



Dublin City University

School of Physical Sciences

Characterising Infiltration Techniques in Polymer Area Selective Deposition

Matthew Snelgrove B.Sc.

Thesis submitted for the award of Doctor of Philosophy (Ph.D.)

January 2022

Supervised by Dr. Robert O'Connor & Prof. Enda McGlynn

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, and 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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ID No.: 14476998

Date: 9th January 2022

Acknowledgements

I'd firstly like to thank my parents, Ann and James Snelgrove, who gave me the opportunity to pursue my dream of studying physics at university. I'd also like to thank my partner Deana Crowe and all my close friends – especially Matthew Connolly for helping me get my chemistry up to scratch!

This was a big project, and I was fortunate to be able to work with a variety of wonderful and talented people. This includes all my collaborators in the AMBER centre, particularly Ross Lundy and Pravind Yadav, whom without their knowledge in polymer chemistry, the experiments in this work would never have come to fruition. I also wish to thank the invaluable assistance from Intel, especially to Matt Shaw, Jennifer McKenna, and Peter Gleeson. I am extremely lucky to have worked with the beamline scientists Jean-Pascal Rueff in SOLEIL synchrotron, and Conan Weiland and Joe Woicik at Brookhaven National Laboratory. Finally, to my good friend Pierre Giovanni Mani González – you are the epitome of a passionate researcher, and I am extremely grateful for the assistance (and laughs) you have provided me over the years.

I would also like to thank the wonderful people I got to work with in DCU. This goes especially to my close colleagues (and friends!) Feljin, Caitlin and Shane; You've been a big part of my life and made things easier in unprecedented global circumstances. To Justin – who's passion for surface science was one of the main reasons why I am here now. To Kyle, Pat and Des, whose ability and willingness to help in a variety of problems I would throw at them was so important. And of course, to Greg Hughes for his guidance, support, and amazing opportunities he provided for me.

Last – but definitely not least – I am beyond grateful to my supervisors Dr. Robert O’Connor and Prof. Enda McGlynn, who gave me the tools and knowledge to shape my research, while always being there to help and support me. I hope this work makes you proud!

Finally, I’d like to acknowledge Science Foundation Ireland and Intel for the financial support of this work.

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List of Abbreviations

A non-exhaustive list of common-occurring abbreviations that appear throughout the text.

AFM	: Atomic Force Microscopy
ALD	: Atomic Layer Deposition
ALE	: Atomic Layer Epitaxy
AMBER	: Advanced Materials and BioEngineering Research
ARXPS	: Angle Resolved X-ray Photoelectron Spectroscopy
ASD	: Area Selective Deposition
ATR	: Attenuated Total Reflectance
BCP	: Block Copolymer
B_E	: Binding Energy
BJT	: Bipolar Junction Transistor
C_{acc}	: Accumulation Capacitance
CAE	: Constant Analyser Energy
CD	: Critical Dimension
C_{FB}	: Flat-band Capacitance
CMOS	: Complementary Metal–Oxide–Semiconductor
CV	: Capacitance Voltage (Sweep)
CVD	: Chemical Vapor Deposition
D_{it}	: Interface Trapped Charge
DCU	: Dublin City University
EAL	: Effective Attenuation Length
E_B	: Breakdown Field
EDX	: Energy Dispersive X-ray Spectroscopy
EPE	: Edge Placement Error
EUV	: Extreme Ultraviolet (Lithography)
FIB	: Focused Ion Beam
FTIR	: Fourier Transform Infrared Spectroscopy
FWHM	: Full Width Half Maximum
GA-FTIR	: Grazing Angle Attenuated Total Reflectance FTIR
GPC	: Growth per Cycle
HAXPES	: Hard X-ray Photoelectron Spectroscopy
HV	: High Vacuum
IC	: Integrated Circuit
IMFP	: Inelastic Mean Free Path
IPA	: Isopropyl Alcohol
IR	: Infrared
IV	: Current Voltage (Sweep)
K_E	: Kinetic Energy
MOS	: Metal–Oxide–Silicon (Transistor)
MOSCAP	: Metal Oxide Semiconductor Capacitor
MOSFET	: Metal–Oxide–Semiconductor Field-Effect Transistor

