure 2.26. The minority carriers begin to be attracted to the semicon-



Figure 2.25: Energy band diagram showing depletion in a p-type MOS^{20}

ductor/dielectric interface and this reduces the surface charge lowering E_i below E_F . The minority carriers now act as the other plate of the capacitor, but the capacitance value is lower than in accumulation as, although the plate separation d is the same, the charge Q is lower due to the lower number of minority carriers. This results in a U-shaped graph, as shown in figure 2.27. The bias voltage at which inversion occurs is known as the threshold voltage (V_T) . The inversion region of the semiconductor now shows electrical behaviour similar to that of an n-type device; strong inversion occurs when the surface region is as strongly n-type as the rest of the semiconductor is p-type.

2.4.2 Defects

In the simplified ideal case shown in figure 2.23 no band-bending occurs in the absence of a bias voltage. However, in general, a number of defects such as trapped charge or interface defects cause band-bending in the case of an unbiased device. In this case a voltage must be applied to get to the situation seen in the figure, this is known as the flat band voltage V_{FB} . The presence of band-bending in the case of an applied bias is apparent in C-V measurements as a shift in the C-V



Figure 2.26: Energy band diagram showing inversion in a p-type MOS^{20}



Figure 2.27: Quasistatic C-V graph of a p-type SiO_2/Si based MOS capacitor structure showing the characteristic U-shape. The regions of accumulation, depletion and inversion are highlighted.



Figure 2.28: C-V graph of a n-type SiO_2/Si based MOS capacitor structure showing the presence of defects.

curve along the x-axis.

Interface defects may create a measurable capacitance that can be viewed as another parallel plate capacitor in series with the oxide capacitance, and in parallel with that of the semiconductor. While the oxide capacitance dominates the C-V spectra, if the density of interface defects is sufficiently high it will deform the C-V profile as a 'bump' in the spectra, as seen in figure 2.28. High interface densities $(>10^{12} \text{ cm}^{-2})$ may be measured with C-V. By performing multi-frequency C-V sweeps (1 kHz - 1 MHz) the frequency dependency of the defects can be measured. More charge can 'follow' the voltage variation as the frequency of oscillation is reduced, leading to the greater prominence of defects at low frequency. This can result in the spreading out of the spectra taken at different frequencies, known as frequency dispersion. Fermi level pinning may result in a device not being able to reach accumulation or inversion; this will result in a reduction in the difference between C_{max} and C_{min} .

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Chapter 3

Initial Investigations of the Measurement Capabilities of HAXPES

3.1 Introduction

This section details the initial experiments performed using hard x-ray photoelectron spectroscopy (HAXPES) in order to understand the capabilities and limits of both the technique and the systems used. As the DCU research group was only the second user of a new HAXPES end station on beamline X24a at the NSLS, it was necessary to undertake a number of baseline experiments in order to determine the measurement capabilities of this system.

Firstly, the increase in sampling depth and energy resolution over conventional x-ray photoelectron spectroscopy (XPS) is explored. The sampling depths available at these higher photon energies was investigated in order to understand the layer thicknesses which are measurable with this technique. These experiments were performed at a range of photon energies and compared with conventional XPS in order to demonstrate the advantage of HAXPES in the characterisation of bulk material properties and multilayer structures with device relevant thick-

nesses. The relationship between energy resolution and photon energy is also demonstrated. This shows the advantage of conventional XPS in the characterisation of the sample surface and thin deposited films, while HAXPES is better suited to the study of bulk material properties or chemical changes in multilayer structures and at buried interfaces.

The next study involved the extension of the conventional application of XPS, in the chemical characterisation of surfaces, to the study of buried interfaces in $Al/SiO_2/Si$ structures. The motivation behind this study was the investigation of Al diffusion and Al-silicide formation at the buried SiO_2/Si interface. The advantage of HAXPES in this particular study is that the silicide formation was driven by the thermal annealing of pre-formed $Al/SiO_2/Si$ MOS structures. Conventional XPS studies of this system would involve the measurement of samples following each step in the fabrication process and subsequent thermal anneal. The limited sampling depth would also necessitate the fabrication of multilayer structures with sufficiently thin layers. HAXPES, however, can measure pre-fabricated and annealed structures, thus simplifying the experiment.

A novel application of HAXPES in the evaluation of the electronic properties of metal-oxide-semiconductor (MOS) structures is demonstrated. The capability of HAXPES in providing chemical and electronic information on much larger depth scales than conventional XPS¹⁻³ has potential application in the study of buried interfaces, as found at the oxide/semiconductor interface, particularly if changes at this interface are of interest following the subsequent deposition of a metal capping layer in the fabrication of MOS structures. Photoemission sampling depths in excess of 10 nm⁴ allow for direct comparison between results obtained from electrical characterisation techniques and photoemission experiments, as these measurements can be made on identical structures, thereby bridging the gap between interface chemistry and electrical properties at buried interfaces. Both n and pdoped substrates were investigated before and after the deposition of a metal gate in order to study any difference in Fermi level behaviour between the different doping types. The use of n and p-doped substrates also ensured samples with both a small and large difference between the substrate and metal workfunction for both Al (whose workfunction is close to the flatband position of n-InGaAs)

and Ni (whose workfunction is close to the flatband position of p-InGaAs). This enables the Fermi level movement through the entire bandgap to be investigated. Initial experiments were performed on HfO₂/InGaAs based MOS structures, where high (Pt) and low (Al) workfunction metals are deposited as the gate metal in order to induce band-bending in the valence and conduction bands of the InGaAs, thus resulting in the Fermi level moving towards the valence or conduction bands respectively. These results were compared with surface potential measurements derived from capacitance-voltage profiling (C-V), the conventional method by which to determine the electrical performance of a MOS structure, on near identical samples in order to evaluate the accuracy of the HAXPES method. While Fermi level differences are detected for both n and p-InGaAs samples, and the samples capped with high and low workfunction metals, an issue with photon energy drift was encountered and this issue along with a working solution will be discussed.

Finally, the complementary HAXPES and C-V method of characterising the electrical structure of MOS devices was employed to characterise SiO_2/Si based structures. For this study, exploring the combination of HAXPES and electrical characterisation techniques, the experiments were performed on SiO_2/Si MOS structures. This system was selected as the interpretation of the multi-frequency C-V response is well developed,⁵ the interface is representative of an unpinned surface Fermi level, and the structure allows accurate determination $(\pm 50 \text{ meV}^6)$ of surface potential for a given gate voltage based on C-V measurements. The samples were formed over n and p-doped silicon substrates and were capped with high (Ni) and low (Al) work function metals to induce surface potential shifts at the SiO_2/Si interface for examination by the HAXPES and C-V methods. Using a photon energy of 4150 eV in these investigations allowed for the simultaneous detection of photoemission signals from metal, oxide and substrate core levels. The band gap of Si (1.1 eV) is wide enough to allow differences in the binding energy (BE) of the n and p-doped substrate core levels to be detected, which directly reflect different Fermi level positions in the band gap.⁷ Attempts were made to perform similar experiments on forming gas (H_2N_2) annealed SiO₂/Si based structures in order to obtain the ideal Fermi level behaviour seen in C-V measurements of identical samples.⁸ The issues encountered in the performance of these anneals are explained.

3.2 Experimental Details

All of the samples described below were fabricated in the Tyndall National Institute, where transmission electron microscopy (TEM) and C-V measurements and analysis were also performed.⁹

Al-Silicide Samples

High quality thermally grown SiO₂ layers, with a thickness of 8 nm, were grown using a dry oxidation process in a furnace at 850 °C on both n (2-4 Ω cm, 1x10¹⁵ cm⁻³ Phosphorus) and p (10-20 Ω cm, 1x10¹⁵ cm⁻³ Boron) doped silicon(100) substrates following a standard silicon surface clean. The samples were capped with 5 nm Al blanket films by electron beam evaporation. These samples were either left unannealed or annealed at 350 or 450 °C in a UHV system so as to limit the further oxidation of the Al cap.

HAXPES measurements were carried out on the National Institute of Standards and Technology (NIST) beamline X24a at the National Synchrotron Light Source at Brookhaven National laboratory, as described in section 2.2. Samples were fixed on a grounded Al sample holder with stainless steel clips, which connected the front of the samples to the sample holder. The sampling depth for the HAXPES measurements is estimated to be no more than 24 nm¹⁰ for the substrate Si 1s which has a kinetic energy of 2310.5 eV for the 4150 eV photon energy used in these studies,¹¹ where the total sampling depth includes the ability to detect the whole of the 5 nm of metal, 8 nm of oxide, and no more than 11 nm sampling depth into the Si. The sampling depths of the Si 1s for the 2140 eV, and 3000 eV photon energies are approximately 10 nm, and 15 nm respectively. The energy resolution and the method used to measure it will be described later in this chapter.

HfO₂/InGaAs Samples

The HfO₂/InGaAs samples used epitaxial n (S-doped at $4 \times 10^{17} \text{ cm}^{-3}$) and p (Zndoped at $4 \times 10^{17} \text{ cm}^{-3}$) In_{0.53}Ga_{0.47}As (hereafter referred to as InGaAs), grown on lattice matched InP. The InGaAs surfaces were initially degreased by sequentially rinsing for 1 minute each in acetone, methanol, and isopropanol. The InGaAs samples were immersed in (NH₄)₂S solutions (10% in deionized H₂O) for 20 minutes at room temperature (295 K), which was found to be the optimum approach to suppress the formation of native oxides and to reduce the high- κ /III-V interface state density, as reported previously.¹² Samples were then introduced to the atomic layer deposition (ALD) chamber load lock after the removal from the 10% (NH₄)₂S surface passivation solution. The transfer time from the aqueous (NH₄)₂S solution to the ALD chamber was kept to a minimum (3 minutes) in order to minimise the formation of native oxides resulting from air exposure.

The 5 nm HfO₂ was deposited by ALD at 250 °C using Hf[N(CH₃)C₂H₅]₄ (TEMAH) and H₂O precursors. Some samples were left without a metal gate, while others were capped with 5 nm Al or Pt blanket films. All metal depositions were achieved by electron beam evaporation. Additional samples were produced for electrical characterisation analysis in an identical fashion to that mentioned above, although the metal caps were 110 nm thick so that they could be used as contacts in the C-V measurement process. The metal gate areas for C-V characterisation were defined by a lithography and lift-off process.

SiO_2/Si Samples

The SiO₂/Si based MOS structures were prepared in an identical manner to the Al-silicide samples previously described, with the exception that some samples were left without metal gates and some were capped with 5 nm Ni blanket films by electron beam evaporation instead of Al, as shown in figure 3.1. The sample set measured by HAXPES is shown in table 3.1. For electrical characterisation, Ni/Au (90 nm/70 nm) and Al (160 nm) gate electrodes were formed by electron beam evaporation and a lift off lithography process. The Si/SiO₂ samples did not



Figure 3.1: SiO_2/Si samples for HAXPES and C-V characterisation. Si substrates were capped with an 8 nm SiO_2 layer and either left without a metal gate or capped with a 5 nm Al or Ni gate.

Substrate	Dopant type	Dielectric	Metal
Si	n-type	SiO_2 (8 nm)	none
Si	n-type	SiO_2 (8 nm)	Al (5 nm)
Si	n-type	SiO_2 (8 nm)	Ni (5 nm)
Si	p-type	SiO_2 (8 nm)	none
Si	p-type	SiO_2 (8 nm)	Al (5 nm)
Si	p-type	SiO_2 (8 nm)	Ni (5 nm)

Table 3.1: SiO_2/Si samples for HAXPES analysis

receive a final forming gas (H_2/N_2) anneal.

In order to ensure correct energy calibration throughout the experiment, metallic Ni Fermi edge reference spectra were acquired immediately before and after the acquisition of the SiO₂ and Si substrate core level peaks. The resultant error associated with this photon energy correction procedure is estimated to be no more than ± 50 meV. The maximum depletion region width for the 1×10^{15} cm⁻³ doped Si substrate is 800 nm, and the total sampling depth of the HAXPES measurements is estimated to be no more than 23 nm¹⁰ for the substrate Si 1*s* which has a kinetic energy of 2310.5 eV for the 4150 eV photon energy used in these studies.¹¹ The total sampling depth includes the ability to detect the whole of the 5 nm of metal, 8 nm of oxide, and no more than 11 nm sampling depth into the Si. Therefore, the BE of the acquired Si substrate core level peaks directly reflect the position of the Fermi level in the silicon at the SiO_2/Si interface i.e. the surface Fermi level position. However, it is noted that for Si samples in inversion, which exhibit strong surface band-bending, the sampling depth of the HAXPES may cause the peaks to shift by up to 0.1 eV to lower BE.¹³

The C-V measurements were recorded using an Aligent C-V-enabled B1500A semiconductor device analyser following an open correction and performed in a Cascade Microtech probe station (model Submit 12971B) in a dry air, dark environment. The B1500A analyser allows for C-V measurements performed at a wide range of AC frequencies (1 kHz to 5 MHz). All the C-V responses were measured starting from inversion and sweeping towards accumulation in order to reduce the effect of border traps, which shift the measured C-V curve.¹⁴ An AC frequency of 1 MHz was used in order to minimise the contribution of an interface state capacitance to the overall capacitance of the MOS capacitor. Under this condition, the primary effect of the interface states is to stretch out the C-V along the gate voltage axis so that Fermi level position can be determined, using the measured capacitance providing that the MOS capacitor is in depletion at $V_g = 0$ V. Multiple sites with different areas were examined in order to ensure the C-V results are representative of the sample behaviour.

3.3 Results and Discussion

3.3.1 Energy Resolution as a Function of Photon Energy

In a non-monochromated XPS system the energy resolution is determined by the anode material and electron analyser, while in a HAXPES system it is determined by the monochromator and electron analyser, as described in section 2.2. The overall instrumental energy resolution is the product of the convolution of the monochromator energy bandwidth and analyser resolution. The energy bandwidth of the monochromator is described as:

Energy bandwidth =
$$\frac{\Delta E}{E} = \frac{\Delta \lambda}{\lambda} \approx 0.1\%$$
, (3.1)

where E is the photon energy and λ is the wavelength. The monochromator energy bandwidth is usually approximated as 0.1% of the photon energy, and as such an increase in the photon energy results in an increase in the energy bandwidth, and thus a decrease in the resolving power of the instrument (increase in absolute resolution).

This energy resolution dependence on photon energy can be seen clearly in Si 2p spectra, as shown in figure 3.2. Uncapped SiO₂/Si structures identical to those shown in figure 3.1 were measured using photon energies of 2140, 3000, and 4150 eV. In the Si 2p spectra, the doublet $(2p_{3/2} \text{ and } 2p_{1/2})$ corresponding to substrate Si (at BE of 100 eV) becomes less well resolved as the photon energy is increased. Similarly the full-width half-maximum (FWHM) of measured peaks should increase as the resolution decreases, as can be seen in the Al 1s spectra of Al capped SiO₂/Si samples, shown in figure 3.3. As the photon energy is increased from 2140 eV to 3000 eV and finally to 4150 eV, the FWHM of the Al oxide peak, originating from the Al₂O₃ layer, increases from 1.56 to 1.65 to 1.76 eV.

The resolution of the HAXPES system is estimated by the measurement and fitting of the Fermi edge of a reference metallic sample; Ni was used in this study. The acquired spectra are then fitted with a convolution of a simulated step function and Gaussian curve, as shown in figure 3.4. The FWHM of the Gaussian curve



Figure 3.2: Normalised Si 2p spectra of Si substrates displaying the decrease in the FWHM of the oxide peak as the photon energy is varied.



Figure 3.3: Al 1s spectra of oxidised 5 nm Al metal films, normalised to the oxide peak. The change in the oxide peak FWHM is highlighted.



Figure 3.4: Ni Fermi edge spectrum, acquired at 4150 eV, fitted with a convolution of a 0.52 eV Gaussian and step function in order to measure the system resolution.

is adjusted until good agreement is reached in the fit of the simulation to the experimental Fermi edge. This FWHM is the resolution of the system at that photon energy. As can be seen in figure 3.4, the resolution for spectra acquired at 4150 eV is 0.52 eV; similar measurements have been performed for photon energies of 2140 eV and 3000 eV, giving energy resolutions of 0.27 eV and 0.39 eV respectively.

3.3.2 Investigation of Sampling Depth

An investigation of the sampling depth achievable with HAXPES was performed. Al/SiO₂/Si samples were studied using photon energies of 2140 eV, 3000 eV and 4150 eV. The layer thicknesses are the same as those in figure 3.1, however the Al cap has a surface oxide present which increases the cap thickness. The wide energy range survey scans of the samples are shown in figure 3.5. It is clear from these that a photon energy of 2140 eV is insufficient to detect the Si 1s peak originating from the SiO₂ layer beneath the Al; the 3000 eV survey shows both the presence of the Al and SiO₂ layers, while the 4150 eV survey scan shows the presence of Al, SiO₂ and Si substrate peaks, indicating that a sufficient number of electrons are escaping from each layer in the structure to provide a measurable signal. While the Si 2p has a greater sampling depth than the Si 1s, due to its greater kinetic energy, the photoionisation cross section of the Si 2p is much lower than the Si 1s, and thus the advantage gained from a greater sampling depth is negated by the decrease in the number of Si 2p electrons detected. In summary, the Si 1s core level grants the greatest possibility of detecting the SiO₂ and Si substrate layers within the survey spectrum.



Figure 3.5: Survey spectra for $Al/SiO_2/Si$ samples at photon energies of 2140 eV, 3000 eV and 4150 eV demonstrating the change in sampling depth.

Theoretical calculations of the inelastic mean free path (IMFP) of high energy electrons in materials indicate that the sampling depth into the Si substrate for the 4150 eV photon energy is 11 nm.¹⁵ Using the information gained from the survey scans, the combined sampling depth into the $Al/SiO_2/Si$ structures is approximately 4 nm, 12 nm and 23 nm for photon energies of 2140 eV, 3000 eV and

4150 eV respectively. The large difference in sampling depth between the 3000 eV and 4150 eV measurements is due to the sampling depth into the Si substrate. The sampling depth into substrate Si is approximately 10 nm at 4150 eV, so once electrons from this layer are detected at a sufficient intensity to rise above the background they are being emitted from within this sampling depth. The sampling depth can also be demonstrated by the investigation of the Al 1s peak at each photon energy, as shown in figure 3.6. As previously stated, the Al cap undergoes surface oxidation due to air exposure, and as such the 5 nm deposited Al film expands, with oxidised Al on the surface. As the photon energy, and thus the sampling depth, is increased the metal signal increases relative to the oxide signal.



Figure 3.6: Normalised Al 1s spectra of oxidised 5 nm Al metal films displaying the relative change in intensity in the metal and oxide peak as the photon energy, and thus the sampling depth, are varied.

3.3.3 Al-Silicide Study at the Al/SiO₂ Interfaces

The extended sampling depth and greater energy resolution of HAXPES over conventional XPS was applied in the study of Al-silicide formation in Al/SiO₂/Si structures identical to those shown in figure 3.1. Previous investigations of the Al/SiO₂ interface in the literature describe the dissociation of the SiO₂ by metallic Al and the subsequent formation of Al₂O₃ and 'free' Si.^{16–20} A study by *Hentzell et. al*²¹ did report the formation of Al-silicide between Al and Si layers by x-ray diffraction and Auger spectroscopy, although there are no XPS studies showing similar results.

The Si 1s spectra, shown in figure 3.7, show that in the sample prior to anneal the peak profile can be fitted by two peaks relating to Si-Si bonds from the substrate Si, and oxidised Si from the SiO₂ layer. Following an anneal in a UHV environment at 350 °C, two additional peaks, one at 1848.5 eV and one peak at 1852.5 eV appear. By investigation of the electronegativities of the elements present: Al (1.61), O (3.44), Si (1.90) and C (2.55),²² it is clear that aluminium is the only element which after bonding with Si would result in a peak at a lower BE position than Si-Si bonds. The small peak at 1852.5 eV is harder to absolutely identify as it could be due to either a Si suboxide state, such as Si_2O_3 , or an Al-silicate. An increase in anneal temperature to 450 °C results in an increase in the Al-silicide peak; the peak also shifts to higher BE by approximately 0.5 eV. This shift is thought to be due to the fact that the Al-silicide present in the 350 °C spectra is of mixed stoichiometry, and the increase in anneal temperature results in the conversion of all of the Al-silicide to a single stoichiometry, possibly $AlSi_2$. The large heat of formation of $AlSi_2$ as compared to other metal silicides may explain the lack of evidence for its formation in the literature.²³ Analysis of the Si spectra also show a slight increase in the bulk Si peak following the $350 \,^{\circ}\text{C}$ anneal, which agrees with the SiO_2 dissociation seen in previous XPS studies.^{16–19} However, following the 450 °C anneal a reversal in this trend is seen due to the consumption of the excess 'free' Si in the Al-silicide formation.



Figure 3.7: Normalised Si 1s spectra of Al/SiO₂/Si samples, before anneal (20 °C), and following 350 °C and 450 °C anneals, acquired at a photon energy of 4150 eV.

The Al 1s spectra of the same samples are shown in figure 3.8. The peak profile of all samples can be fitted with three peaks: Al metal at 1559 eV, Al_2O_3 at 1562.3 eV and an Al suboxide at 1560.2 eV. The oxidised Al peaks are due to the surface oxidation of the deposited Al layer. Any Al-silicide peak should appear between the Al metal and Al_2O_3 peaks, and as such it can be difficult to distinguish between Al-silicide and Al suboxides. The consumption of Al metal, and subsequent increase in Al_2O_3 seen in the Al 1s spectra is also due to the SiO₂ dissociation and subsequent formation of Al_2O_3 .



Figure 3.8: Al 1s spectra of Al/SiO₂/Si samples, before anneal (20 °C), and following 350 °C and 450 °C anneals, acquired at a photon energy of 4150 eV.

The location of the Al-silicide can be investigated by acquiring a more bulk sensitive Si peak in order to alter the sampling depth of the measurement. To this end the Si 2p peak was acquired at both 4150 eV and 2140 eV, as shown in figures 3.9 and 3.10. The Si 1s acquired at 4150 eV has a sampling depth of approximately 11 nm, while the Si 2p peaks acquired at 4150 eV and 2140 eV (with kinetic energies of 4050 eV and 2040 eV) have a sampling depth of 20 nm and 10 nm, respectively. In a comparison of the intensity of the substrate Si and the Alsilicide peaks for the 350 °C sample acquired at the bulk sensitive 4150 eV, and the surface sensitive 2140 eV photon energies, the silicide peak in the surface sensitive data is larger with respect to the bulk Si, indicating the Al-silicide is located above the substrate Si layer. Comparison between the silicide and the SiO₂ peaks shows that the silicide peak decreases in size relative to the SiO₂ in the more surface sensitive (2140 eV) spectra, indicating that the silicide is present below the SiO₂ layer, at the SiO₂/Si interface, as shown in figure 3.11. This suggests diffusion of Al through the SiO₂ to form Al silicide at the Si/SiO₂ interface.


Figure 3.9: Bulk sensitive Si 2p spectra of Al/SiO₂/Si samples, before anneal (20 °C), acquired at 2140 eV, and following 350 °C and 450 °C anneals acquired at a photon energy of 4150 eV.



Figure 3.10: Surface sensitive Si 2p spectra of Al/SiO₂/Si samples before anneal (20 °C), and following 350 °C and 450 °C anneals, acquired at a photon energy of 2140 eV.



Figure 3.11: Diagram of the structure of the $Al/SiO_2/Si$ sample following thermal anneal, showing the location of the Al-silicide at the SiO_2/Si interface.

This work has shown the formation of an Al silicide in $Al/SiO_2/Si$ MOS structures. While this formation has been shown on multiple samples more work is required to fully explain both the formation process and the stoichiometry of the silicide.

3.3.4 HAXPES Characterisation of HfO₂/InGaAs Based MOS Structures

While conventional laboratory based XPS continues to be of great use in the area of surface science in understanding chemical interactions and electronic structure, of both Si and III-V based semiconductors, one of the main weaknesses is that all layers must be no more than 2 to 3 nm thick in order to stay within the limited probing depth of 4 to 5 nm of standard X-ray sources (1 to 1.5 keV). This limitation is particularly relevant in measuring complete MOS structures. While a certain amount can be understood from the measurement of thinner layer structures, there

are problems in ensuring the uniformity of thin (2 to 3 nm) deposited layers. This gap in knowledge is one of the key contributions HAXPES can make to current understanding, as due to the much higher energies achievable with HAXPES, penetration depths of up to 30 nm are achievable, hence thicker metal and oxide layers can be probed.

In XPS measurements, if the sample is in electrical contact with the spectrometer, and is adequately grounded, the Fermi level of the sample and the spectrometer are at the same energy, as shown in figure 2.2. As such, the binding energy of every core level is measured relative to this Fermi level, so if for any reason the Fermi level in the sample 'moves', the core level binding energies should also shift correspondingly. It was decided to investigate the ability of HAXPES to determine Fermi level differences between heavily n and p-doped InGaAs substrates with 5 nm HfO_2 layers on top, which should have Fermi levels near the conduction and valence bands respectively, and subsequently investigate the Fermi level movement in both following the deposition of either high (Pt) or low (Al) workfunction metals on top of the HfO_2 layers. The use of high and low workfunction metals should be able to induce band-bending in the n or p-InGaAs, to move the Fermi level toward the conduction band for the low workfunction metal, or the valence band for the high workfunction metal, if the Fermi level is not pinned at the $HfO_2/InGaAs$ interface. The sweeping of the Fermi level from the conduction band to the valence band is intended to mimic a C-V measurement, which uses a bias to sweep the Fermi level through the bandgap, as described in section 2.4. The idea is then to perform C-V characterisation to investigate the Fermi level movement in a MOS structure, on near identical samples, with only the metal thickness (110 nm as opposed to 5 nm) differing. The C-V results would thus be used to verify the HAXPES results of Fermi level movements.

TEM images of the samples show the actual thickness of the Pt caps was 6 nm and show the extensive oxidation of the Al cap which acts to increase the cap thickness to 10 nm, as seen in figure 3.12.²⁴

Spectra of the As 2p and Ga 2p (not shown) core levels were acquired for each sample as shown in figure 3.13. It was noticed that the photon energy, and thus



Figure 3.12: TEM images of $HfO_2/InGaAs$ samples (a) without a metal cap, (b) with an Al cap, and (c) with a Pt cap. Layer thicknesses as measured by TEM are indicated.

the peak position varied as a function of time which will be discussed in detail later in this chapter. In order to account for this temporal variation of the photon energy, reference Ag 3d and Fermi edge spectra were acquired before and after each sample was measured in order to determine the precise photon energy. This enabled the InGaAs core level positions to be corrected to a precision of $\pm 150-200$ meV. The band-gap of InGaAs is 0.75 eV so ideal results for the uncapped n and p-InGaAs samples should measure a peak separation of approximately 0.68 eV for these doping levels.⁵ The Fermi level of the uncapped p-doped samples appears at lower binding energy than the respective n-type sample, as expected, although the magnitude of the difference (0.31 eV) is smaller than would be expected for heavily doped n and p-InGaAs if the Fermi levels were in their flat band positions.

The next important measurement is the determination of the absolute position of the n and p-InGaAs Fermi levels within the InGaAs bandgap. Valence band edge spectra are used for this purpose, as they allow the offset between the valence band and the Fermi level of the sample to be determined. This, combined with the knowledge of the InGaAs bandgap (0.75 eV), allows the absolute position of the Fermi level to be determined. The valence band spectra for the uncapped, Al capped, and Pt capped n-InGaAs MOS structures are shown in figure 3.14.



Figure 3.13: Normalised As 2p core level spectra acquired at a photon energy of 4150 eV for the uncapped HfO₂/InGaAs, Pt (5 nm) capped HfO₂/InGaAs, and Al (5 nm) capped HfO₂/InGaAs samples, showing the shifts in the core level after metal deposition for (a) n-InGaAs, and (b) p-InGaAs substrates. The dotted lines show the energy separation between n and p-type samples without metal gates.



Figure 3.14: Normalised valence band spectra of uncapped, Al, and Pt capped $HfO_2/InGaAs$ MOS structures on n-InGaAs.

In the uncapped sample the valence band maximum (VBM) of the n-InGaAs can be clearly seen. Extrapolation of this feature to zero on the y-axis yields a value of 0.82 eV, this is the offset between the valence band and the Fermi level in the n-InGaAs.²⁵ Combining this measurement with a bandgap of 0.75 eV for InGaAs, we estimate the Fermi level of the n-InGaAs sample to firstly lie above its flatband position of approximately 0.72 eV, and also to lie 0.07 eV above the conduction band minimum, suggesting that the Fermi level of the n-InGaAs is in the conduction band. This is consistent with previous reports of the InGaAs Fermi levels residing in the conduction band, as measured by the combined split capacitance-voltage method and Hall measurements. InGaAs has a high density of interface states (D_{it}) in the conduction band, leading to Fermi level pinning there.²⁶ Similar measurements on p-InGaAs samples yield a value of 0.45 eV for the valence band offset from the Fermi level position, which is in the middle of the InGaAs bandgap, once again indicating the presence of band-bending in the InGaAs Fermi level prior to any metal deposition, most likely due to D_{it} at the $HfO_2/InGaAs$ interface.

The effect of metal deposition on the BE position of the As 2p core level can be seen in figure 3.13. If the Fermi level at the $HfO_2/InGaAs$ interface is free to move, it would be expected to align with the metal Fermi level resulting in an increase in band-bending (increase in BE) for the n-InGaAs with the low work function Al (4.08 eV) contact, and an increase in the n-InGaAs band-bending in the opposite direction (reduction in BE) for the high work function Pt (6.35 eV) contact. For the p-InGaAs, an increase in band-bending (increase in BE) with the low work function Al contact, and a decrease in the band-bending (reduction in BE) for the high work function Pt contact would be expected. HAXPES measurements show that for the p-InGaAs sample the core level peaks shift 0.33 eV to higher BE, and for the n-InGaAs sample the peaks shift 0.16 eV to lower BE, following the deposition of Al contact. Following the deposition of Pt the peak positions shift 0.39 eV for n-InGaAs and 0.29 eV for p-InGaAs to lower BE. The directions of the BE shifts observed in n-InGaAs following Pt deposition, and p-InGaAs following Al and Pt deposition, are consistent with the differences in the Fermi level positions for the InGaAs substrates and metals, however the magnitudes differ. However, the shift seen following Al deposition on n-InGaAs is opposite to the expected shift direction, especially seeing as the electron affinity of InGaAs is 4.5 eV, which is far below the workfunction of Al (4.08 eV). This shift is most likely due to the large error in measuring peak BE positions.

Upon analysis of the HAXPES data it was realised that the correction procedure used, whereby Ni reference scans are taken before and after each sample, was insufficient to account for the photon energy drift. The correction procedure used gave an accuracy in determining the peak position of approximately ± 150 -200 meV, which is close to the magnitude of shifts which would be expected across a 0.75 eV bandgap. As such, none of the measurements on this sample set were accurate enough to warrant the performance of the equivalent C-V measurements.

3.3.5 Photon Energy Drift

The photon energy drift issue was a result of the high intensity synchrotron radiation striking the first crystal in the double crystal monochromator arrangement described in section 2.2. At the National Synchrotron Light Source the beam is injected twice daily in the x-ray ring. As a result the beam current, and thus it's intensity, is at a maximum after injection and decays throughout the 12 hour run time. The intensity of the radiation heats up the first crystal which expands, thereby increasing the lattice spacing (d) in the Bragg equation:

$$n\lambda = 2d\sin(\theta),\tag{3.2}$$

where θ is the angle of incidence between the crystal and the incoming radiation, n is the order number, and λ is the wavelength of the light. In the Bragg equation the angle θ is chosen so as to diffract the desired wavelength (and thus energy) photons through the exit slit of the monochromator; these photons are then used to perform HAXPES measurements. However, if d changes then the angle (θ) needed to produce a desired energy changes. As can be seen from the above equation, as the beam intensity decays the first crystal cools, and so d decreases as does λ for fixed angle θ . The energy of a photon is inversely proportional to its wavelength, as described by Max Planck:

$$E = \frac{hc}{\lambda} \tag{3.3}$$

As the wavelength decreases the photon energy in the HAXPES measurement should increase.

The first crystal is water cooled in an attempt to control the heating issue, though the water cooling does slow down the heating it is not sufficient to negate the problem. A feedback system is used which adjusts the angle and height of the the second crystal in order to ensure that the photons which are focussed on the exit slit of the monochromator are of the desired energy. Once again this method does help but is not sufficient to keep the photon energy constant throughout the beam fill. In order to quantify the drift, the photon energy was measured throughout a beam fill, by acquisition of Pt Fermi edges, and the results are plotted in figure 3.15. The photon energy drift is approximately linear in nature, with a drift of 0.18 eV an hour. In the $HfO_2/InGaAs$ MOS measurements described in the previous section, acquisition of all of the relevant core levels in a sample took 30 to 40 minutes, so by taking reference scans before and after each sample we could only



Figure 3.15: Graph of the photon energy as a function of time, as measured by the Ni Fermi edge, showing an approximately linear nature.

determine the photon energy to within 150 to 200 meV. This error is too large, so it was decided that in future sample sets it would be necessary to acquire reference metallic spectra before and after every core level. The acquisition of an individual core level takes 3 to 5 minutes, and the photon energy drift in that time is <50meV which was a more acceptable level of uncertainty in the measurements.

3.3.6 A Combined HAXPES and Electrical Characterisation Study of SiO₂/Si(100) Based MOS Structures

After the photon drift issues encountered in the $HfO_2/InGaAs$ MOS measurements, it was decided that the first joint C-V and HAXPES experiment should be performed on an electrically well understood system, and so the SiO₂/Si system was chosen. This is the most widely studied and used MOS material system, therefore it gives a benchmark by which the joint C-V and HAXPES method can be verified. As mentioned earlier, Ni reference peaks were acquired before and after the acquisition of each core level in order to minimise the affect of photon energy drift on the measured BE positions. The samples used were n and p-doped Si substrates with an 8 nm SiO₂ layer and the samples were left without a metal gate or capped with a 5 nm Al or Ni gate. The sample structure can be seen in figure 3.1.

Figure 3.16 shows the Si 1s core level spectra originating from the substrate and the 8 nm SiO₂ layer for both n and p-Si, with and without the presence of a metal gate. The BE positions of the core level peaks are measured, and the difference between the n and p-Si substrates is used to estimate the Fermi level separation at the SiO₂/Si interface. HAXPES measurements on the uncapped SiO₂/Si samples revealed that the BE position for the p-Si peaks was 0.32 eV lower than the n-Si, consistent with the Fermi level residing closer to the valence band edge for p-type, and closer to the conduction band edge for n-type. The difference is, however, less than the expected value of 0.57 eV, which is calculated from the theoretical Fermi level position difference for n and p-Si with a doping concentration of 1×10^{15} cm⁻³.⁵

The reduction in measured difference in the Si 1s core level BE indicates that there is band-bending present at the SiO_2/Si interface, even in the absence of a metal overlayer. In order to establish the approximate position of the Fermi level in the band gap with respect to the valence band edge prior to metal deposition, valence band spectra were acquired at the same photon energy. A linear extrapolation of the Si valence band to a zero signal intensity yields the approximate position of the valence band edge,²⁷ as shown in figure 3.17. Although more accurate methods have been recently employed,²⁸ this method is sufficient to provide the accuracy required here. Reference spectra of a sample with a Ni gate were subsequently taken, and the Ni metallic edge was used to establish the Fermi level position at 0 eV BE on the x-axis. These measurements show that the Fermi level of the n-type sample is 0.95 eV above the valence band edge, indicating an accumulated surface with the surface Fermi level above its flat band position of 0.85 eV above the valence band. Similar measurements for the p-type sample show the Fermi level is 0.66 eV above the valence band edge, which is above its flat band position of 0.28 eV, indicating that the p-type surface is weakly inverted. Both



Figure 3.16: Normalised Si 1s core level spectra acquired at a photon energy of 4150 eV for the uncapped SiO₂/Si, Ni (5 nm) capped SiO₂/Si, and Al (5 nm) capped SiO₂/Si samples, showing the shifts in the core level after metal deposition, and the changes in the potential across the SiO₂ layer caused by different work function metals for (a) n-Si, and (b) p-Si substrates. The dotted lines show the energy separation between n and p-type samples without metal gates.



Figure 3.17: Valence band spectra of an n-type SiO_2/Si sample, showing the measured valence band offset.

of these observations are consistent with fixed positive charge in the SiO₂, which is expected based on the oxidation temperature of 850 °C and the absence of any post deposition annealing.²⁹

The effect of the deposition of high (Ni 5.15 eV²²) and low (Al 4.1 eV²²) work function metals (5 nm), on the SiO₂ surface, on the Si 1s BE is also shown in figure 3.16. If the Fermi level at the SiO₂/Si interface is free to move, it would be expected to align with the metal Fermi levels, resulting in a slight increase in band-bending (increase in core level BE) for the n-type substrate with the low work function Al contact, given that the electron affinity of Si is 4.05 eV. For the Ni contact, a large increase in band-bending (reduction in core level BE) would occur as Ni has a high work function. Alternatively, for the p-type substrate, an Al contact would result in an increase in band-bending (increase in core level BE), while a Ni contact would result in a decrease in band-bending (decrease in core level BE). HAXPES measurements in figure 3.16 for samples with Al gates show that the Si 1s signal originating from the silicon substrate, located at a BE of 1839 eV, shifts 0.14 eV for the p-type and 0.08 eV for the n-type to higher BE. While for the Ni gate, the Si 1s peak shifts 0.12 eV for the p-type, and 0.22 eV for the n-type to lower BE. The experimentally observed shifts for the samples with metal gates are therefore consistent with the direction of expected surface Fermi level movement, while not matching the expected shift magnitudes.

The limited ability to move the Fermi level closer to the valence band edge with the high work function Ni is consistent with fixed positive charge in the SiO₂ which will tend to accumulate electrons at the SiO₂/Si interface. In addition, as the samples received no final forming gas (H₂/N₂) anneal, it is expected that interface defects originating from silicon dangling bonds (P_b centres) will be present, which will also restrict somewhat the movement of the surface Fermi level. The P_b centres at the SiO₂/Si(100) interface have levels in both the lower and upper energy gap regions.^{30–32}

Work function differences between the metal and the partially pinned Si Fermi level should also result in a potential difference across the oxide layer which should manifest as a BE shift of the associated oxide core levels.^{3, 7} These changes would be expected to be most apparent between the n-Si and the Ni, or the p-Si and the Al, as these both represent the largest difference in work functions. The spectra in figure 3.16 also show the changes in BE of the Si 1s oxide peak (located at 1844) eV) for both dopant types resulting from metal deposition. For a p-type sample the deposition of the low work function Al results in an increase in the Si 1s oxide peak BE of 0.31 eV, reflecting a potential decrease consistent with the alignment of the metal work function and semiconductor Fermi level. For the Ni capped p-type sample, a decrease in the BE of 0.38 eV is measured, reflecting a potential increase across the oxide caused by the high work function Ni contact after Fermi level alignment. The corresponding BE shifts for the n-type sample were 0.09 eV to higher BE, and 0.67 eV to lower BE for the Al and Ni cap, respectively. All of these changes are consistent with the expected polarity of the potential difference across the oxide layer, caused by the low and high work function metals. Figures 3.18(a) and (b) show a schematic diagram illustrating the changes in BE due to Fermi level movements and potential differences across the SiO_2 for a p-Si substrate following the deposition of Al and Ni contacts, respectively. The centre of the Si 1s oxide peak is located at a weighted average of the photoemission signal

intensity from the different depths into the oxide.³ Note that the shift resulting from Fermi level movement in the bulk Si is also present in the oxide peaks, so any shift in the oxide peaks is a combination of the Fermi level movement and a potential difference across the oxide.