MPI	: Multiple Pulsed Infiltration
MPL	: Multiple Patterning Lithography
MSE	: Mean Squared Error
NA	: Numerical Aperture
NIST	: National Institute of Standards and Technology
N _{OT}	: Density of Trapped Oxide Charge
OH	: Hydroxyl Group
P2VP	: Poly-2-vinyl pyridine
P4VP	: Poly-4-vinyl pyridine
PDI	: Polydispersity Index
PDLA	: Poly(d-lactide)
PDMS	: Polydimethylsiloxane
PEALD	: Plasma Enhanced Atomic Layer Deposition
PEO	: Polyethylene glycol
PMMA	: Poly (methyl methacrylate)
PS	: Polystyrene
PVP	: Polyvinylpyridine (P2VP & P4VP, not to be confused with Polyvinylpyrrolidone)
RMS	: Root Mean Square
SAM	: Self Assembled Monolayer
SCCM	: Standard Cubic Centimetres per Minute
SEM	: Scanning Electron Microscope
SH	: Thiol Group
SIS	: Sequential Infiltration Synthesis
STEM	: Scanning Transmission Electron Microscope
TDDDB	: Time Dependent Dielectric Breakdown
TEM	: Transmission Electron Microscope
THF	: Tetrahydrofuran
TMA	: Trimethylaluminum
UHV	: Ultra High Vacuum
UV	: Ultraviolet
V _B	: Breakdown Voltage
V _G	: Gate Voltage
VPI	: Vapor Phase Infiltration
XPS	: X-ray Photoelectron Spectroscopy

Publications Arising from this Work

- 1. Electrical Properties of P4VP-Mediated Hafnium Oxide Films**
M. Snelgrove, P. Yadav, K. Shiel, C. Weiland, P. Gleeson, G. Hughes, M.A. Morris, J.C. Woicik, E. McGlynn and R. O'Connor. *In Preparation*.
- 2. Growth Chemistry and Electrical Performance of Ultrathin Aluminium Oxide Films Formed by Vapour Phase Infiltration of Poly-2-vinylpyridine**
M. Snelgrove, C. McFeely, G. Hughes, C. Weiland, J.C. Woicik, K. Shiel, P.G. Mani Gonzalez, O. Solis-Canto, C. Ornelas, K. Cherkaoui, P. Yadav, M.A. Morris, E. McGlynn, and R. O'Connor. *In Preparation*.
- 3. Use of Plasma oxidation for conversion of metal salt infiltrated thin polymer films to metal oxide.**
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- 4. Fabrication of High-k Dielectric Metal Oxide Films on Patterned Substrates: Polymer Brush Assisted Depositions for Modern Device Architectures**
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- 5. Polymethyl Methacrylate Template Assisted Deposition of Uniform Zirconium Oxide Films on Copper Substrate through liquid phase for Area Selective Deposition Application.**
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- 8. Precise Definition of a “Monolayer Point” in Polymer Brush Films for Fabricating Highly Coherent TiO₂ Thin Films by Vapor-Phase Infiltration**
R. Lundy, P. Yadav, N. Prochukhan, E. C. Giraud, T. F. O'Mahony, A. Selkirk, E. Mullen, J. Conway, M. Turner, S. Daniels, P. G. Mani-Gonzalez, M. Snelgrove, J. Bogan, C. McFeely, R. O'Connor, E. McGlynn, G. Hughes, C. Cummins and M. A. Morris, *Langmuir*, 2020, **36**, 12394–12402.