Figure 3.18: (a) Band diagram, illustrating the BE shifts due to an electric field across the oxide caused by metal deposition, for p-Si showing a potential difference across the oxide for a p-type sample with an Al gate. (b) Band diagram showing a potential difference of the opposite polarity for a p-type sample with a Ni gate.

The C-V responses recorded at an AC signal frequency of 1 MHz for the corresponding Al (160 nm) and Ni/Au (160 nm) gate SiO_2/Si MOS capacitors for the n

and p-Si are shown in figures 3.19 (a) and (b), respectively.⁹ The multi-frequency C-V responses from 1 kHz to 1 MHz, as seen in figure 3.20 (a)-(d), do exhibit the features associated with P_b defects at the SiO₂/Si interface, consistent with previous publications.³¹ The presence of unpassivated silicon dangling bonds (P_b defects) is expected as the samples did not receive a final forming gas anneal. The AC signal frequency of 1 MHz was selected to minimise the effect of the silicon dangling bond defects on the C-V response. Considering first the surface potential at 0 V, which is the condition for the HAXPES measurements, the C-V observations match the expected results, and are consistent with the HAXPES measurements, indicating the following: surface accumulation for the Al gate over the n-type, inversion of the surface for the Al gate over p-type, and depletion of the surface for the Ni gate over both n and p-type. From the C-V responses, the surface potential at 0 V can also be calculated by fitting the C-V with a Poisson C-V solver.^{33, 34} From the resulting surface potentials (ϕ_s) , the values of $E_f - E_v$ at 0 V are shown in figure 3.19, and compared with the corresponding HAXPES measurements in table 3.2. The shift in surface potential for the Al with respect to the Ni gate samples on n-Si is 0.36 eV, which compares to the value of 0.3 eV from HAXPES. For the p-type sample the surface potential shift from the Al to the Ni gate is 0.28 eV, which compares to 0.26 eV from the HAXPES as shown in table 3.2. When taking into account the errors in surface potential for the two methods which are ± 50 meV for both the HAXPES and C-V fitting, this is a good agreement between the HAXPES and C-V analysis. Note that the E_f - E_v result for Al/SiO₂/Si on p-Si is given as a range, due to the fact that HAXPES is measuring 11 nm into the Si substrate, and the strong surface band-bending present in this sample may result in the core level peaks shifting by up to 0.1 eV to lower BE, as modelled by numerically solving Poissons equation to produce a band-bending profile.¹³ The increase in capacitance, observed in figure 3.19 (b) for the p-type $Al/SiO_2/Si MOS$ structure at positive gate bias, is attributed to peripheral inversion effects.³⁵



Figure 3.19: C-V characteristics (1 MHz) for the metal/SiO₂/Si samples with Al and Ni gates for both (a) n-type, and (b) p-type substrates, displaying both the flat band shifts ΔV_{fb} and the calculated surface Fermi level (E_f) position at zero gate voltage. The Fermi level position is with respect to the valence band (E_f-E_v)



Figure 3.20: Multi-frequency (1 kHz - 1 MHz) C-V characteristics for (a) $Al/SiO_2/n-Si$, (b) $Ni/SiO_2/n-Si$, (c) $Al/SiO_2/p-Si$ and (d) $Ni/SiO_2/p-Si$ samples, clearly displaying the presence of interface defects.

Sample	E_f - E_v	E_f - E_v	E_f - E_v	ΔE_f	Flat-band
	(SiO_2/Si)	$(Al/SiO_2/Si)$	$(Ni/SiO_2/Si)$	(Al-Ni shift)	(Al-Ni shift)
n-type	n/a	1.00 eV	$0.64 \mathrm{~eV}$	$0.36 \ \mathrm{eV}$	$0.7 \ \mathrm{eV}$
(C-V)					
n-type	$0.95~{\rm eV}$	$1.03 \ \mathrm{eV}$	$0.73~{ m eV}$	$0.3 \ \mathrm{eV}$	$0.76~{\rm eV}$
(HAXPES)					
p-type	n/a	$1.05 \ \mathrm{eV}$	$0.77~{\rm eV}$	$0.28 \ \mathrm{eV}$	$0.66 \ \mathrm{eV}$
(C-V)					
p-type	$0.66 \ \mathrm{eV}$	$0.8\text{-}0.9~\mathrm{eV}$	$0.54 \ \mathrm{eV}$	$0.26\text{-}0.36~\mathrm{eV}$	$0.69~{\rm eV}$
(HAXPES)					

Table 3.2: Summary of the HAXPES and C-V results for SiO_2/Si samples

As well as providing information on the surface potential at zero gate voltage, the HAXPES method can also detect the flat band voltage difference between the Ni and Al gate samples. The flat band voltage in a MOS capacitor is the gate voltage required to offset the built in potential, which is across the oxide and the silicon substrate at 0 V, to achieve a flat band condition. As a consequence, the difference in the flat band voltage in the C-V for the Ni and Al gate samples should relate to the BE shifts measured in the HAXPES Si 1s oxide signal, as these spectra include both the Fermi level shifts in the substrate and the potential difference across the oxide. The calculated flat band capacitance (C_{fb}) is indicated on figures 3.19 (a) and (b), and the flat band voltage difference for the Al and Ni gate samples is 0.7 V for the n-type and 0.66 V for the p-type. This is in very good agreement with the combined Al-Ni shifts in the Si 1s oxide spectra in figure 3.16, which are 0.76 eV and 0.69 eV for the n and p-type substrates, respectively. The agreement between the surface potential differences and the flat band voltage differences for the two measurement techniques are shown in table 3.2. There is very good agreement in the relative shifts between samples with Al and Ni gates, however, there is a discrepancy between the p-type Fermi level positions determined by the two techniques. The results in figure 3.19 provide a possible explanation. The p-type samples are either at the onset of strong inversion (Ni) or in strong inversion (Al) at 0 volts and consequently have larger surface bandbending than the n-type samples which are in depletion (Ni) or slight accumulation (Al). If we assume a maximum sampling depth into the Si substrate of 11 nm, the band-bending will vary by 0.1 to 0.15 eV for a p-type sample in inversion based on a Poisson-Schrodinger simulation.¹³ This variation would be apparent in the HAXPES measurement, and will result in a lower $E_f - E_v$ than obtained from the C-V analysis.

3.3.7 Forming Gas Anneal Attempts

The SiO₂/Si samples electrically characterised using the joint C-V and HAXPES method did not receive forming gas anneal (FGA), which is commonly used to reduce the fixed charge present in the SiO₂ and passivate dangling bonds (P_b defects)

at the SiO₂/Si interface, thus reducing D_{it} . The next logical step in the study of this joint C-V and HAXPES method was to attempt to obtain measurements on an ideal interface, and thus it was decided to study SiO₂/Si based MOS structures following forming gas anneal. The measurement of MOS structures following FGA cannot be accomplished in conventional XPS as the FGA is normally performed post-fabrication. Forming gas is a mixture of hydrogen and nitrogen (H₂/N₂), where the ratio of gases can vary, though conventional SiO₂/Si FGA consists of 5% H₂ and 95% N₂.⁸

The first attempt at using FGA as a sample treatment involved the fabrication of samples identical to those used in the previous section, and the post-fabrication annealing of these samples in a furnace at 450 °C under 5% $H_2/95\%$ N₂ gas flow for 30 minutes, which has been shown to provide optimum results³⁶.³⁷ While the C-V characteristics of the samples,⁹ shown in figure 3.21, showed marked improvement over non-FGA samples and the expected ideal MOS behaviour, the HAXPES of equivalent samples showed extensive oxidation of the Ni cap, as shown in figure 3.22, and oxidation of the Al cap combined with Al-silicide formation, as described in section 3.3. The extensive oxidation of the 5 nm Ni cap in particular, where no metallic Ni can be detected following FGA, indicates that oxygen was leaked into the chamber along with H_2/N_2 mix. The conversion of the metallic layers to oxide results in no metallic Ni layer to move the Si Fermi level, thus making the experiment impossible. The C-V samples did not suffer as badly from the cap oxidation as it is likely that only the first 5 to 10 nm of the Ni/Au or Al contacts (160 nm) used in the C-V samples oxidised. The next attempt involved the performance of the FGA under the same conditions, but prior to metal deposition in order to prevent metal cap oxidation. While the HAXPES spectra looked fine the C-V results showed little improvement in device performance compared to the samples without FGA, suggesting the metal layer acts as a catalyst in the FGA passivation process.

The final attempt involved the performance of the FGA prior to metal deposition, but as only a small improvement was seen in the electrical behaviour of the device after performing the pre-metal FGA for 30 minutes, it was decided to perform the FGA for 3 hours, in an attempt to achieve the ideal results without



Figure 3.21: Multi-frequency (1 kHz - 1 MHz) C-V characteristics for (a) $Al/SiO_2/n-Si$, (b) $Ni/SiO_2/n-Si$, (c) $Al/SiO_2/p-Si$ and (d) $Ni/SiO_2/p-Si$ samples following post-metallisation FGA.



Figure 3.22: Normalised spectra of the Ni 2p spectra before and after postmetallisation FGA showing the oxidation of the Ni cap.

metal cap oxidation. Spectra of the metal layers showed no signs of metal oxidation, though the core level shifts observed in the HAXPES, and the behaviour measured with the C-V profiling, showed unexpected behaviour. From the Si 1sspectra, shown in figure 3.23, it is clear that the separation between uncapped n and p-Si has reduced from 0.32 to 0.07 eV. If the FGA was working correctly this separation should increase towards the flatband conditions for n and p-Si. The shifts following metal deposition are also very similar for both n and p-Si. Valence band scans similar to those in figure 3.17 were acquired in order to estimate the absolute Fermi level position within the bandgap. The results indicated that the Fermi level position for both uncapped n and p-Si samples were at the top of the Si bandgap, near the conduction band. This indicates that p-Si has been doped n-type by the 3 hour FGA. C-V measurements of equivalent samples showed similar 'dopant switching' behaviour, as seen in figure 3.24, where the p-Si samples are behaving similar to the equivalent n-Si samples. The absolute Fermi level positions from HAXPES measurements are summarised in table 3.3. Although this experiment failed to produce the expected results, the fact that agreement was



Figure 3.23: Normalised Si 1s core level spectra for the 3 hour pre-metallisation uncapped SiO₂/Si , Ni/SiO₂/Si and Al/SiO₂/Si samples, showing the shifts in the core level after metal deposition, and the changes in the potential across the SiO₂ layer caused by different work function metals for (a) n-Si, and (b) p-Si substrates. The dotted lines show the energy separation between n and p-type samples without metal gates.

obtained on the Fermi level behaviour of the samples between the HAXPES and C-V measurements further validates the technique.



Figure 3.24: 100 kHz C-V characteristics for (a) $Al/SiO_2/n-Si$, (b) $Ni/SiO_2/n-Si$, (c) $Al/SiO_2/p-Si$ and (d) $Ni/SiO_2/p-Si$ samples following a 3 hour pre-metallisation FGA. The dashed lines indicate zero bias voltage. The multiple traces are from different devices on the same wafer.

Sample	E_f - E_v	E_f - E_v	E_f - E_v	ΔE_f	Flat-band
	(SiO_2/Si)	$(Al/SiO_2/Si)$	$(Ni/SiO_2/Si)$	(Al-Ni shift)	(Al-Ni shift)
n-type	1.12 eV	$0.94 \mathrm{~eV}$	$0.69~{\rm eV}$	$0.25 \ \mathrm{eV}$	$0.68 \mathrm{~eV}$
(HAXPES)					
p-type	$0.98 \mathrm{~eV}$	0.84 eV	$0.47 \ \mathrm{eV}$	$0.37 \ \mathrm{eV}$	$0.75 \ \mathrm{eV}$
(HAXPES)					

Table 3.3: Summary of the HAXPES results for 3 hour pre-metallisation FGA samples

3.4 Chapter Conclusion

This chapter details the initial studies performed using HAXPES. The increase in sampling depth possible with HAXPES measurements performed at synchrotron sources was demonstrated. This was used to investigate the diffusion of Al into SiO_2 following thermal anneal, and the subsequent formation of Al-silicide in $Al/SiO_2/Si$ structures. Spectra taken at different photon energies was used to locate the Al-silicide within the structure. Initial attempts at joint HAXPES and C-V measurements of HfO₂/InGaAs based MOS structures were detailed, and the photon energy drift issue encountered in the measurement process was explained. The successful application of the same joint HAXPES and C-V characterisation was performed on Si based MOS structures. The HAXPES measurements of the Si core levels have been shown to be sensitive to changes in band-bending at the SiO_2/Si interface due to the presence of high (Ni) and low (Al) work function metal overlayers. The Si 1s core level originating from the SiO₂ layer indicates the presence of a potential difference across the SiO_2 layer. The changes in the band-bending at the SiO_2/Si interface, and the potential difference across the SiO_2 , are consistent with the difference in metal work functions, and are in agreement with the results derived from C-V measurements. Finally, the performance of various forming gas anneal techniques, and the issues encountered with each one, are described. The experimental findings validate the capability of HAXPES measurements to investigate both chemical interactions and Fermi level movements at buried interfaces, and have been shown to replicate the electrical understanding of MOS structures derived from C-V measurements.

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Chapter 4

Combined HAXPES and C-V Characterisation of III-V Based MOS Structures

4.1 Introduction

The innovation and scaling of complementary metal-oxide-semiconductor field effect transistors (MOSFET) at the heart of integrated circuits has led to the search for alternative substrate materials to replace Si, as described in section 1.3. However, issues still remain with these systems due to the high interface state density (D_{it}) present at the high- κ /III-V interface, which restrict efficient III-V surface Fermi level movement, as well as the other issues discussed in chapter 1. One of the main issues, in the electrical characterisation of these systems, associated with the accurate extraction of D_{it} concentrations (D_{it} distribution as a function of energy in the III-V bandgap, i.e. $D_{it}(E)$) for the high- κ /III-V metal-oxide-semiconductor (MOS) system, is the question of how each gate voltage (V_g) is related to the corresponding surface Fermi level position (E_f) relative to the valence band edge (E_v). For a $D_{it}(E)$ which changes density exponentially with E_f - E_v , this is clearly a potential source of error and variation between research groups. Moreover, the relationship between E_f - E_v and V_g is further complicated in the case of high D_{it} systems, such as GaAs, and those where the semiconductor has a low conduction band density of states, such as InGaAs. Other defects in high- κ /III-V MOS systems include fixed charges within the high- κ oxide and border traps near/at the high- κ /III-V interface transition layer.^{1, 2} These defects affect MOSFET performance in a range of detrimental ways,³ and possible methods to remove these defects from these systems have been extensively studied.⁴⁻⁷

As a traditional method, C-V analysis is widely used to investigate the high- κ /III-V electrical defects.^{8, 9} However the difficulty in characterising high D_{it} interfaces has led to a need for an alternative technique which is unaffected by D_{it}. Hard x-ray photoelectron spectroscopy (HAXPES) has the capability to solve this issue. The increase in the analysis depth, from 5 to 7 nm for conventional XPS up to 15 to 30 nm for HAXPES,^{10–13} facilitates the measurement of core level signals from all the relevant layers in MOS structures. The ability of HAXPES measurements to provide information on band-bending at the semiconductor/dielectric interface and to detect the presence of a potential difference across the dielectric provides complementary information on the electronic structure of the MOS to that deduced from C-V measurements.¹⁴

Having proven the validity of this joint HAXPES and C-V characterisation method with the SiO₂/Si system in chapter 3, it was decided to study the GaAs MOS system, which is known to display C-V characteristics indicative of a high D_{it} , which restricts the movement of the Fermi level at the oxide/GaAs interface upon application of a gate voltage.^{15–17} To fully characterise the interfacial electronic properties in high- κ /GaAs MOS system it is necessary to determine the energy distribution of the interface states. In the case of a MOS system with a high D_{it} , such as GaAs, the conversion of the gate voltage in the C-V response to the corresponding energy position in the interface state analysis is an established problem.⁸ It would be highly beneficial to the community working in the electrical characterisation of III-V MOS interface states to have an independent method of evaluating the surface potential for a given gate voltage, as this would provide a higher degree of certainty for energy mapping of the interface states. $In_x Ga_{1-x} As$ with a 53% Indium concentration ,i.e. $In_{0.53} Ga_{0.47} As$, was also chosen as a substrate material to be studied using this technique due to its position as the prime candidate to replace Si in future MOSFETs. The high- κ /InGaAs MOS system is known to have a relatively high D_{it} , however the InGaAs surface Fermi level is generally not fully pinned as compared to high- κ /GaAs MOS system.¹⁸

In this chapter, a study exploring the application of HAXPES analysis to determine the surface Fermi level positions in n and p-doped GaAs and InGaAs based MOS structures is reported, where the oxide is an Al_2O_3 (8 nm) thin film deposited by atomic layer deposition (ALD). The samples studied included structures with no metal gates and samples capped with 5 nm thick high (Ni) and low (Al) workfunction metals, to explore if the low and high workfunction metal layers modulate the surface Fermi level position. Using a photon energy of 4150 eV in these investigations allowed the detection of photoemission signals from metal, oxide and substrate core levels. The relatively wide band gaps of GaAs (1.42 eV) and InGaAs (0.75 eV) are sufficient to enable the detection of differences in the binding energy (BE) of the n and p-doped substrate core levels which directly reflect different Fermi level positions in the band gap.¹⁹ The surface Fermi level positions obtained from the HAXPES analysis are compared to the reported location of the pinning positions in the GaAs band gap for n and p-doped substrates from other studies.^{16, 20, 21}

In conjunction with the HAXPES analysis, GaAs and InGaAs based MOS capacitor structures were examined using C-V analysis. The C-V and HAXPES analysis was performed on near-identical samples, with the only difference being the metal gate thickness, as the C-V measurement uses the metal gate as a probing contact. On the premise that a true high frequency C-V can be obtained, the surface potential and thus the Fermi level position can be determined, and compared with the equivalent HAXPES measurements. The results presented in this section illustrate the ability of HAXPES to detect Fermi level positions at the high- κ /III-V interface, regardless of the levels of D_{it}, and the presence of any potential differences across the dielectric layers in MOS structures. The results from the HAXPES analysis are also compared to the analysis of the C-V response.

4.2 Experimental Details

All of the samples described below were fabricated in the Tyndall National Institute, where transmission electron microscopy (TEM) and C-V measurements and analysis were also performed.^{22, 23}

The n (Si - $5x10^{17}$ cm⁻³) and p (Zn - $5x10^{17}$ cm⁻³) doped GaAs samples consisted of 400 nm thick GaAs layers grown by metal organic vapour-phase epitaxy (MOVPE) on epi-ready GaAs substrates. The GaAs surfaces were initially degreased by sequentially rinsing for 1 min each in acetone, methanol, and isopropanol. Prior to the ALD of the high- κ oxide, the samples were immersed in (NH₄)₂S solutions (10% in deionized H₂O) for 20 min at room temperature (295 K), which was found to be the optimum approach to suppress the formation of native oxides and to reduce the high- κ /III-V interface state density, as reported previously.⁵ Samples were then introduced to the ALD chamber load lock after the removal from the 10% (NH₄)₂S surface passivation solution. The transfer time from the aqueous (NH₄)₂S solution to the ALD chamber was kept to a minimum (3 minutes) in order to minimise the formation of native oxides resulting from air exposure.

The 8 nm Al₂O₃ was deposited by ALD at 300 °C using alternating TMA $(Al(CH_3)_3)$ and H₂O pulses. The samples were split into three groups, A, B, and C, each containing one n and one p-type substrate. Group A were left without a metal gate, group B were capped with a 5 nm Ni blanket film, while group C were capped with a 5 nm Al blanket film, as shown schematically in figure 4.1. All metal deposition was achieved by electron beam evaporation. Additionally, two further groups, D and E were produced for C-V analysis in an identical fashion to that mentioned above, with group D samples capped with a 160 nm Al film, while group E were capped with a 70/90 nm Ni/Au film for electrical probing. The metal gate areas for the C-V characterisation were defined by a lithography and lift-off process.

The $In_{0.53}Ga_{0.47}As$ (hereafter referred to as InGaAs) samples studied in this work were heavily n-doped (S at $2x10^{18}$ cm⁻³) and heavily p-doped (Zn at $2x10^{18}$



Figure 4.1: InGaAs and GaAs samples for HAXPES and C-V characterisation. Substrate materials were capped with an 8 nm Al_2O_3 layer and either left without a metal gate or capped with a 5 nm Al or Ni gate.

cm⁻³) InP (100) substrates with 2 μ m n-type (S at 4x10¹⁷ cm⁻³) and p-type (Zn at 4x10¹⁷ cm⁻³) InGaAs epitaxial layers respectively, grown by MOVPE. The InGaAs surfaces were initially degreased by sequentially rinsing for 1 min each in acetone, methanol, and isopropanol. The (NH₄)₂S passivation, Al₂O₃ growth, and metal deposition were performed identically to those for the GaAs samples previously described. The InGaAs sample matrix was also identical to that described for GaAs.

HAXPES measurements were carried out on the National Institute of Standards and Technology (NIST) beamline X24a at the National Synchrotron Light Source at Brookhaven National laboratory, as previously described in section 2.2. Samples were fixed on a grounded Al sample holder with stainless steel clips, which connected the front of the samples to the sample holder. In order to ensure correct energy calibration throughout the experiment, metallic Ni Fermi edge reference spectra were acquired immediately before and after the acquisition of the Al₂O₃, GaAs, and InGaAs core level peaks. The resultant error associated with this photon energy correction procedure is estimated to be no more than ± 50 meV. The maximum depletion region width for the 5×10^{17} cm⁻³ doped GaAs substrate is calculated to be 61 nm, while for the 4×10^{17} cm⁻³ doped InGaAs it is 51 nm. The total sampling depth of the HAXPES measurement using a photon energy of 4150 eV is estimated to be 23 nm²⁴ which ensures the detection of photoemitted electrons from the 5 nm metal and 8 nm dielectric layers, as well as approximately 10 nm into the GaAs and InGaAs, which is obtained from the inelastic mean free path of the Ga 2p and As 2p photoemitted electrons, which have kinetic energies of 2827 eV and 3033 eV, respectively.²⁵ Therefore, the acquired peaks directly reflect the binding energy (BE) of the core levels with respect to the Fermi level near the top of the depletion region, adjacent to the dielectric interface. The XPS core level spectra were curve fitted, using Voigt profiles composed of Gaussian and Lorentzian line shapes in a 3:1 ratio with a Shirley-type background, to increase the accuracy of locating the peak centres.

The C-V measurements were recorded using an Aligent CV-enabled B1500A semiconductor device analyser following an open correction and performed in a Cascade Microtech probe station (model Submit 12971B) in a dry air, dark environment.²² The B1500A analyser allows for C-V measurements performed at a wide range of AC frequencies (1 kHz to 5 MHz). All the C-V responses were measured starting from inversion and sweeping towards accumulation in order to reduce the effect of border traps, which shift the measured C-V curve. Multi-frequency (1 kHz to 1 MHz) and 1 MHz C-V measurements were carried out at both room temperature and -50 °C. The C-V characteristics measured at both temperatures were compared in order to rule out the possible contribution of an interface state capacitance to the overall measured capacitance of the MOS capacitors at room temperature. For comparison between HAXPES and C-V measurements an AC frequency of 1 MHz was used to minimise the contribution of an interface state capacitance to the overall capacitance of the MOS capacitor. Under this condition, the primary effect of the interface states is to stretch out the C-V along the gate voltage axis so that the Fermi level position can be determined using the measured capacitance, provided that the MOS capacitor is in depletion at $V_q =$ 0 V. Multiple sites with different areas were examined in order to ensure the C-V results are representative of the sample behaviour. The oxide capacitance and flatband capacitance used for C-V analysis are calculated using a dielectric constant value of 8.6 for Al_2O_3 and accurate oxide thicknesses obtained from high-resolution cross-sectional transmission electron microscopy (HR-TEM).
4.3 Results and Discussion

4.3.1 Al₂O₃/GaAs(100) Based MOS Structures

Figure 4.2 shows the As 2p core level spectra acquired at 4150 eV photon energy for both n and p-GaAs with the 8 nm Al₂O₃ dielectric layer, with and without the presence of a metal overlayer. Measurements on the uncapped samples reveal that the BE position for the p-GaAs peaks was found to be 0.6 eV lower than the n-GaAs substrate, consistent with the Fermi level residing closer to the valence band maximum. The difference is, however, less than the expected value of 1.34 eV, which is based on the calculated Fermi level position difference for n and p-GaAs with a doping concentration of 5×10^{17} cm⁻³, indicating that there is band-bending at the Al₂O₃/GaAs interface for both dopant types, even in the absence of a metal contact.³

Using an identical method to the SiO₂/Si study in chapter 3, high (Ni 5.01 eV) and low (Al 4.08 eV) workfunction metal films 5 nm thick were deposited on the dielectric²⁶ in order to determine whether the band-bending displayed at the interface reflected Fermi level pinning. If the Fermi level at the Al₂O₃/GaAs interface is free to move, it would be expected to align with the metal workfunction, resulting in a reduction in band-bending (increase in core level BE) for the n-type substrate with the low workfunction Al contact and an increase in the band-bending (reduction in core level BE) for the high workfunction Ni contact. The same dependence of core level BE on metal workfunction would be expected for the p-type substrate, however, the magnitude of the shifts would differ, so for a Ni gate a much larger core level BE shift should be recorded for n-type than for p-type, while for an Al gate a larger shift for p-type than for n-type would be expected.

HAXPES measurements for samples with an Al gate show that the peaks shift 0.11 eV and 0.15 eV to higher BE, for n and p-type samples respectively, with no detectable change for the Ni gate. The limited ability to move the Fermi level of either dopant type suggests high D_{it} at the Al₂O₃/GaAs interface. The small



Figure 4.2: Normalised As 2p core level spectra acquired at a photon energy of 4150 eV for the uncapped Al₂O₃/GaAs, Ni (5 nm) capped and Al (5 nm) capped Al₂O₃/GaAs samples, showing the shifts in the core level after metal for (a) n-GaAs, and (b) p-GaAs substrates. The dotted lines show the energy separation between n and p-type samples without metal gates.

shift in the GaAs core levels following the deposition of the low workfunction Al contact indicates that there is a limited ability to move the Fermi level towards the conduction band. These combined results indicate that the band-bending observed at the $Al_2O_3/GaAs$ interface for the n and p-doped substrates, in the absence of a metal contact, broadly reflects the position of the partially pinned Fermi level, as no significant Fermi level movements occurred following the deposition of metals with different workfunctions. The measurements also suggest that the partial Fermi level pinning for n and p-doped substrates at different positions in the band gap are caused by different interface state defects consistent with previous studies.^{16, 27, 28} This result is in agreement with the recent work of Caymax et al,¹⁶ for electrical measurements on sulphur treated Al₂O₃/GaAs MOS capacitors on n and p-doped substrates, which reported different defect state distributions in the GaAs band gap and the limited ability of sulphur treatment to passivate the mid-gap defect states. The reduction in signal to noise apparent in the spectra for the GaAs substrate peaks following the metal deposition reflects an intensity attenuation of 84% in the case of the Al contact and a 91% reduction for the Ni contact which highlights the necessity for the large sampling depth and high brilliance capabilities of HAXPES measurements.

Following the work of *Kraut et. al.*,²⁹ the position of the valence band maximum (VBM) in relation to a reference metallic Fermi level was determined by theoretically calculating the density of states (DOS) from first principles.³⁰ The theoretical DOS is then weighted by the cross section of each atomic orbital, and convolved with a Gaussian curve, $\sigma = 0.5$ eV full width at half maximum (approximately the energy resolution of the HAXPES measurements), in order to accurately model the valence band (VB) as measured by photoemission.³¹ Figure 4.3 shows the good agreement between the calculated DOS and the VB spectrum for n-type Al₂O₃/GaAs as measured by photoemission. The VBM for this n-doped substrate is determined to be approximately 1.0 ± 0.1 eV below the reference Fermi level, which would be at zero BE on the x-axis, while the corresponding VBM for the p-type Al₂O₃/GaAs, determined using the same method, was 0.4 ± 0.1 eV below the Fermi level.



Figure 4.3: Total theoretical DOS, convolved cross-section weighted DOS and experimental photoemission valence band spectra of n-GaAs/Al₂O₃. A Gaussian of $\sigma = 0.5$ eV was used in convolution. The VBM position is indicated by the vertical line. The Ni Fermi edge was used to determine zero BE on this scale which reflects the Fermi level position.

In order to assess the magnitude of the error in determining the Fermi level position from the HAXPES measurement, a simulation of the band-bending for 5×10^{17} cm⁻³ doped p-GaAs resulting from a 0.4 eV surface potential was performed by numerically solving Poissons equation.³² The resulting band-bending diagram, shown in figure 4.4, indicates that for a sampling depth into the GaAs substrate of 10 nm, the error in determining the VBM position is a maximum of 0.15 eV. However, due to the exponential fall off in the weighting of the photoemitted electron contribution with depth, as shown in figure 2.3, it would be reasonable to assume that the actual error is likely to be less than 0.1 eV. By including this error the Fermi level position for the p-type sample without a metal cap, or with a Ni cap, can be determined to be in the range of 0.4 to 0.5 eV above the VBM, while for the sample with the Al cap the Fermi level is 0.55 to 0.65 eV above the



Figure 4.4: Simulation of the band-bending in a p-type GaAs MOS structure based on 0.4 eV band-bending, as measured by HAXPES

VBM. For the equivalent n-type sample, assuming a similar band-bending derived error, the Fermi level is in the range of 0.9 to 1.0 eV above the VBM for uncapped and Ni capped samples, and 1.01 to 1.11 eV for Al capped samples.

In order to quantify any surface photovoltage (SPV) related effect,³³ caused by the generation of electron hole pairs in the GaAs by a high incident photon flux, the following analysis has been undertaken. SPV effects are characterized by a rigid shift of both semiconductor substrate and metal derived peaks towards the flat band positions.³³ This has the effect on p-type substrates of shifting the metallic Fermi edge above the reference Fermi level by an amount equivalent to the band flattening cause by SPV, but no such shift was observed in this work. In addition, the relatively high doping density (5x10¹⁷ cm⁻³), and the fact that measurements were performed at room temperature both act to minimize any SPV effect.³⁴ Deriving similar Fermi level positions from both metal capped and uncapped samples also indicates that a significant SPV effect.³⁴ In any case, studies by Bauer et al^{34} would indicate that for the photon flux used in these measurements (maximum of 10^{11} photons/s) and the doping density of the GaAs substrates, an upper estimate of the SPV effect would result in no more than 0.1 eV shift towards the flat band positions. Even taking these SPV induced shifts into account, and adding this to the error as a result of the band-bending, the results suggest that the Fermi level of the p-type sample is in the range 0.4 to 0.6 eV above the valence band maximum (VBM) for uncapped and Ni capped samples, and 0.55 to 0.75 eV for Al capped samples, above its calculated position of 0.04 eV above VBM. The corresponding analysis for the n-type Fermi level position is in the range 0.8 to 1.0 eV from the VBM for uncapped and Ni capped samples, and 0.91 to 1.11 eV for Al capped samples, below its calculated position of 1.38 eV above VBM, which agree with the n-p Fermi level separation of 0.6 eV as determined from the core level peak shifts. These Fermi level positions are in good agreement with those previously reported for p-type GaAs, 0.4 to 0.6 eV,²⁰ and 0.33 eV^{17} above the VBM. However there is a greater discrepancy in the ntype Fermi levels, with previous values of 0.61 eV^{17} and 0.7 eV^{35} . The presence of two pinning positions close to the midgap is however consistent with the unified defect model (UDM), which explains the two pinning states as being related to acceptor (missing As atom) or donor-like (missing Ga atom) states which are due to missing atoms at the semiconductor/oxide interface.^{16, 36}

In order to fully characterise the presence of interface states at the dielectricsemiconductor interface, both high and low AC frequency C-V measurements are required. The C-V responses recorded at a range of AC signal frequencies (1 kHz to 1 MHz) for the corresponding Al (160 nm) and Ni/Au (70/90 nm) gate Al₂O₃/GaAs MOS capacitors for the n and p-type GaAs are shown in figure 4.5 (a)-(d).²² A large frequency dispersion at positive gate voltages is observed in the C-V for the n-GaAs, which is consistent with the high interface state density in the upper half of the GaAs bandgap. The accumulation capacitance is not seen from the 1 MHz C-V, suggesting that the Fermi level is pinned at a fixed energy level at the Al₂O₃/GaAs interface for n-type and cannot move towards the conduction band to accumulate electrons. The accumulation-like capacitance measured at 1 kHz is not only due to the differential capacitance (C_s) of the n-type GaAs but is a



Figure 4.5: Multi-frequency (1 kHz to 1 MHz) C-V response at room temperature (295 K) for (a) Al/Al₂O₃/n-GaAs (b) Al/Al₂O₃/p-GaAs (c) Ni/Al₂O₃/n-GaAs and (d) Ni/Al₂O₃/p-GaAs MOS capacitors.

consequence of a capacitance contribution of an interface state capacitance (C_{it}) in parallel with C_s . As C_{it} is large compared to C_s and C_{ox} , according to the equivalent circuit of a MOSCAP with the presence of interface states, a capacitance that approaches C_{ox} can be observed but does not indicate that accumulation is achieved. Because the Fermi level is pinned at the fixed energy level, all the additional gate charge is compensated by charging $Al_2O_3/GaAs$ interface defects. A similar C-V response was also observed for a $HfO_2/GaAs$ MOS capacitor at 295 K.¹⁸ The multi-frequency C-V response for the p-type GaAs MOS capacitors shows much smaller frequency dispersion at negative gate voltages, with a maximum capacitance that approaches C_{ox} at both 1 kHz and 1 MHz, implying that the interface state density is reduced in the lower half of the GaAs bandgap in comparison to the upper half, thus the p-type can more easily reach accumulation than n-type.

The effect of the Al and Ni on the GaAs Fermi level position is estimated from the C-V at 1 MHz as shown in figure 4.6 (a) and (b) for p and n-type, respectively. In order to obtain the Fermi level position, the GaAs surface potential is calculated based on the measured capacitance at 1 MHz and zero gate voltage, as the HAXPES measurement is carried out without applying a gate voltage. It is crucial to do the calculation on the premise that a true high frequency capacitance is obtained at $V_g = 0$ V, otherwise the measured capacitance comprises a C_{it} term



Figure 4.6: Comparison of 1 MHz C-V between Al and Ni gate for (a) p-GaAs and (b) n-GaAs.

which leads to an incorrect surface potential. A model by Brammertz et al.¹⁵ that determines the interface trap response at 295 K using a capture cross section of 1×10^{-14} cm² is shown in figure 4.7.³⁷ This model shows the range of positions within the bandgap in which interface states much reside so that they can respond to the AC frequency applied during the C-V measurement. Only the interface defects in the energy range E_v to $E_v + 0.31$ eV and $E_c - 0.27$ eV to E_c can respond to an AC frequency of 1 MHz. All the interface states outside this energy range will only affect the C-V though a stretch-out along the gate voltage axis without the addition of C_{it} to the total capacitance of the MOS capacitor. As discussed earlier, the HAXPES measurements indicate that the Fermi level is located in the range of 0.8 to 1.11 eV and 0.4 to 0.75 eV above the VBM for n and p-type respectively. It is noted that these energy positions are in the region where interface states cannot respond, giving us confidence in calculating the surface potential using the 1 MHz capacitance at $V_g = 0$ V. In addition, it is worth highlighting that for GaAs, the capture cross section can vary over orders of magnitude.³⁸ The calculations for the model have been performed for capture cross sections which span 3 orders of magnitude $(1 \times 10^{-17} \text{ to } 1 \times 10^{-14} \text{ cm}^2)$, which all show that no interface states at those energy levels can respond to 1 MHz at $V_g = 0$ V. From the C-V at 1 MHz the corresponding semiconductor depletion capacitance can be calculated from the total measured capacitance $(C_{it} = 0)$ and an oxide capacitance value C_{ox} = 9.5x10^{-7} \mathrm{~F/cm^2} assuming an $\mathrm{Al_2O_3}$ layer with nominal thickness of 8 nm is formed during the ALD. This value can then be used to determine the surface potential and hence the surface Fermi level position with respect to the VBM. The C-V based calculations indicate that for n-type the Fermi level is 0.86 eV and 0.78 eV above the VBM with Al and Ni gates, respectively, and for the p-type, it is 0.41 eV and 0.30 eV above the VBM with Al and Ni gates, respectively, which are in good agreement with the HAXPES measured Fermi level positions. The comparative HAXPES and C-V results ($V_q = 0$) for the surface Fermi level position are presented in table 4.1. The difference between the Fermi level position of Al and Ni is thus 0.08 eV over n-type and 0.11 eV over p-type, which are consistent with the Fermi level shift between Al and Ni from HAXPES over both n-type, of 0.11 to 0.31 eV, and p-type, of 0.15 to 0.35 eV as shown in table 4.1.



Figure 4.7: Simulation of trap response using the model by Brammertz et al.¹⁵ associated with the measurement at 295 K, assuming a capture cross section of 1×10^{-14} cm⁻². The horizontal dashed line corresponds to the high frequency of 1 MHz in the C-V measurement and circled regions represent the energy levels of interface states (E_t) in the GaAs bandgap measured by HAXPES, which are in the ranges 0.8 to 1.11 eV and 0.4 to 0.75 eV above VBM for n and p-type, respectively, with and without the presence of a metal gate. For smaller values of capture cross section the region of the energy gap over which the interface states can respond is reduced.

Workfunction differences between the metal and the pinned GaAs Fermi level should be reflected in a potential difference across the dielectric layer resulting in a BE shift, and broadening of the associated dielectric core levels.¹² These changes would be expected to be most apparent between the n-type GaAs and the Ni, or the p-type GaAs and the Al, as these both represent the largest potential difference, given the electron affinity of GaAs is 4.07 eV. Figure 4.8 shows the changes in BE of the Al 1s oxide peak (located at 1562 eV) for the n and p-type GaAs substrate resulting from metal deposition. For the n-type sample the deposition

Table 4.1: Comparison of Fermi level positions recorded by HAXPES and C-V measurements at $V_g=0$ V. E_f is the Fermi level energy, E_v is the valence band energy.