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- 10. Analysis of Al and Cu salt infiltration into a poly 2-vinylpyridine (P2vP) polymer layer for area selective deposition applications**
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- 1. Photoemission Study of the Growth of Cobalt Nitride by Plasma Enhanced Atomic Layer Deposition**
M. Snelgrove, K. Shiel, C. Weiland, G. Hughes, J. Woicik, and R. O'Connor
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- 2. Investigation into the effect of Molecular Weight on the thickness of Polymer Brush Monolayers Suitable for Area Selective Deposition**
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5th Area Selective Deposition Workshop, Virtual Meeting, 2021.
- 3. Use of a Reactive ion etch plasma system for conversion of thin salt infiltrated polymer films to metal and metal oxide layers**
J. Conway, M. Snelgrove, R. Lundy, P. Yadav, M. Turner and S. Daniels
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- 4. Use of a Reactive ion etch plasma system for conversion of thin salt infiltrated polymer films to metal and metal oxide layers**
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- 5. Application of Plasma processing for conversion of salt infiltrated polymer films to metal oxide films**
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- 6. In situ XPS Characterization of Al_xO_y growth by ALD**
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- 7. Aluminium Infiltration of Poly(2-vinylpyridine) via Atomic Layer Deposition**
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*Underscore denotes speaker

8. Hard X-ray Photoelectron Spectroscopy Study of Copper Formation by Metal Salt Inclusion in a Polymer Film

M. Snelgrove, P G. Mani-Gonzalez, J. Bogan, R. Lundy, J.-P. Rueff, G. Hughes, P. Yadav, E. McGlynn, M. Morris and R. O'Connor

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9. Angle-Resolved HAXPES analysis of Al_xO_y and Cu_xO_y layers formed by metal salt infiltration into a poly 2-vinylpyridine (P2vP) polymer layer

P.G. Mani-Gonzalez, M. Snelgrove, J.-P. Rueff, R. Lundy, J. Bogan, R. O'Connor, M.A. Morris and G. Hughes

4th Area Selective Deposition Workshop, Leuven, 2019.

10. Formation and in-situ Characterisation of Metal Oxides from Infiltrated Polymers

M. Snelgrove, P.G. Mani-Gonzalez, J. Bogan, R. Lundy, J.-P. Rueff, G. Hughes, P. Yadav, P. Swift, E. McGlynn, M.A. Morris and R. O'Connor

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Characterising Infiltration Techniques in Polymer Area Selective Deposition

Matthew Snelgrove

Abstract

The integrated circuit (IC) and the vast number of transistors that each one contains has revolutionised how humanity lives in the 21st century. Key to the near constant progress in modern electronics is the photolithography process of ‘top down’ patterning an IC with the use of light, interconnecting the millions of transistors together so that the device can perform a rich variety of roles. However, the increasing demand for faster, more efficient technology while ensuring costs are kept to a minimum, has caused photolithography to fast approach its technological and financial limitations. Research into ‘bottom-up’ methods as an alternative to photolithography for next-generation electronic devices has led to major efforts in identifying suitable polymers for area selective deposition (ASD) and block copolymer (BCP) lithography. These patterning approaches rely on a self-assembled surface containing ‘active’ or ‘inactive’ polymer regions. When the sample is exposed to a metal in solvent or chemical-precursor form, the solvent/precursor will either be incorporated or rejected by the active or inactive polymers, respectively. Subsequent polymer removal can be achieved through an oxygen rich process, leaving a metal oxide patterned in such a way that imitates the original morphology of the polymer structure to which the metal was exposed. This work focuses on developing and characterising metal infiltration techniques into various polymers that have shown the capability to be used in ASD and BCP sectors. Both liquid and vapor infiltration processes are investigated using X-ray photoelectron spectroscopy as the core analysis method, alongside techniques such as atomic force microscopy, transmission electron microscopy, ellipsometry and thin film electrical measurements.

1 Introduction

1.1 Current Challenges in IC Fabrication

1.1.1 Moore's Law

It is impractical and arguably impossible to discuss research related to the semiconductor industry without addressing one of the most important predictions made in modern electronics, physics and engineering; Moore's Law.¹ In 1965, Dr. Gordon E. Moore claimed that the number of components on integrated circuits would double every year from 1965 - 1975. This claim was then revised in 1975 - becoming what is known as Moore's Law - that the number of transistors on integrated circuits will double every two years.