Sample	E_f - E_v	E_f - E_v	E_f - E_v	ΔE_f
	(no cap)	(Al cap)	(Ni cap)	(Al-Ni shift)
n-type	n/a	0.86 eV	$0.78 \ \mathrm{eV}$	0.08 eV
(C-V)				
n-type (HAXPES)	$0.8 \rightarrow 1.0 \text{ eV}$	$0.91 \rightarrow 1.11 \text{ eV}$	$0.8 \rightarrow 1.0 \text{ eV}$	$0.11{\rightarrow}~0.31~{\rm eV}$
(HAXPES)				
p-type (C-V)	n/a	0.41 eV	$0.3 \mathrm{~eV}$	0.11 eV
(C-V)				
p-type (HAXPES)	$0.4 \rightarrow 0.6 \text{ eV}$	$0.55{\rightarrow}~0.75~{\rm eV}$	$0.4 \rightarrow 0.6 \text{ eV}$	$0.15{\rightarrow}~0.35~{\rm eV}$
(HAXPES)				

of the low workfunction Al results in a small increase in the Al 1s peak BE (0.09) eV), which is less than the workfunction difference in the range of 0.3 to 0.5 eV. It is thought that this discrepancy is partly due to trapped charge in the Al_2O_3 , which has previously been measured in the case of Al₂O₃/InGaAs systems.^{1, 4} If there is positive charge already present in the oxide then the potential field needed to equalise the metal workfunction and Fermi level in the semiconductor is less in the case of an Al cap, and greater in the case of a Ni cap, which is the case in our results as shown in table 4.2. The presence of a metallic Al 1s signal at 1559.4 eV BE originates from the gate metal. For the Ni capped n-type sample, a significant decrease in the BE (-0.59 eV) of the Al 1s oxide peak reflects a potential difference of the opposite polarity across the dielectric caused by the high workfunction Ni contact, as previously explained in chapter 3. Table 4.2 compares the experimental potential fields as measured from the Al 1s peak and compares them to calculated potential fields, as determined from the energy difference between the measured Fermi level position of the InGaAs and the metal workfunction. This shift agrees well with the theoretical workfunction difference in the range of -0.52 to -0.32 eV. The corresponding BE shifts for the p-type sample were 0.54 eV to higher BE with the Al cap and -0.26 eV for the Ni cap, which show reasonable agreement with the expected shifts of 0.66 to 0.86 eV and -0.12 to 0.08 eV, respectively. Note that the shift resulting from Fermi level movement in the GaAs is also present in the oxide peaks, so any shift in the oxide peaks is a combination of the Fermi level



Figure 4.8: Al 1s spectra showing BE shift due to the changes in the potential across the Al₂O₃ layer caused by different workfunction metals for (a) n-type and (b) p-type GaAs. The presence of a metallic Al 1s signal at 1559.5 eV BE originates from the metal cap.

movement, and a potential difference across the oxide.

All of these changes are consistent with the difference in the polarity of the potential difference in the dielectric layer caused by the low and high workfunction metals and further reflect the restricted nature of the Fermi level movement in the GaAs, as the workfunction difference between GaAs and metal caps is manifest as a potential difference across the dielectric layer.¹² The Al 1s peak widths for the metal capped samples broaden when compared to the samples without metal

due to the presence of a potential field across the oxide layer.							
	Sample	Calculated Al_2O_3 shift (eV)	Experimental Al_2O_3 shift (eV)				
	$Al/Al_2O_3/n$ -GaAs	$0.3 \rightarrow 0.5$	0.09				
	Ni/Al ₂ O ₃ /n-GaAs	$-0.52 \rightarrow -0.32$	-0.59				
	$Al/Al_2O_3/p$ -GaAs	$0.66 \rightarrow 0.86$	0.54				
	Ni/Al ₂ O ₃ /p-GaAs	$-0.12 \rightarrow 0.08$	-0.26				

Table 4.2: Comparison of the calculated and measured shifts in the Al oxide peak due to the presence of a potential field across the oxide layer.

gates, reflecting the gradient in the potential across the dielectric layer. The small potential difference of 0.09 eV measured across the Al_2O_3 layer for the Al on n-type results in negligible broadening while a full width half maximum (FWHM) increase of 0.36 eV for Ni on n-type reflects the larger potential difference across the dielectric. In the case of the p-type sample, again negligible differences in FWHM were measured for the Al contact, but a 0.18 eV FWHM increase was found for the Ni capped sample. While these differences are smaller than would be expected, this can be partially accounted for by the limited extent to which these potential changes can be quantified by measuring photoemission peak line shapes.³⁹

In summary, the large sampling depth of HAXPES has been used to characterise band-bending in metal/Al₂O₃/GaAs structures fabricated with both high (Ni) and low (Al) workfunction metals. The results are consistent with different Fermi level positions for n and p-doped substrates which are largely independent of metal workfunction. Valence band measurements indicate that the Fermi level positions in the band gap are in the range of 0.4 to 0.75 eV and 0.8 to 1.11 eV above the valence band maximum for p-type and n-type GaAs, respectively. C-V analysis of near identical samples yield very similar surface Fermi level positions at zero gate voltage for the n and p-type GaAs samples. The C-V responses also indicate an $Al_2O_3/GaAs$ interface with a higher D_{it} in the upper half of the bandgap. A potential difference across the Al_2O_3 layer consistent with the difference in metal workfunctions was also measured. The ability of HAXPES measurements to allow the extraction of Fermi level positions at buried metal/dielectric interfaces in the presence of metal capping layers facilitates the study of MOS structures which are difficult to analyse by C-V electrical characterisation methods due to the limited Fermi level movement.

4.3.2 $Al_2O_3/In_{0.53}Ga_{0.47}As$ Based MOS Structures

Figure 4.10 shows the HAXPES As 2p core levels acquired at 4150 eV photon energy for both n and p-InGaAs with an Al₂O₃ dielectric layer with and without the presence of the metal gate. For the unmetallised samples, the binding



Figure 4.9: (a) Band diagram, illustrating the BE shifts due to an electric field across the oxide caused by metal deposition, for p-GaAs showing a potential difference across the oxide for a p-type sample with an Al gate. (b) Band diagram showing a potential difference of the opposite polarity for a p-type sample with a Ni gate.

energy position for the p-InGaAs peaks was found to be 0.28 eV lower than the n-InGaAs substrate, consistent with the Fermi level residing closer to the valence band maximum (VBM). The difference is, however, less than the expected difference of 0.68 eV, which is calculated from the difference in Fermi level position for n and p-InGaAs for a doping level of 4×10^{17} cm⁻³,³ indicating that there is band-bending present at the Al₂O₃/InGaAs interface prior, to the deposition of the metal contacts.



Figure 4.10: Normalised and fitted As 2p core level spectra acquired at a photon energy of 4150 eV for the uncapped, Ni (5 nm) capped, and Al (5 nm) capped Al₂O₃/InGaAs samples, showing the shifts in the core level BE after metal deposition for (a) n and (b) p-InGaAs substrates. The dotted lines show the energy separation between n and p-InGaAs samples without metal gates.

In order to establish the absolute position of the Fermi level in the band gap with respect to the VBM, valence band spectra were acquired at the same photon energy, as shown in figure 4.11. An extrapolation of the InGaAs valence band to a zero signal intensity yields the approximate position of the valence band edge.⁴⁰ Although a more accurate method was employed in the GaAs based samples, in

the previous section, this method is sufficient to provide an accuracy of approximately $\pm 50 \text{ meV}$ in these studies, as absolute Fermi level pinning positions are not being obtained as they were in the GaAs case. Reference spectra of the nickel metallic edge were subsequently acquired in order to establish the Fermi level position. From the valence band spectra of the uncapped Al_2O_3/n -InGaAs sample, the Fermi level is 0.67 eV above the VBM and the equivalent measurement for the p-type (not shown) Fermi level position is 0.39 eV above the VBM. Therefore the Fermi level is 0.09 eV below flatband position for n-InGaAs and is 0.31 eV above flatband position (i.e. near mid-gap) for the p-InGaAs, indicating that the n-InGaAs surface is slightly depleted and the p-InGaAs surface is strongly depleted. Figure 4.12 (a) and (b) schematically illustrate the band-bending occurring for the non-metallised samples and the respective Fermi level positions (E_f) determined by HAXPES. The depletion of both the n-type and p-type surface cannot be explained by one net oxide charge type. Therefore, the band-bending occurring at the InGaAs surface in the absence of metal gates are attributed to a combination of fixed charge in the Al_2O_3 layer and the interface states with energy levels within the InGaAs bandgap, which deplete both the n-type and p-type surfaces. Based on the work by R. D. Long et. al^4 , the fixed oxide charge in ALD deposited Al₂O₃ is comprised of negative interface fixed charge that exists near the Al₂O₃/InGaAs interface and positive fixed charge distributed through the bulk of the Al_2O_3 . For a relatively thin oxide of 8 nm, the net fixed oxide charge (Q_f) could be negative for n-type sample and positive for p-type samples, as discussed in the work by R.D. Long et. al.⁴ In addition, previous studies^{4, 41, 42} have reported the evidence that the net interface states type for Al_2O_3 on $In_xGa_{1-x}As$ is donor type (+/0). If this is the case, for an n-type sample at flatband where the E_f is close to conduction band edge and the interface state energy levels in the bandgap are occupied, the interface defects (Q_{it}) are neutral. The combination of negatively charged Q_f and neutral Q_{it} is a negative charge which slightly depletes the n-type surface as shown in figure 4.12 (a). For a p-type sample at flatband where E_f is close to the VBM, the donor-type interface defects have a net associated positive charge as their energy levels in the bandgap are empty. The positively charged interface states plus the positively charged Q_f results in the depletion of the p-type surface, as shown in figure 4.12 (b). Confirming the sign of Q_f and Q_{it} requires an Al₂O₃

thickness series as described in the report by R. D. Long et. al,⁴ which is beyond the scope of this work.



Figure 4.11: Valence band spectra of an n-type $Al_2O_3/InGaAs$ sample, showing the measured valence band offset.

In order to determine whether the band-bending displayed at the interface reflects Fermi level pinning, both high (Ni) and low (Al) work function metals of 5 nm in thickness were deposited on the dielectric. By ensuring electrical contact between the metal overlayer and the InGaAs substrate, Fermi level equalisation across the MOS structure occurs. If the Fermi level at the $Al_2O_3/InGaAs$ interface is free to move, it would be expected to align with the metal Fermi level resulting in an increase in band-bending (increase in BE) for the n-InGaAs with the low work function Al contact and an increase in the n-InGaAs band-bending in the opposite direction (reduction in BE) for the high work function Ni contact. The same dependence of core level binding energy on metal work function would be expected for the p-type substrate, however, the magnitude of the shifts would



Figure 4.12: Band diagrams of (a) unmetallised Al_2O_3/n -InGaAs, (b) unmetallised Al_2O_3/p -InGaAs MOS capacitors, (c) Al_2O_3/n -InGaAs following Al deposition, (d) Al_2O_3/p -InGaAs following Al deposition, (e) Al_2O_3/n -InGaAs following Ni deposition and (f) Al_2O_3/p -InGaAs following Ni deposition. The band-bending occurring in the absence of a metal contact shown in (a) and (b) are due to a combined effect of fixed oxide charges and interface states. E_f represents the Fermi level position, E_c represents the conduction band edge, E_v represents the valence band edge and E_i represents the InGaAs midgap energy level. The surface E_f - E_v values shown are determined by HAXPES.

differ, so for a Ni gate a much larger core level binding energy shift should be recorded for n-type than for p-type, while for an Al gate we would expect a larger shift for p-type than for n-type. The changes in band-bending and InGaAs surface Fermi level when the metal contacts are present can be visualised using the schematic band diagrams and the Fermi levels presented in figure 4.12 (c)-(f). HAXPES measurements in figure 4.10 show that, for the p-InGaAs sample the core level peaks shift 0.21 eV, and for the n-InGaAs sample the peaks shift 0.02 eV, both to higher BE, following the deposition of the Al contact. Following the deposition of a Ni contact the peak positions shift 0.11 eV for n-InGaAs and 0.03 eV for p-InGaAs, to lower BE. The directions of all the BE shifts observed in the HAXPES spectra are consistent with the differences in the Fermi level positions for the InGaAs substrates and metals.

The corresponding Fermi level positions in the InGaAs bandgap following either Al or Ni deposition are calculated from the HAXPES to be 0.69 eV above the VBM for the Al gate, and 0.56 eV above VBM for Ni gate, over n-InGaAs. For the HAXPES p-InGaAs samples, the Fermi levels are determined to be 0.6 eV above VBM with the Al gate and 0.36 eV above the VBM with the Ni gate.

In the HAXPES measurements, any large degree of band-bending at the $Al_2O_3/$ InGaAs interface may lead to an error in the surface Fermi level measurement, as HAXPES has a sampling depth into the substrate of approximately 10 nm, so the Fermi level is being measured up to 10 nm below its surface position. In order to assess the magnitude of this error in determining the Fermi level position from the HAXPES measurement, a simulation of the band-bending for $4x10^{17}$ cm⁻³ doped p-InGaAs resulting from a 0.31 eV surface potential was performed by numerically solving Poissons equation. The resulting band-bending diagram (not shown) indicates that for a sampling depth into the InGaAs substrate of 10 nm, the error in determining the VBM position is a maximum of 0.1 eV. As described earlier in this chapter the actual error is likely to be less than 0.1 eV. This error can thus be taken into account when comparing the results of the approximate Fermi level position of each sample in the InGaAs bandgap.

The C-V characteristics at 1 MHz and 295 K for Al (160 nm) or Au (90 nm)/Ni (70 nm) metal gate MOS capacitors are shown in figure 4.13 (a) and (b) for Al₂O₃/p-InGaAs and Al₂O₃/n-InGaAs, respectively.²² If interface states can respond at these measurement conditions, the measured capacitance (C_m) will have a contribution from interface states (C_{it}), which is frequency and temperature dependent, and can be suppressed at a higher frequency and/or lower temperature.^{3, 18} This will especially affect the C-V responses in terms of frequency

dispersion in the accumulation region at different temperatures. Therefore, a significantly higher level of accumulation frequency dispersion and a decrease in the 1 MHz C_m are expected at a lower temperature when compared to the measurements at room temperature. It is believed that a true high frequency C-V is achieved at 1 MHz, measured at room temperature, as the multi-frequency (1 kHz to 1 MHz) and 1 MHz C-V measured at room temperature have very similar characteristics when compared to the C-V measured at -50 °C (not shown). The ability to achieve a true high frequency C-V response at 1 MHz and room temperature in the InGaAs MOS system using ALD deposited Al₂O₃ is attributed to the self-cleaning process of ALD Al₂O₃, which has been reported to be effective at removing the InGaAs native oxide and thus reducing the D_{it}, improving the efficiency of surface Fermi level movement.^{43, 44} The removal of the InGaAs native oxide has been confirmed by HR-TEM shown in figure 4.14.

Using the oxide thickness measured by HR-TEM, the oxide capacitance (C_{ox}) is calculated and used to determine the flatband capacitance (C_{fb}) ²³ Furthermore, the calculated C_{fb} can be used to determine whether the MOS capacitor is operating in the non-accumulation region at $V_g = 0$ V, thus validating the calculation of Fermi level positions using the depletion capacitance. From the C-V plot for n-InGaAs in figure 4.13 (b), the measured capacitance for Ni gate sample is below the calculated C_{fb} (0.0073 F/m²) and is thus operating in depletion at V_g = 0 V. The corresponding InGaAs depletion capacitance (C_s) can be calculated using the measured capacitance C_m ($C_{it}=0$) and an oxide capacitance value of $1.27 \mathrm{x} 10^{-6}~\mathrm{F/cm^2}.$ The C_s value can be used to calculate the surface Fermi level position with respect to the valence band maximum (VBM), for Ni gate n-InGaAs this yields a value of 0.71 eV. For the Al gate n-InGaAs sample shown in figure 4.13 (b), the C_m at V_g = 0 V approximately equals the C_{fb} value (0.00615 F/m²), which indicates that the sample is in the near flatband condition and its surface potential is approximately zero at $V_g = 0$ V. Thus the Fermi level position for this sample is 0.76 eV above the VBM, at the flatband condition for n-InGaAs. Both of these Fermi level positions are in reasonable agreement with the HAXPES measurements where the Fermi level is 0.59 to 0.69 eV above the VBM, for the Al gate, and 0.46 to 0.56 eV above the VBM, for the Ni gate. From the C-V for Ni gate



Figure 4.13: C-V responses at 1 MHz and 295 K for Al gate and Au/Ni gate over (a) Al_2O_3/n -InGaAs and (b) Al_2O_3/p -InGaAs MOS capacitors.



Figure 4.14: HR-TEM images of the MOS capacitors under investigation. Note that the InGaAs native oxide is removed due to the self-cleaning process of ALD deposited Al_2O_3 .

Table 4.3: Surface Fermi level positions obtained from C-V analysis at $V_g = O$ V and HAXPES measurements for uncapped, Al gate and Ni gate Al₂O₃/InGaAs samples

Sample	E_f - E_v	E_f - E_v	E_f - E_v	ΔE_f
	(no cap)	(Al cap)	(Ni cap)	(Al-Ni shift)
n-type	n/a	$0.76 \ \mathrm{eV}$	$0.71 \ \mathrm{eV}$	$0.05 \ \mathrm{eV}$
(C-V)				
n-type	$0.57{\rightarrow}~0.67~{\rm eV}$	$0.59{\rightarrow}~0.69~{\rm eV}$	$0.46{\rightarrow}~0.56~{\rm eV}$	$0.03 \rightarrow 0.23 \text{ eV}$
(HAXPES)				
p-type (C-V)	n/a	$0.73 \ \mathrm{eV}$	$0.55 \ \mathrm{eV}$	0.18 eV
(C-V)				
p-type	$0.39 \rightarrow 0.49 \text{ eV}$	$0.6 \rightarrow 0.7 \text{ eV}$	$0.36{\rightarrow}~0.46~{\rm eV}$	$0.14 \rightarrow 0.34 \text{ eV}$
(HAXPES)				

and Al gate over p-InGaAs shown in figure 4.13 (a), both samples are operating in depletion at $V_g = 0$ V. Using the same method of surface Fermi level calculation for n-InGaAs, the Fermi level is determined to be 0.55 eV and 0.73 eV above VBM with Ni and Al gates, respectively. This is also in reasonable agreement with the HAXPES measurments for identical samples, where the Fermi level positions are estimated to be 0.46 to 0.56 eV and 0.6 to 0.7 eV above the VBM, for Ni and Al gates, respectively.

A comparison between the Fermi level positions at the Al₂O₃/InGaAs interface derived from C-V analysis at $V_g = 0$ V and the HAXPES measurements, shown in table 4.3, displays that a reasonable agreement is achieved between the two techniques. The difference between the Fermi level positions of Al and Ni capped samples, obtained from C-V analysis, is also consistent with that determined by HAXPES measurements. The difference between the C-V and HAXPES values for E_f - E_v are in the range 0.1 to 0.2 eV. This is comparable to the results obtained in the case of the Al₂O₃/GaAs MOS system, as described in the previous section, but in the case of the InGaAs this error represents a larger percentage of the energy gap.