Moore's Law effectively became a self-fulfilling prophecy, with the semiconductor industry increasing their IC transistor count at the predicted rate (Figure 1.1²⁻¹⁶). In doing so, many sectors of humanity have reaped the rewards of modern electronics, which include the obvious advantages visible in our daily lives from improved communication

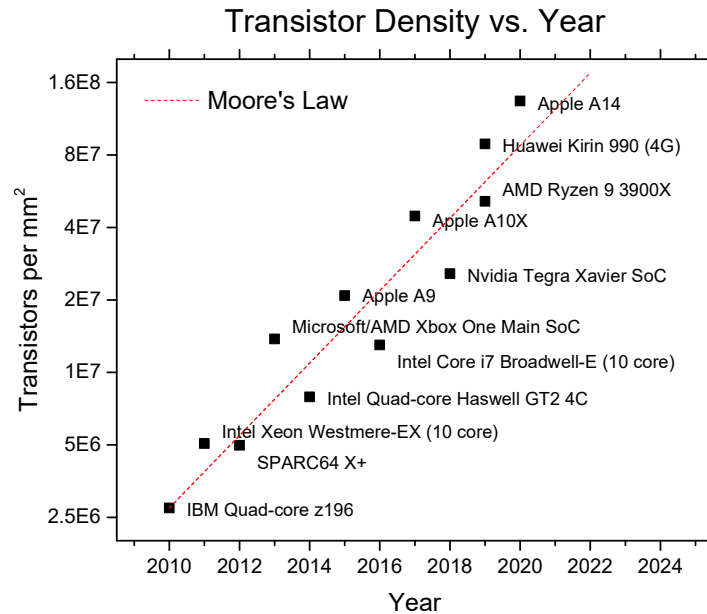


Figure 1.1: A non-exhaustive plot of a selection of microprocessors from the period 2010 – 2020. The dashed line is an equation representing Moore's law, where the transistor density for processors in 2010 is doubled every two years.

technology and personal electronic devices such as phones/laptops/computers, to changes we take for granted such as medical devices (e.g. implants) and improved computer systems (e.g. climate change modelling).

The constant improvement in technology and hence lifestyle, understanding and health, has resulted in our current life being claimed as a 'golden age of technology' by some. However, the rate at which technology improves is beginning to show signs of strain as technological limits are being approached.

1.1.2 The Integrated Circuit

An integrated circuit (IC) is a single substrate (commonly silicon) device that contains multiple semiconductor components – such as transistors, resistors and condensers – interconnected upon it in such a way as to perform a rich variety of tasks. Often referred to as 'chips' in the industry, ICs have become the cornerstone in all modern electronic devices, reaching a large and complex scale (e.g. The A14 chip that provides the processing power for the iPad Air contains 11.8 billion transistors in a chip that is 88 mm^2 in area).⁷

Present day IC components are dominated by the metal–oxide–semiconductor field–effect transistor (MOSFET), alternatively known as the metal–oxide–silicon transistor (MOS).¹⁷ A schematic of a conventional enhanced mode N-channel MOSFET (N-type MOS) is shown in Figure 1.2. The MOSFET is a three-terminal device, comprised of a drain, source and gate. Below a certain gate voltage, current does not flow between the drain and source due to the creation of a semiconductor depletion zone. However, applying a larger voltage to the gate results in the creation of a capacitor like effect between the metal electrode and P-type substrate due to the presence of an oxide insulator as Figure 1.2 implies. The capacitor-like behaviour between the metal electrode and P-

type region results in the creation of an oversaturated electron region within the P-type material, referred to as an N-channel, which facilitates current flow between the drain and source. Compared to other transistors such as the bipolar junction transistor (BJT), MOSFETs are a smaller, cheaper and a less power demanding alternative. Both N-type and P-type MOSFETs (nMOS, pMOS respectively) can be symmetrically combined to form complementary metal–oxide–semiconductor (CMOS) inverters. CMOS logic has a low static power consumption (power consumed while there is no circuit activity) when compared to other logics such as transistor – transistor logic (TTL), which uses bipolar junction transistors. CMOS devices have thus become the ideal device for high density ICs, such as microprocessors and memories, as minimal power loss/waste heat is produced.¹⁸