Further insight into the $Al_2O_3/InGaAs$ interface properties can be obtained from the HAXPES measurements in relation to the extent of the Fermi level movements at the InGaAs surface, when a metal layer is deposited. Following the deposition of the Al gate, the n-InGaAs Fermi level position moves towards the conduction band. For the p-InGaAs following Al deposition, the Fermi level also moves towards the conduction band edge, residing slightly below the conduction band minimum. These experimental observations confirm the ability of the Fermi level in the InGaAs bandgap to move towards the conduction band edge, attempting to align with the Al Fermi level (see figure 4.12). They are also consistent with the fact that movement of the Fermi level is restricted if the Fermi level is very close to the conduction band edge or already resides within the conduction band. The small shift seen for the p-InGaAs sample with a Ni cap is to be expected, as the Fermi level of Ni and uncapped p-InGaAs are already close to each other (the difference is 0.18 eV). The inability to move the n-InGaAs Fermi level to align with the Ni workfunction suggests a peak D_{it} distribution where the density increases in the lower half of the bandgap, consistent with previous publications.⁴⁵⁻⁴⁷

Work function differences between the metal (Φ_m) and the InGaAs Fermi level (Φ_s) should be reflected in a potential difference across the dielectric layer resulting in an energy broadening and a binding energy shift of the associated dielectric core levels.^{12, 14, 48} The presence of interface states which restrict the movement of the Fermi level at the oxide/InGaAs interface will increase the fraction of Φ_{ms} which falls across the oxide. Based on the difference in work functions, these changes would be expected to be more apparent in the p-type sample than in the n-type with an Al gate, and more apparent in the n-type sample than in the p-type with a Ni gate. Note that the shift resulting from Fermi level movement in the InGaAs is also present in the oxide peaks, so any shift in the oxide peaks is a combination of the Fermi level movement and a potential difference across the oxide after Fermi level alignment.

Figure 4.15 shows the changes in binding energy of the Al 1s oxide peak (at 1562 eV) for the n and p-InGaAs substrate resulting from metal deposition. For n-InGaAs the deposition of the low work function Al only results in a small increase in the Al 1s peak binding energy in the Al_2O_3 (0.18 eV), while for the p-InGaAs the deposition of Al results in a more significant increase in the binding energy (0.36 eV), reflecting the large work function difference between p-InGaAs and the



Figure 4.15: Al 1s spectra showing BE shift due to the changes in the potential across the Al₂O₃ layer caused by different work function metals for (a) n-InGaAs and (b) p-InGaAs. The presence of a metallic Al 1s signal at 1559.5 eV in the Al/Al₂O₃/InGaAs spectra originates from the metal cap.

low work function Al. For n-InGaAs the deposition of the high work function Ni results in a decrease in the Al 1s peak binding energy (0.43 eV), while for the p-InGaAs the deposition of Ni results in a smaller decrease in the binding energy (0.3 eV), consistent with the larger work function difference between n-InGaAs and the high work function Ni compared to the case of p-InGaAs. All of these changes are consistent with the expected polarity of the potential difference across the dielectric layer, caused by the workfunction difference between the InGaAs and the low and high work function metals.

The Al 1s peak widths (FWHM) for the metal capped samples broaden when compared to the samples without metal gates, reflecting the gradient in the potential across the dielectric layer. The small potential difference of 0.18 eV measured across the Al₂O₃ layer for the Al on n-type results in a broadening of 0.09 eV, while a full width half maximum (FWHM) increase of 0.62 eV for Ni on n-type reflects the larger potential difference across the dielectric. In the case of the ptype sample, a negligible difference in FWHM was measured for the Al contact, but a 0.46 eV FWHM increase was found for the Ni capped sample. While these differences are smaller than would be expected, this can be partially accounted for by the limited extent to which these potential changes can be quantified by measuring photoemission peak line shapes,³⁹ as well as the reduction in signal to noise especially in the case of the Ni capped samples.

4.4 Chapter Conclusion

The complimentary HAXPES and C-V characterisation technique outlined in chapter 2 was applied to the high $D_{it} Al_2O_3/GaAs$ sample set, as the high D_{it} present at the $Al_2O_3/GaAs$ interface makes this a particularly difficult sample to measure using conventional electrical characterisation techniques. Good agreement on the measured Fermi level positions was achieved between the two techniques. The results indicate different pinning positions within the GaAs bandgap for n and p-type samples, in agreement with previous studies, and the presence of higher D_{it} in the upper half of the GaAs bandgap.

It was also applied to the $Al_2O_3/InGaAs$ sample set, as this system is of technological relevance due its position as the prime candidate to replace Si in future MOSFET devices. Reasonable agreement between the HAXPES and C-V was found on Fermi level positions in all cases. HAXPES was also used to measure the potential difference across the dielectric layer, resulting from the workfunction difference between the partially pinned Fermi levels and the metal workfunctions. The results point to a partially pinned $Al_2O_3/InGaAs$ interface and suggest a peak interface state density near the midgap.

The ability of HAXPES to measure structures regardless of D_{it} was shown, proving its usefulness in the cases of samples with high D_{it} which are difficult to measure using electrical characterisation methods. These simple measurements of electronic structure combined with the standard chemical characterisation ability of photoemission, show the strengths of this technique, as applied to a range of MOS structures.

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Chapter 5

Novel salicide materials for source/drain regions in InGaAs MOSFETs

5.1 Introduction

The III-V materials, such as GaAs and InGaAs, show promise as an alternative (to Si) channel material in n-MOSFETs due to their higher injection velocities and electron mobilities. Research has recently focused on InGaAs due to promising improvements in the InGaAs/high- κ interface,¹⁻⁶ however the issue of source/drain (S/D) contacts in InGaAs based MOSFETs remains. A possible solution is to find a self-aligned silicide-like material (salicide), to act as the S/D contacts.⁷ Self-aligned source/drain materials allow the source/drain regions to be formed after the gate stack has been processed, as shown in figure 5.1. This ensures minimal overlap between the source/drain regions and the gate stack, which minimises the parasitic capacitance which this overlap usually generates.^{8, 9} The optimum material would ideally display an abrupt ordered interface with InGaAs, low sheet resistance (R_{sh}) (less than $1 \times 10^{-8} \Omega \text{cm}^2$), as well as achieving the thermal stability to withstand the temperatures involved in current MOSFET fabrication processes.

The material chosen should also have a Schottky barrier height of less than 0.2 eV, as predicted by intrinsic interface state theory,¹⁰ in order to from an Ohmic contact with the InGaAs. The search for this material has recently focused on the Ni-InGaAs system, due to its low R_{sh} and its apparent sharp interface with InGaAs.^{7, 11, 12} Previous measurements of the Schottky barrier height between Ni-InGaAs and p-InGaAs have yielded values of 0.6 to 0.8 eV, indicating that Ni-InGaAs froms an Ohmic contact on n-InGaAs and a Schottky contact on p-InGaAs.^{13, 14} In addition, investigations have been performed on the ability to incorporate this material system into standard device processing procedures.^{11, 15} There is a large body of work detailing the chemical interaction between Ni and GaAs, and Ni and InP, yet there is significantly less published data on the Ni-InGaAs system which is known to form a mixed metallic alloy phase.^{16–19} Previous studies have shown a trend of decreasing R_{sh} with increasing post deposition anneals, although there is a reversal in this trend between 450 to 500 °C.¹¹ While it has been suggested that this behaviour could be attributed to the thermal desorption of the III-V elements at this anneal temperature, more detailed work is needed to definitively prove this. The aim of this study is to address this issue by exploring the details of the chemical bond formation resulting both from the initial Ni deposition as well as the structural changes which occur after a range of thermal anneals up to 500 °C.

The Mo-InGaAs system is also studied as a possible S/D material for InGaAs MOSFETs. The thermal stability of Mo and the alignment between the work-function of Mo (4.65 eV) and the conduction band of InGaAs (4.5 eV) make Mo a good candidate for the formation of an Ohmic contact with n-InGaAs.²⁰ Sheet resistance values of 1 to $1.5 \times 10^{-8} \ \Omega \text{cm}^2$, and the ability to incorporate Mo-InGaAs into current device processing techniques have been demonstrated.^{8, 20–23} However, similar to the Ni-InGaAs system there has been no definitive study on the chemical bonds formed and the physical structure of the Mo-InGaAs alloy system. The aim of this preliminary work is to study the chemical bonds formed and the changes in physical structure of the Mo/InGaAs system at room temperature and following a 450 °C anneal.

X-ray photoelectron spectroscopy (XPS) is a widely used technique for the iden-



Figure 5.1: The processing involved in the formation of self-aligned NiInGaAs source/drain regions.

tification of chemical changes at metal/semiconductor interfaces, and can readily detect the oxidation state of the chemical species present. Additionally, XPS can be used to quantitatively determine non-destructive depth-dependent composition due to the well characterized photoelectron attenuation lengths. As mentioned in chapter 1, hard x-ray XPS (HAXPES), using x-ray photons of higher energy than conventional XPS, can increase the effective sampling depth of the photoemission measurement to greater than 20 nm into the material. Chemical speciation in XPS, however, is complicated by the dependence of peak energies and shapes on electrostatic interactions such as interfacial dipoles or fixed charges; that is, chemical differences cannot always be judged by apparent binding energy shifts alone. X-ray absorption spectroscopy (XAS) measures the absorption edges of the individual elements in a material to deduce information about their local bonding environment.²⁴ Unlike XPS, XAS is unaffected by sample charge, reducing the uncertainty in chemical speciation. In the analysis of XAS measurements the spectra can be compared with those of reference materials thereby assisting in the identification of the chemical species present. The work presented in this chapter
demonstrates the advantage in combining these two techniques, to obtain a clear chemical and structural model of complex material systems.

In the Ni-InGaAs study, nickel films of different thicknesses were sputter deposited on undoped InGaAs substrates and thermally annealed at a range of temperatures between 250-500 °C in 50 °C steps. These samples were then investigated using sheet resistance, XAS, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and HAXPES measurements in order to obtain information on the electrical resistivity, chemical composition, and physical structure of the Ni/InGaAs interfacial region. Grazing incidence XAS measurements were used to identify the chemical phases present in the Ni/InGaAs interfacial region and compared to more bulk sensitive measurements acquired at normal emission. While for the Mo-InGaAs study 5 nm of Mo was sputter deposited on undoped InGaAs substrates and the effect of thermal annealing at 450 °C was also studied. The Mo samples were only studied using HAXPES measurements in order to gain a preliminary understanding of the chemical and physical structure in the as-deposited sample and after 450 °C anneal.

5.2 Experimental Details

The undoped InGaAs samples consisted of 30 nm thick $In_{0.53}Ga_{0.47}As$ (herefater referred to as InGaAs) layers grown by molecular beam epitaxy (MBE) on InAlAs epi-ready layers on InP substrates. The samples were cleaned for 60 seconds in dilute hydrofluoric acid prior to being loaded into the metal deposition chamber. The samples for electrical and TEM measurements were produced with 5, 15, and 25 nm thick sputter-deposited Ni layers, and separate samples were prepared by annealing at 50 °C steps between 250 and 500 °C for 60 seconds. For HAXPES analysis one sample was left bare to act as a clean InGaAs reference, while all other samples had 5 nm of Ni sputter-deposited. One of these Ni capped samples was left unannealed, while the remaining samples were annealed in situ in 50 °C steps between 250 and 500 °C. In order to study the changes in the relative intensities of the peaks as a function of thermal annealing, which can assist in determining the extent of inter-diffusion and hence the location of the chemical species, an internal reference peak which remains at constant intensity is necessary. This was achieved by capping all of the HAXPES samples with a sputter deposited 3 nm SiN capping layer, after the Ni deposition and anneal, to act both as a barrier to post processing oxidation and as an internal reference. As such the Si 1s peak was acquired at the same time as each core level, with a constant ratio between the number of scans of the Si 1s and the relevant core level of 1:3. This was subsequently used to correct for any photon energy drift during the measurements, and to normalise the core level spectra across all samples. Using the Si 1s reference spectra for each core level, the change in peak intensity of a given chemical species throughout the anneal study can be determined, and thus the diffusion behaviour of the different elements can be investigated. An equivalent sample set, prepared using identical conditions was prepared for the XAS measurements, however, the SiN layer was not present, as a reference layer is not required in XAS.

The Mo-InGaAs samples used the same substrate InGaAs samples. For XPS analysis one sample was left bare to act as a clean InGaAs reference, while the other two samples had 5 nm of Mo sputter-deposited. One of those Mo capped samples was left unannealed, while the other was annealed in-situ at 450 °C. A 3 nm SiN layer was sputter-deposited on all samples, after the Mo deposition and any anneal, for intensity reference purposes.

Electrical sheet resistance (R_{sh}) measurements were performed on these annealed samples using a four-point probe apparatus. The samples for TEM analysis were prepared using a dual beam FIB equipped with an in-situ nano-manipulator. The samples were first protected by applying layers of electron beam deposited carbon and Pt, and then a second layer of Pt was deposited using the ion beam. The samples were thinned to electron transparency using 30 kV and 7 kV Ga ion beams followed by a 2 kV clean up step. The samples were imaged using an STEM apparatus operated at 300 kV and the images were recorded using a beam convergence angle of 8.1 mRad. TEM images were filtered to produce zero-loss images with a 10 eV energy window.

HAXPES measurements were carried out on the NIST beamline X24a at the

National Synchrotron Light Source (NSLS) at Brookhaven National laboratory. A double Si (111) crystal monochromator allowed for photon energy selection in the range of 2.1 to 5.0 keV. An electron energy analyser was operated at a pass energy of 200 eV giving an overall experimental broadening of 0.29 eV at the chosen photon energy of 2200 eV, 0.43 eV at 3000 eV, and 0.52 eV at 4050 eV. The total sampling depth of the HAXPES measurement using a photon energy of 2200 eV is estimated to be 13 nm,²⁵ which ensures the detection of photoemitted electrons from the 3 nm SiN and 5 nm Ni or Mo layers, as well as approximately 5 to 10 nm into the InGaAs, which is obtained from the inelastic mean free paths of the As 2p, Ga 2p, and In 3d photoemitted electrons at this photon energy.²⁶ The sampling depth is estimated to be 18 nm and 21 nm for 3000 eV and 4050 eV, respectively. The XPS core level spectra were curve fitted, using peak profiles composed of Gaussian and Lorentzian line shapes with a Shirley-type background.

XAS measurements were performed on the As, Ga, and In K-edges at room temperature using the NIST beamline X23a2 at the NSLS. A double Si (311) crystal monochromator allowed for photon energy selection in the range of 4.9 to 30 keV. XAS measurements were performed with the angle between the incident beam and sample surface at the critical angle (approximately 0.15°) to produce surface sensitive data and at both 0.5° (Ga and As K-edges) and 1.2° (Ni K-edge) to sample either the entire Ni film and/or a more bulk sensitive InGaAs signal. The grazing incidence angle chosen was at a critical angle of 0.15° where the x-ray photon penetration depth into the sample is 2.5 to 5 nm. Below the critical angle total external reflection occurs. The XAS signal is entirely bulk sensitive at an incidence angle of 1°, normal incidence in this case.²⁷

5.3 **Results and Discussion**

5.3.1 Ni-InGaAs

In order for Ni-InGaAs to be incorporated into the processing of III-V MOSFETs, it is critical to know the effect of both anneal temperature and initial Ni thickness



Figure 5.2: Sheet resistance measurements (a) on 5 nm and (b) 15 nm thick Ni layers as a function of post deposition anneal temperature and (c) as a function of Ni thickness after a 400 $^{\circ}$ C anneal.

 (T_{Ni}) on the electrical resistance. The sheet resistance of the Ni-InGaAs samples over a range of annealing temperatures, was determined by four point probe measurements.²⁸ Figures 5.2 (a) and (b), show the plots of R_{sh} for a 5 nm and a 15 nm thick Ni layer, respectively, annealed in 50 °C steps between 250 and 500 °C. A consistent drop in R_{sh} with increasing anneal temperature up to 400 °C is observed for the 5 nm deposited layer with the trend reversing for higher temperatures. This reversal is not observed for the 15 nm film which is attributed to the decreasing influence of Ni-InGaAs interface effects as the thickness of the deposited layer is increased. The even lower value of sheet resistance for the 25 nm Ni film following a 400 °C anneal, evident from figure 5.2 (c), confirms this trend in agreement with previous studies of the Ni-InGaAs system.^{11, 12, 15}

Cross-sectional TEM measurements of the 5 nm Ni samples following 250 °C,



Figure 5.3: SEM (top) and TEM (bottom) images of 5 nm Ni capped samples after (a) 250 °C, (b) 400 °C, and (c) 500 °C post deposition anneals showing the increasing thickness of the Ni-InGaAs following the 400 °C anneal and the agglomeration/phase separation which occurs following the 500 °C anneal.

400 °C, and 500 °C anneals were taken in order to determine the morphological changes in the Ni-InGaAs layer occurring over the course of the anneal study, and in particular if any significant difference could be observed following the 500 °C anneal.²⁹ In the TEM image in figure 5.3 (a) for the 250 °C anneal sample, a uniform Ni-InGaAs layer can be clearly distinguished. When the anneal temperature is increased to 400 °C the Ni-InGaAs layer thickness increases indicating the continued diffusion of Ni into the InGaAs. After the 500 °C anneal, there is evidence of significant disruption of the ordered layer structure apparent at lower temperatures and agglomeration/phase separation is seen in the Ni-InGaAs layer. This effect is also seen in SEM images, displayed in figure 5.3, which show a substantial increase in surface roughness and evidence of islanding in the 500 °C sample as compared to 250 and 400 °C samples.²⁹ This is a possible reason for the increase in sheet resistivity seen in figure 5.2 (a) following a 500 °C anneal, as the sample surface is not fully covered by a uniform Ni-InGaAs layer due to the disruption of the layered structure, as seen in figure 5.3 (c).

In order to further understand the decrease and subsequent increase in R_{sh}

with increasing anneal temperature for the 5 nm deposited Ni film, it is necessary to determine the changes in the sample chemistry which occur in the Ni-InGaAs interfacial region. The normalised spectra of the In 3*d*, As 2*p*, and Ga 2*p* core levels for the SiN capped InGaAs reference sample with no nickel layer are shown in figure 5.4. The spectra are fitted according to the parameters specified by *Brennan et al*,³⁰ who compiled a wide variety of reported oxide positions for the InGaAs core level peaks. It is clear from the presence of higher binding energy components in the individual elemental spectra that the InGaAs surface was partially oxidised due to air exposure prior to SiN deposition. The corresponding As and Ga absorption K-edges from the XAS measurements of this sample are also shown in figure 5.4 (b). The similarity of surface and bulk sensitive spectra reflect the homogeneous composition within the XAS sampling depth and match reference spectra of GaAs and InAs samples.^{31, 32}



Figure 5.4: (a) Normalised and fitted In 3d, As 2p, and Ga 2p HAXPES spectra acquired at a photon energy of 2200 eV for a SiN/InGaAs sample showing surface oxidation of the InGaAs layer. The spectra are plotted relative to the binding energy of the substrate InGaAs peaks, <u>As</u>-Ga for the As 2p, <u>Ga</u>-As for the Ga 2p and <u>In</u>-As for the In 3d. (b) XAS spectra of As and Ga K-edges showing the similarity in surface and bulk sensitive spectra of the InGaAs material consistent with a uniform chemical composition within the XAS sampling depth.

To understand the change in the chemical structure of the sample throughout the study, it is necessary to study both the chemical species present at each anneal stage and the location and relative concentration of these chemical species within the sample. As stated earlier the use of an internal reference peak, such as the Si 1s peak used here, allows the location of each chemical species to be determined. The Si 1s core level spectra acquired from the SiN capping layers on the bare InGaAs sample and the Ni-InGaAs sample as-deposited and following a 500 °C anneal, as shown in figure 5.5, display a very similar profile, apart from an increase in the higher binding energy shoulder at +1.5 eV. The SiN surface would be expected to oxidise after removal from the deposition chamber forming a thin layer of Si₂N₂O or SiO₂,³³ however, this would be expected to be similar for all samples. Therefore, the increased level of Si oxidation apparent for the samples with the Ni interlayer would suggest that this oxidation has occurred at the SiN/Ni interface which will be discussed later.



Figure 5.5: Normalised Si 1s spectra for the SiN capping layer with (20 °C) and without Ni and after 500 °C anneals. The spectra are plotted relative to the binding energy of the <u>Si</u>-N peak.

Figure 5.6 (a) shows the normalised (to the Si signal in the SiN cap) and curve fitted Ni 2p HAXPES spectra acquired at 2200 eV photon energy for the SiN-Ni-InGaAs samples as-deposited (20 °C) and after 300 and 400 °C anneals. The spectra are fitted with two peaks, the metal Ni peak at 0 eV, and a broad plasmon loss feature at +2.4 eV.³⁴ The metallic peak is fitted using an asymmetric Voigt function with Lorentzian values of $0.46\pm0.05 \text{ eV}$, and Gaussian values of 0.55 ± 0.05 eV. The decrease in the intensity of the Ni 2p peak with successively higher anneals suggests either the diffusion of the Ni into the InGaAs, and/or the diffusion of the InGaAs substrate elements through the Ni. However, there is no obvious change in the lineshape of the Ni 2p throughout the annealing study which indicates that either no strong chemical interaction between the Ni and InGaAs can be detected by HAXPES measurements, or that any chemical reaction between the Ni and InGaAs occurs upon Ni deposition and does not change following subsequent anneal.



Figure 5.6: (a) Normalised and fitted Ni 2p HAXPES spectra for SiN-Ni-InGaAs samples as-deposited (20 °C) and after 300 and 400 °C anneals. The spectra are plotted relative to the binding energy of the main Ni peak. (b) Fourier transformed XAS spectra of the Ni K-edge, for a reference Ni foil and the Ni signal from the as-deposited (20 °C) Ni-InGaAs sample and (c) XAS spectra from the as-deposited (20 °C) Ni-InGaAs sample and after 400 °C anneal showing evidence for NiGa and NiAs compound formation.

Figure 5.6 (b) shows the Fourier transformed Ni K-edge XAS spectrum of a reference polycrystalline metal Ni foil and the Ni-InGaAs sample prior to any anneal.

It is clear that the deposited Ni is not in a metallic Ni chemical environment, suggesting that significant intermixing with the InGaAs has occurred upon deposition. The Ni K-edge spectra for the deposited layer shown in figure 5.6 (c), acquired in both bulk and surface sensitive modes respectively, match the XAS spectrum of NiGa.³⁵ The characteristic two stepped structure (with step features at 8334 and 8342 eV) is weaker in the as-deposited film, possibly due to a mixed NiGa and metallic Ni phase in the reacted layer. This structure becomes more prominent, in both the bulk and surface spectra, after 250 °C anneal (not shown) indicating a continued formation of a NiGa phase. The NiGa formation also indicates that Ga atoms have diffused into the Ni layer at room temperature which is not evident from the apparent abrupt interface observed in the TEM image. Increasing the annealing temperature to 400 °C, as seen in figure 5.6 (c) results in the surface spectrum still resembling a NiGa alloy, but the bulk spectrum begins to show a change consistent with a chemically mixed phase of NiGa and NiAs, or NiAs₂, as suggested by the replacement of the step feature at 8342 eV with the observation of a peak at this position, and the appearance of a feature at 8352 eV in the bulk sensitive spectra consistent with a Ni-As chemical phase.³⁶ This analysis would suggest that the Ga has continued to diffuse through the Ni layer as a function of thermal annealing, leaving a Ga deficient Ni/InGaAs interface which results in NiAs bond formation. After a 500 °C anneal (not shown) the peaks at 8342 and 8352 eV which are assigned to NiAs in the bulk sensitive spectrum become more prominent, while the surface sensitive signal also displays the same NiAs features. Even for the highest anneal temperature, both surface and bulk sensitive spectra display a mix of NiGa and NiAs bonding configurations, once again confirming the diffusion of Ga through the Ni layer, and continued formation of NiAs. There is no evidence of Ni oxidation in any of the samples. It is important to note that the HAXPES measurements show no chemical change in the Ni spectra while the XAS identifies a large Ni-InGaAs interaction resulting in a variety of Ni compounds, which evolve as the anneal temperature increases.

Figure 5.7 (a) shows the HAXPES spectra for the normalised and curve fitted Ga 2p core level acquired at 2200 eV photon energy for the SiN-InGaAs sample and the SiN-Ni-InGaAs sample, as-deposited (20 °C) and after a 400 °C anneal.

The spectrum from the SiN-InGaAs sample is fitted with two peaks, one representing the Ga-As peak present in the InGaAs bulk, and one which is attributed to Ga₂O due to surface oxidation. The spectrum of the as-deposited SiN-Ni-InGaAs sample shows the growth of a broad peak, consistent with an oxidised Ga state, although it is difficult to be definitive as to the exact stoichiometry of the oxide as the attenuation of the substrate Ga-As peak removes the reference by which the oxidation state is normally identified.³⁷ In addition to the oxide growth, the lower binding energy peak at -0.5 eV is attributed to a Ga-Ni bonding interaction at the surface based on the respective electronegativities of both Ga (1.81) and Ni (1.91).³⁸ The reaction between Ga and Ni has been studied previously on GaAs



Figure 5.7: (a) Normalised and fitted Ga 2p HAXPES spectra, and (b) Ga K-edge XAS spectra, for a SiN-InGaAs sample and SiN-Ni-InGaAs samples as-deposited (20 °C) and after a 400 °C anneal. The HAXPES spectra are plotted relative to the binding energy of the substrate <u>Ga</u>-As peak.

and the observed strong interaction between Ni and Ga^{18} was attributed to the large enthalpy of formation for NiGa.³⁹ As the anneal temperature increases to 400 °C a large growth in the Ga oxide peak, at +1.1 eV, is seen, and a decrease in the Ga-Ni intensity. This assignment is consistent with inter-diffusion between the InGaAs and Ni layer as has been previously reported for the interaction between Ni and Ga containing semiconductors.^{39, 40} The subsequent oxidation of

the up-diffused Ga, prior to SiN deposition, results in the formation of a surface oxidised overlayer which acts to suppress the Ga-Ni signal. The Ga 2p spectra following the 500 °C anneal (not shown) is similarly dominated by the Ga oxide peak, indicating the formation of a thick Ga oxide layer prior to the deposition of the SiN cap.

The bulk sensitive Ga K-edge spectra shown in figure 5.7 (b) for InGaAs samples with and without Ni are indicative of the gallium atoms being in either a GaAs or InGaAs bonding environment with the characteristic two peak structure at 10378 and 10384 eV.³¹ However, with Ni deposition, the surface sensitive spectrum shows significant changes, and the appearance of a broad feature at 10380 eV, which could suggest the presence of NiGa or oxidised Ga at the surface of the Ni-InGaAs film.^{41–43} This additional feature in the spectrum is less evident in the bulk sensitive spectra, again suggesting that this species is localised at the SiN-Ni interface. Figure 5.7 (b) also shows the XAS spectra for a Ni-InGaAs sample following a 400 °C anneal where the surface sensitive data is a perfect match to Ga_2O_3 showing the distinct double peak at 10379 and 10382 eV, while the bulk signal shows a weakening of the InGaAs double peak feature, due to the increased formation of NiGa and Ga_2O_3 . Direct evidence for the formation of NiGa bonds cannot be determined from these spectra due to the fact that the primary feature of NiGa appears at 10378 eV,¹⁸ and thus would be difficult to distinguish from the Ga_2O_3 signal. This suggests that upon Ni deposition some Ga atoms diffuse through the Ni layer to the surface where they oxidise, which is assumed to have occurred when the Ni-InGaAs samples were removed from the vacuum system. The 500 °C spectra (not shown) display very similar results to the 400 °C spectra. The Ga K-edge data is thus consistent with the picture provided by the Ni K-edge analysis. Therefore, the Ga K-edge, Ni K-edge and HAXPES spectra can be interpreted in a consistent fashion indicating that the Ga has out diffused through the Ni overlayer resulting in the formation of NiGa within the reacted Ni layer and a Ga_2O_3 overlayer between the reacted Ni layer and the subsequently deposited SiN cap.

The complementary chemical information derived from the HAXPES and XAS spectra is particularly beneficial in the analysis of the Ga 2p. The only evidence in

the HAXPES spectra that this peak represents a different chemical state of the Ga is the large increase in the FWHM (1.38 eV in the oxide, as opposed to 0.78 eV in the Ga-As). The XAS spectra for the same sample acquired in a surface sensitive mode identifies the Ga signal to be in an oxidized state which is further confirmed by the HAXPES and XAS spectra following the 400 °C anneal. It is likely that oxidised Ga seen in the 20 °C spectra is composed of a number of suboxide states, and following anneal at 400 °C the greater concentration of Ga at the Ni-InGaAs surface forms Ga_2O_3 , which is the most stable of the Ga oxides.⁴⁴

The formation of Ga₂O₃ at the surface of the Ni-InGaAs reacted layer can be used to explain the changes in SiN oxidation seen in figure 5.5. The increase in the SiN-O signal in the as-deposited SiN-Ni-InGaAs sample is likely due to oxygen gettering by the SiN layer from the Ga₂O₃ at the SiN/Ni-InGaAs interface. The Gibbs free energies of SiN oxidation products, either SiO₂ ($\Delta G = -802 \text{ kJ/mole}$) or Si₂N₂O ($\Delta G = -1063 \text{ kJ/mole}$),^{33, 45} compared to Ga₂O₃ ($\Delta G = -998.3 \text{ kJ/mole}$)⁴⁶ suggest that Si₂N₂O could form at the SiN/Ni-InGaAs interface. The fact that there is no change in the extent of oxidation after a 500 °C anneal, where the Ga₂O₃ thickness is known to increase, indicates that this gettering behaviour is self-limited.

Figure 5.8 displays the normalised and curve fitted In 3d spectra acquired at 2200 eV for the SiN-InGaAs sample and SiN-Ni-InGaAs sample as-deposited (20 °C) and after a 400 °C anneal. For the reference SiN-InGaAs sample, the presence of a higher binding energy component shifted by 0.46 eV with respect to the In-As peak is indicative of an oxidised surface. A substantial change occurs in the as-deposited Ni sample resulting in the appearance of a very broad spectral feature which can be curve fitted with four component peaks. The two peaks on the lower BE side of the bulk In-As peak, are attributed to In-In bonds, at -1 eV and In-Ni bonds at -0.55 eV consistent with the electronegativity values of In (1.78) and Ni.³⁸ Previous studies on the interaction of a deposited Ni layer with the InP surface, have reported the dissociation of the InP with the appearance of In-In bonds.¹⁶⁻¹⁸ The Ni-In peak at -0.55 eV continues to grow as the anneal temperature increases. The strong increase in intensity of the In-Ni peak over the anneal range is attributed to the diffusion of In into the Ni layer, forming more



Figure 5.8: Normalised and fitted In 3d spectra for sample with (20 °C) and without Ni, and after 400 °C anneal. The spectra are plotted relative to the binding energy of the substrate In-As peak.

In-Ni bonds in the layer below the Ga_2O_3 , while both the In-In and In-As signals are suppressed with increasing anneal temperature as both bonds are localised at the InGaAs interface.

XAS spectra of the In K-edge were recorded but unfortunately due to the high energy (27000 eV) the peak was very broad making it hard to obtain information on the In bonding environment. The interpretation of the Ni K-edge spectra previously discussed suggests that any Ni-In formed is at a lower concentration than both NiAs and NiGa, as both of these alloys dominate the Ni edge spectra at different temperatures. However, due to the lack of XAS data, In chemical assignments are necessarily more speculative.

Figure 5.9 shows the normalised and peak fitted As 2p spectra for the SiN-InGaAs sample and the SiN-Ni-InGaAs sample as-deposited and after 400 °C and 500 °C anneals. For the SiN-InGaAs sample, the As 2p profile has higher binding energy components consistent with an oxidised surface. Although the overall line shape does not significantly change in the as-deposited SiN-Ni-InGaAs sample, the shift of 1 eV to higher binding energy (BE), indicates a possible change in



Figure 5.9: (a) Normalised and fitted As 2p HAXPES spectra for a SiN-InGaAs sample and SiN-Ni-InGaAs samples as-deposited (20 °C) and after 400 °C and 500 °C anneals (b) As K-edge XAS spectra, for a SiN-InGaAs sample and SiN-Ni-InGaAs samples as-deposited (20 °C) and after a 400 °C anneal. The HAXPES spectra are plotted relative to the binding energy of the substrate <u>As</u>-Ga peak.

chemical state of the As located at the surface of the InGaAs, consistent with the formation of NiAs as also seen in the Ni K-edge data. Throughout the anneal study, the As chemical bonding environments do not change, however, there is a significant reduction in the intensities of the overall As 2p peak as the anneal temperature is increased. As in the case for the Ni 2p peak in figure 5.6, this is primarily attributed to the formation of the Ga₂O₃ layer above the InGaAs interface. Additionally, the substantial reduction in the intensity of the total As profile as a function of thermal anneal indicates that the As remains primarily localised at the InGaAs surface throughout the study. The increase in the As intensity for the 500 °C annealed sample is attributed to the agglomeration of the reacted Ni-InGaAs layers, apparent from scanning electron microscopy (SEM) and cross-sectional transmission electron microscopy (TEM) data, where there is evidence of significant disruption of the ordered layer structure apparent at lower temperatures. The agglomeration issue noticed at 500 °C must be taken into account when interpreting the HAXPES spectra acquired at this temperature.

As K-edge spectra were acquired to confirm the sample composition profile, as shown in figure 5.9 (b). The spectra of bare InGaAs are characteristic of a clean InGaAs, or a GaAs As K-edge spectrum, with a double peak structure at 11870 and 11875 eV^{31} and the bulk spectra of the Ni-InGaAs sample show no change with anneal. The surface sensitive spectra do show a change indicative of a chemical interaction at the InGaAs surface; however, it has not been possible to identify the precise chemical species present, as the layer may consist of a number of As species, such as As-As, AsNi, and AsOx. Upon annealing at 400 °C, there is a significant change in the surface sensitive spectra with a strong peak emerging at 11868 eV corresponding to NiAs or NiAs₂ phases,^{37, 47} while the bulk sensitive signal still matches InGaAs. Following the 500 °C anneal (not shown), the surface sensitive spectrum becomes less well defined, while the bulk signal still resembles InGaAs. This suggests the formation of NiAs at the Ni-InGaAs interface, in agreement with the HAXPES results.

As in the case of the Ni 2p spectra, no obvious change in the As 2p peak lineshape indicative of a chemical interaction with Ni is seen in the HAXPES spectra. Therefore in this case, the XAS analysis has informed the HAXPES data interpretation. A clear existence of NiAs in the Ni and, to a lesser degree, the As K-edges, indicates that the dominant peak seen in the As 2p spectra can be attributed to a NiAs bonding interaction.

In order to determine the location of the As-Ni reacted phase with respect to the InGaAs substrate the As 3d peak was measured at higher photon energies, thereby increasing the sampling depth from 5 nm into the InGaAs layer for the As 2p peak acquired at 2200 eV photon energy, to 11 nm, 15 nm, and 20 nm for the As 3d taken at 2200, 3000 and 4050 eV respectively, as shown in figure 5.10.²⁵ If the proposed structure of an As-Ni overlayer on the InGaAs substrate is correct, then a more bulk sensitive measurement should be able to detect both As-Ni bonds and As-Ga bonds, attributed to the bulk InGaAs. As can be seen in figure 5.10, in the SiN-Ni-InGaAs sample an As-Ga bonding component can be identified at 0.48 eV lower BE than the As-Ni component peak, with the As-Ga peak area increasing with increasing photon energy, as the measurement becomes increasingly bulk sensitive. This confirms the presence of an As-Ni bonding interaction in a layer at



Figure 5.10: Normalised and fitted As 3d spectra for an as-deposited SiN-Ni-InGaAs sample taken at 2200 eV, 3000 eV, and 4050 eV photon energy. The spectra are plotted relative to the binding energy of the substrate <u>As</u>-Ga peak.

the surface of the InGaAs substrate.

In order to determine the relative positions of the NiIn and In-In bonding interactions within the Ni-InGaAs structure, HAXPES spectra were also taken at 3000 eV photon energy. This increases the sampling depth of the In 3*d* from 10 nm at 2200 eV to 13 nm at 3000 eV. From comparison of the normalised spectra following a 300 °C anneal, acquired at the two photon energies, as shown in figure 5.11, the change in the relative intensity between the In-In and In-Ni can be seen as the photon energy is varied. The results indicate that the In-In is located below the In-Ni, as in the more bulk sensitive (3000 eV) measurement the In-In intensity increases relative to the In-Ni. Similar comparison for the Ga 2*p* spectra of the as-deposited SiN-Ni-InGaAs sample, where the sampling depth is increased from 7 nm at 2200 eV to 11 nm at 3000 eV, demonstrate the Ga-Ni intensity increasing relative to the Ga₂O₃ in the more bulk sensitive measurement, indicating the Ga-Ni is located below the Ga₂O₃ in the structure as expected.

In order to produce an accurate model of the sample structure throughout the anneal study, it is important to understand the location of each chemical



Figure 5.11: Normalised and fitted Ga 2p spectra for an as-deposited (20 °C) SiN-Ni-InGaAs sample and In 3d spectra for a SiN-Ni-InGaAs sample after a 300 °C anneal, acquired at 2200 and 3000 eV photon energy.

species. To this end the photoionisation cross section, and inelastic mean free path (IMFP) normalised HAXPES peak areas have been plotted as a function of anneal temperature for each sample and displayed in figure 5.12. The steady decrease in the Ni 2p signal intensity as a function of anneal temperature is consistent with both the diffusion of Ni into the InGaAs layer as well as the growth of an overlayer of Ga_2O_3 . Conversely, the increase of the Ga signal over the course of the anneal study agrees with the continual up-diffusion of Ga through the Ni layer, forming a Ga_2O_3 overlayer between the SiN and Ni layers. The Ga area begins to decrease after the 450 °C anneal, which can be explained by the agglomeration of the Ni-InGaAs layer at this temperature, resulting in the unreacted substrate InGaAs moving toward the sample surface around the agglomerated region. A steady decrease in both the In 3d and As 2p signals up to 400 °C agrees with both of these elements out-diffusing less than the Ga and remaining closer to the InGaAs surface. Once again the increases seen in both peaks between 450 to 500 °C are due to the Ni-InGaAs agglomeration at these temperatures which significantly disrupts the overall film structure.



Figure 5.12: Plots of the normalised HAXPES peak areas as a function of temperature, of (a) As 2p, (b) Ga 2p, (c) In 3d, and (d) Ni 2p peaks. All areas have been normalised by photoionisation cross-section, and inelastic mean free path.

Combining the results from both XAS and HAXPES measurements, a model of the Ni-InGaAs system over the course of the anneal study can be produced. All of the chemical interactions observed appear to initiate upon Ni deposition, contrary to previous results,¹² and only the volume of the reacted layers changes as the anneal temperature increases. Upon Ni deposition there is a large diffusion of Ga into and through the Ni layer, resulting in the segregation of a Ga layer on top of the Ni, which subsequently oxidises to form Ga oxide. Beneath this layer there is a reacted NiGa phase which is intermixed with NiIn and NiAs chemical phases. These results would suggest that closer to the InGaAs surface there is a thin metallic In layer as a consequence of preferential out diffusion of Ga and a strong chemical interaction between the residual As and Ni resulting in the formation of Ni-As. The Ga oxide layer is believed to form the stable Ga_2O_3 upon anneal. Figure 5.13 shows the diffusion behaviour of the Ni and Ga in the sample, where Ni is seen to diffuse into the InGaAs forming the reacted Ni-InGaAs region and Ga diffuses through this reacted layer to form Ga_2O_3 at the sample surface. All of the chemical species formed, Ga oxide/Ga₂O₃, NiGa, NiIn, and NiAs increase in volume throughout the anneal study as Ni continues to diffuse into the InGaAs layer. The HAXPES and XAS experimental data can be used to construct a schematic model of the sample structure prior to Ni deposition, upon Ni deposition, and after a 400 °C anneal, as shown in figure 5.14. The diverse range of the chemical species formed coupled with their physical location in relation to the original Ni-InGaAs interface makes this a challenging experimental study which necessitated the enhanced sampling depth of HAXPES and the definitive chemical species identification capabilities of XAS. Previous studies have described a very abrupt Ni-InGaAs/InGaAs interface, and constant composition throughout the Ni-InGaAs layer.^{7, 11, 12} The results in this study are in contrast with these findings, as significant diffusion of certain species throughout the anneal study indicate a graded layered structure within the reacted region. These previous studies used secondary ion mass spectroscopy (SIMS) to characterise the diffusion profile of each element as well as the abruptness of the interface. While SIMS is a powerful method in determining the diffusion profile for a given element, the measurement in itself can cause intermixing and it does not provide chemical speciation. The key point in this study is that the combination of HAXPES



Figure 5.13: Schematic diagram showing the diffusion behaviour of the Ni and Ga in the sample.

measurements to identify reactions between Ni and InGaAs, and the diffusion profile of the elements throughout the Ni-InGaAs layer, and XAS measurements to provide chemical speciation allows the chemical compositional structure of this complex material system to be investigated.

5.3.2 Mo-InGaAs

Preliminary studies of the interaction of sputter-deposited Mo layers with InGaAs as studied by HAXPES measurements has been undertaken. Figure 5.15 shows the normalised (to the SiN overlayer) As 2p core level spectra acquired at 3000 eV for the SiN-InGaAs reference sample and the SiN-Mo-InGaAs sample as-deposited and following a 450 °C anneal. The spectrum for the SiN-InGaAs sample shows the presence of As-Ga bonds from the InGaAs substrate and a number of peaks at higher binding energy which are due to surface oxidation prior to SiN deposition. Note that all of the SiN-InGaAs reference spectra in this study were acquired at 2200 eV photon energy so are more surface sensitive. In the as-deposited SiN-Mo-InGaAs sample the most noticeable effect is the substantial suppression of the As peak due to the presence of the Mo layer, suggesting that the As remains primarily localised at the Mo/InGaAs interface. As shown in the As 2p peakfit for the reference sample the main peak is attributed to As-Ga bonds. The electronegativities of As (2.18), Ga (1.81) and Mo (2.16) indicate that any Mo-As



Figure 5.14: Schematic diagram showing the deduced Ni-InGaAs sample structure and composition before and after (20 $^{\circ}$ C) Ni deposition and following 400 $^{\circ}$ C anneal.

interaction peak should occur at higher BE than the As-Ga peak. There is no large change in peak shape upon deposition suggesting that the small peak observed was attributed to the suppressed InGaAs signal, although the shift to higher BE may suggest that this peak is actually As-Mo. After the 450 °C anneal the increase in the peak intensity indicates the diffusion of As into the Mo layer which would be expected to lead to interaction between the Mo and As. The As 2p core level spectra of the same samples were also acquired at 4000 eV photon energy, as shown in figure 5.16, which increases the sampling depth into the InGaAs layer from approximately 10 nm at 3000 eV to 13 nm at 4000 eV photon energy. Although little difference between the 3000 and 4000 eV spectra is seen for the SiN-InGaAs sample and the as-deposited SiN-Mo-InGaAs sample, the presence of a peak at lower BE in the SiN-Mo-InGaAs sample following a 450 °C anneal is attributed to an InGaAs substrate signal. The evidence of this peak at 0 eV suggests that the large peak (+0.6 eV) seen in the 3000 eV spectra is due to an As-Mo interaction. The fact that the As-Ga peak increases in intensity after anneal may also suggest that it is the Mo which diffuses down into the InGaAs.



Figure 5.15: Normalised and fitted As 2p HAXPES spectra for a SiN-InGaAs sample and SiN-Mo-InGaAs sample as-deposited (20 °C) and after 450 °C anneal, acquired at 3000 eV photon energy.



Figure 5.16: Normalised and fitted As 2p HAXPES spectra for a SiN-InGaAs sample and SiN-Mo-InGaAs sample as-deposited (20 °C) and after 450 °C anneal, acquired at 4000 eV photon energy.

The Ga 2p spectra of the SiN-InGaAs reference sample and the SiN-Mo-InGaAs sample as-deposited and following a 450 °C anneal in figure 5.17 show a partially oxidised surface for the SiN-InGaAs sample. The as-deposited SiN-Mo-InGaAs spectra is fitted with a single peak, which can be attributed to either Ga-As or Ga-Mo, as As and Mo have very similar electronegativites, 2.18 and 2.16 respectively. After the 450 °C anneal there is a growth of a large broad peak, consistent with oxidised Ga. The peak at lower BE is attributed to the same Ga-As/Ga-Mo peak as in the as-deposited sample. The spectra acquired at 4000 eV photon energy, as shown in figure 5.18, show the presence of a small peak at lower BE in the as-deposited SiN-Mo-InGaAs sample consistent with Ga-Ga bonds. Upon anneal at 450 °C the lower BE Ga-As/Ga-Mo peak is shown to increase relative to the oxidised Ga indicating that the Ga_2O_3 is located above the Ga-As/Ga-Mo layer within the sample structure. This interpretation suggests the diffusion of Ga through the Mo layer following thermal anneal, resulting in a layer of Ga at the surface of the sample which oxidises, similar to the behaviour seen in the Ni-InGaAs study.



Figure 5.17: Normalised and fitted Ga 2p HAXPES spectra for a SiN-InGaAs sample and SiN-Mo-InGaAs samples as-deposited (20 °C) and after 450 °C anneal, acquired at 3000 eV photon energy.



Figure 5.18: Normalised and fitted Ga 2p HAXPES spectra for a SiN-InGaAs sample and SiN-Mo-InGaAs samples as-deposited (20 °C) and after 450 °C anneal, acquired at 4000 eV photon energy.

The In 3d spectra acquired at 3000 eV, as shown in figure 5.19, indicate a partially oxidised surface for the SiN-InGaAs sample. The as-deposited SiN-Mo-InGaAs sample shows a substantial suppression of the In 3d peak, indicating little or no diffusion into the Mo layer. The peak fit is composed of one large peak, attributed to In-As, and a small component at lower BE, consistent with metallic In (In-In). Although no obvious change in lineshape is seen between the SiN-InGaAs and as-deposited SiN-Mo-InGaAs sample, the single peak can be attributed to either In-As or In-Mo. Following the 450 °C anneal there is a substantial change in the peak profile, with the growth of an In-In peak, and the appearance of a peak at higher BE, which is likely due to oxidised In, possibly In_2O_3 as this is the most stable In oxide. This suggests a small amount of interdiffusion between the In and Mo occurs, forming an In-In layer at the Mo surface, which oxidises when the sample is removed from the metal deposition chamber, similar to the Ga oxide in the Ni-InGaAs study. The In 3d spectra acquired at 4000 eV photon energy, as shown in figure 5.20, show the growth of the In-As/In-Mo sample with respect to the oxidised In peak in the 450 °C sample. This suggests that the In-In remains at the InGaAs interface, the In-As/In-Mo lie above this in an intermixed Mo-InGaAs layer and the oxidised In is located above this, at the SiN/Mo-InGaAs interface.



Figure 5.19: Normalised and fitted In 3d HAXPES spectra for a SiN-InGaAs sample and SiN-Mo-InGaAs samples as-deposited (20 °C) and after 450 °C anneal, acquired at 3000 eV photon energy.



Figure 5.20: Normalised and fitted In 3d HAXPES spectra for a SiN-InGaAs sample and SiN-Mo-InGaAs samples as-deposited (20 $^{\circ}$ C) and after 450 $^{\circ}$ C anneal, acquired at 4000 eV photon energy.

The Mo 3d spectra of the SiN-Mo-InGaAs sample both as-deposited (20 °C) and after 450 °C anneal are shown in figure 5.21. As these spectra are not fitted it is the change in peak intensity which will provide the most insight as to the change in chemical and physical structure. A decrease in the intensity of the Mo peak is seen following thermal anneal, which suggests a diffusion of Mo into the InGaAs layer following thermal anneal, as suggested by the As, Ga and In core level spectra.



Figure 5.21: Normalised Mo 3d HAXPES spectra for a SiN-Mo-InGaAs sample as-deposited (20 °C) and after 450 °C anneal, acquired at 3000 eV photon energy.

The chemical information deduced from the core level spectra is used to assemble a schematic diagram of the Mo-InGaAs system for the sample as-deposited and following a 450 °C anneal sample, as shown in figure 5.22. The reaction of As and Ga with the Mo results in an excess of In at the Mo/InGaAs interface, resulting in a thin In-In layer. The reacted Mo-In, Mo-As and Mo-Ga species form an intermixed layer with amorphous Mo on top of the InGaAs substrate. Both Ga, and to a lesser extent In, diffuse through this reacted Mo-InGaAs layer to form In and Ga oxides at the sample surface.

5.4 Conclusion

The change in chemical composition, physical structure and the accompanying change in resistivity of a Ni-InGaAs interface was studied as a function of post deposition anneal temperature. It was found that while the resistivity steadily decreases as the anneal temperature increases for thick films, thinner films show a reversal of this trend at 450 °C due to the agglomeration/phase separation of



Figure 5.22: Schematic diagram showing the deduced Mo-InGaAs sample structure and composition before and after (20 $^{\circ}$ C) Ni deposition and following 450 $^{\circ}$ C anneal.

the Ni-InGaAs film. The analysis of both the chemical and structural composition of Ni-InGaAs contacts has been shown to significantly benefit from the use of two complementary measurement techniques. While XAS can readily identify the chemical species present, HAXPES is required to determine the relative concentrations and diffusion trends throughout the annealing study. The combination of XAS and HAXPES analysis is necessary to fully describe the chemical composition and structure of the Ni-InGaAs layer. The Ni-InGaAs model derived from the experimental results reveals a highly reactive and interdiffused interface with substantive Ga out-diffusion and the formation of Ni-In and Ni-As alloy phases closer to the Ni-InGaAs interface. These studies provide a detailed understanding of this material system and have potential application for fabrication strategies for S/D contacts in future InGaAs MOSFETs. The chemical structure of Mo-InGaAs system was also studied in order to understand the chemical bonds present upon formation of the Mo-InGaAs alloy. The results show the extensive interaction between the Mo and InGaAs suggesting Mo compound formation with all three substrate elements and the diffusion of Ga and, to a lesser extent, In through the Mo layer to form surface oxides.

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Chapter 6

Conclusions and Future Work

6.1 Conclusions

In this thesis the advantages of hard x-ray photoelectron spectroscopy (HAXPES) over conventional x-ray photoelectron spectroscopy for various applications in the study of Si and III-V based MOS structures have been explored. In addition to the use of HAXPES complementary techniques such as capacitance-voltage (C-V) profiling and x-ray absorption spectroscopy have been employed.

In chapter 3, accurate changes in the binding energy positions of Si and SiO₂ core levels from HAXPES measurements have been used to determine Fermi level movement as a function of metal workfunction along with a potential difference across the oxide layer, due to the remaining separation of the Si Fermi level and the metal workfunction, which manifested as a shift of the SiO₂ peak in the Si 1s spectrum. C-V analysis on near-identical samples (only the metal thickness differed) showed good agreement with the HAXPES results, both in Fermi level positions and flatband shifts. This system therefore acted as proof of principle for the experimental method.

In chapter 4, this method was subsequently applied to the high D_{it} Al₂O₃/GaAs system for high and low workfunction metals in order to study the behaviour of

a system with a pinned Fermi level. As expected little Fermi level movement was measured, regardless of the metal workfunction, indicating a pinned or partially pinned Fermi level. As a result a large potential difference was observed in the Al_2O_3 peak due to the large separation between the GaAs Fermi level and metal workfunction. The identification of different pinning positions for n and p-doped GaAs showed reasonable agreement with previous theories and experiments.^{1–7} The measurement of pinning positions allowed the 1 MHz C-V analysis to be confidently fitted, in order to obtain Fermi level positions. Good correlation between C-V and HAXPES measurements was obtained for both the $Al_2O_3/GaAs$ and finally the $Al_2O_3/InGaAs$ MOS systems. This method has shown particular promise in high D_{it} systems which are difficult to measure using conventional electrical measurements (such as C-V).

In chapter 5 the Ni-InGaAs self aligned salicide was investigated as a possible material for use as the source/drain region in future InGaAs based MOS field effect transistors (MOSFETs). Electrical measurements showed the low sheet resistivity of this system, and how this resistivity evolves with increasing anneal temperature. SEM and TEM images showed the growth of the Ni-InGaAs layer as a function of anneal temperature and showed the physical disruption which occurs after a 500 °C anneal. Complementary HAXPES and XAS analysis were performed on samples and showed the reaction between Ni and all three component elements of the InGaAs, resulting in the formation of an extensively intermixed Ni-InGaAs reactive layer. A large scale diffusion of Ga through this intermixed layer was observed, resulting in an oxidised Ga layer on the surface of the Ni-InGaAs layer. The strength of using a chemical compound specific technique such as XAS combined with HAXPES, which can give information on the diffusion behaviour of various elements and the evolution of the sample structure, was demonstrated, and used to assemble a schematic model of the sample structure as a function of anneal temperature.

The Mo-InGaAs salicide was also studied using HAXPES. Similar to the Ni-InGaAs, a large scale reaction between the InGaAs and Mo was seen, once again accompanied by the diffusion of Ga and In through the reacted layer.

6.2 Future work

The aspects of this work which require further study are outlined in this section.

6.2.1 HAXPES measurements of in-situ biased samples

The combined C-V and HAXPES characterisation of MOS structures performed in chapters 3 and 4, used high and low workfunction metals to sweep the Fermi level through the bandgap of the semiconductor substrate. The next logical step in this experiment is to measure the movement of the semiconductor Fermi level in a more dynamic manner, through the use of an applied bias voltage, similar to that used in C-V profiling.

Initial attempts have been made to measure $Al_2O_3/GaAs$ based MOS structures, similar to those measured previously in chapter 4, using a nickel capping layer. In order to apply an in-situ bias, samples were required which had a thicker metal region to act as the metal probe contact, and a thinner metal region on which HAXPES analysis could be performed. The workfunction of the metal top contact is not as important in these experiments as the Fermi level movement will be caused by the applied bias. Therefore the primary concern in choosing a metal was air stability, in order to have a minimum surface oxide on the sample. Ni was the chosen material. The sample design decided upon is shown in figure 6.1. The bias was applied to the semiconductor, while the capping metal was grounded.



Figure 6.1: Sample design chosen for the biased HAXPES samples.

Previous studies of the application of an in-situ bias voltage to MOS structures have shown the ability to extract information on the energy mapping of interface $states^{8-10}$ in MOS structures. In the biased HAXPES measurements the substrate material (semiconductor) is biased, while the metal gate is grounded, so the nickel workfunction (Φ_{Ni}) is in alignment with the Fermi level of the spectrometer. When no bias is applied the Fermi level of the semiconductor (E_f) and the workfunction of the metal are in alignment, however, when a bias voltage is applied this decouples the semiconductor Fermi level and nickel workfunction. The energy difference between Φ_{Ni} and the conduction band minimum and valence band maximum of the semiconductor are fixed values, and as the core level peak is also at a fixed energy difference from the valence band maximum, Fermi level movement cannot alter the position of the semiconductor core level with respect to Φ_{Ni} . As shown in figure 6.2 the energy difference (x) between Φ_{Ni} and the semiconductor core level , is not affected by movement of the semiconductor Fermi level due to the applied bias voltage. Thus movement of the semiconductor Fermi level in the bandgap, due to band-bending, will not result in the shift of the substrate core level. However, if the bias voltage results in charge at the interface due to charging interface states, or generating a potential difference across the oxide layer, a shift in the core level peak will be observed. In this scenario, shown in figure 6.3, the accumulation or release of charge at the oxide/semiconductor interface results in a shift of the core



Figure 6.2: Band diagram of MOS structure with and without an applied positive bias voltage, assuming all bias voltage results in Fermi level movement.

level by a value y, related to the magnitude of potential drop at the interface.

Figures 6.4 (a) and (b) show the Ga 2p spectra of a Ni/Al₂O₃/n-GaAs sample with an applied negative and positive bias, respectively. In the measurement of the GaAs samples it was noticed that small bias voltage ranges produced little noticeable effect. The likely cause of this is that during the growth or deposition of the Al_2O_3 an oxide was formed on the back of the sample. Therefore, it was necessary to use much large bias voltage ranges than those used in previous studies in order to ensure that the bias voltage was falling across the region of interest, i.e. the sample substrate and dielectric layer. The application of larger bias voltage did result in shifting of the core level Ga 2p peaks. The dependence of core level peak binding energy position as a function of applied bias is plotted in figure 6.5. It was found that for the n-doped samples a positive bias voltage resulted in a large peak shift, while a negative bias voltage resulted in either no shift or a very small shift, as shown in figure 6.4 where the peak shift as a function of bias voltage is plotted. As explained previously the shift of the Si 1s substrate peak indicates the potential field across the dielectric layer. As such it is not clear why only one bias polarity should result in a peak shift. The opposite behaviour was observed for the



Figure 6.3: Band diagram of MOS structure with and without an applied positive bias voltage, assuming all bias voltage results in accumulation or release of charge at the oxide/semiconductor interface.

p-type samples. It is clear from these measurements that while the application of a negative bias voltage results in a potential drop across the dielectric, the applied forward bias does not show an equivalent oxide field.

In addition figure 6.6 shows the large increase in the FWHM of the Al 1s oxide peak which is consistent with a large potential difference falling across the Al₂O₃ layer at large positive bias voltages, however, the same trends are seen regarding a negative bias voltage, where little broadening or peak shifts are seen. Indeed the spectra in figure 6.6 seem to show the presence of two peaks in the Al 1s spectra, this could be caused by the very large potential difference present at bias voltages above 3 V, where there is such a large potential difference falling across the dielectric that separate peaks can be detected from both the Ni/Al₂O₃ interface and the Al₂O₃/GaAs interface.

The results from the initial attempt at biased HAXPES measurements of MOS structures are still not fully understood although it is clear there were a number of issues with the experiment which need to be addressed for future studies. In order to ensure electrical contact on the back of the samples ohmic contacts should



Figure 6.4: Ga 2p spectra of Ni/Al₂O₃/n-GaAs samples with (a) a negative and (b) a positive applied bias voltage.



Figure 6.5: Plot of the Ga 2p positions as a function of applied bias voltage



Figure 6.6: Al 1s spectra of Ni/Al₂O₃/n-GaAs samples with a negative applied bias voltage.

be fabricated. In addition the voltage supply used in this study was not accurate enough to indicate the precise magnitude of the leakage current, which would give an indication of a breakdown of the oxide. It is possible that the large bias voltages used resulted in oxide breakdown in some cases. However, these initial studies indicate that further investigation of in-situ bias studies could yield important information about Fermi level movements resulting from an applied voltage, particularly for highly pinned systems.

6.2.2 Further analysis of the Mo-InGaAs salicide

In chapter 5 a preliminary study of the Mo-InGaAs salicide was performed using HAXPES. The measurement of only three samples: no Mo, as-deposited Mo, and after a 450 °C anneal is not sufficient to give a full understanding on the evolution of the sample system as a function of anneal temperature. It would be of interest to analyse this system using HAXPES at a range of intermediate temperatures similar to those measured in the more comprehensive Ni-InGaAs sample set.

In addition, the performance of XAS on identical samples would also be of interest to unambiguously identify the chemical bonds present in the HAXPES spectra. Finally structural (SEM and TEM) analysis, and electrical data on the sample set would also aid in providing a full study of the suitability of Mo-InGaAs as a possible source/drain material in future InGaAs MOSFETs.

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