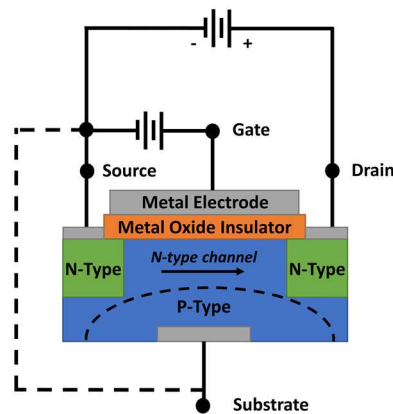


Figure 1.2: A N-channel MOSFET.

In the context of this work, it is worth summarising the importance of the metal-oxide insulator, located between the gate and channel of the device – known the gate oxide, or gate dielectric. Historically made from SiO_2 , characteristics of the gate oxide should include the ability to be fabricated defect free, thin and have a low leakage current. A thin film allows for a higher capacitance during the MOSFET operation, with defect heavy and/or poor insulators resulting in leakage current flowing via the gate. A perfect gate oxide insulator therefore results in zero current flow under all static biasing conditions.

As the trend in scaling followed Moore's Law, the gate oxide thickness was also required to be scaled down to generate higher capacitance devices and thereby device performance. The decrease in oxide thickness led to the effects of leakage current due to electron tunnelling, reducing the reliability of MOSFETs with SiO₂ gate oxides. By ignoring quantum mechanical effects, the capacitance of the gate oxide is given by:

$$C = \frac{k\epsilon_0 A}{t} \quad (1.1)$$

Where k is the relative dielectric constant, ϵ_0 is the permittivity of free space and t is the thickness of the gate oxide. As equation (1.1) shows, an alternative method of increasing device capacitance is the selection of materials with a higher k value. A high k value allows for a greater capacitance, while also allowing for the gate oxide to be thicker which reduces tunnelling current. This led to the development of high k materials, which increased the gate capacitance in MOSFETs without the issue of leakage current. Materials used in this role include Al₂O₃, ZrO₂, TiO₂ and HfO₂.¹⁹

1.1.3 Techno-economic and Financial Limitations

The success in following Moore's Law was achieved through the scaling of devices and interconnects, constantly making them smaller in accordance with Dennard Scaling.²⁰ This scaling observation, made in 1974 by Richard Dennard, showed that the power density for a given area of an IC remained constant – the power loss caused by the decreasing transistor size (thus causing current and voltage reductions) was combated by the increasing transistor count. This held true through the 1970s and 1980s, however by the late 1990s, limits imposed by dopant clustering, gate oxide electron tunnelling and dopant distribution became issues as the industry moved into the sub-100 nm device regime.^{21,22} Downscaling continued until devices became so thin that leakage current prevented further scaling in gate and capacitor dielectrics. The introduction of high k

materials helped to continue this scaling,²³ however the trend eventually moved away from Dennard scaling, with processes relying on inventive device geometries and circuit architecture in order to continue the adherence to Moore's Law, while maintaining reasonable power limits, at a manufacturable chip area and acceptable cost.²⁴

It is worth also noting in brief the concept of node and feature sizes in the semiconductor industry. The node, referred also as technology/process node, historically matched the length of the gate in CMOS based processing and the half pitch (the distance between two identical features on the IC).²⁵ This definition held true until 1997 with the introduction of Intel's 0.25 μm node, which had a gate length of 0.20 μm . Up to this point, node size had been decreasing rapidly (Intel had a processing node of 10 μm in 1972, reducing to 0.35 μm in 1995).²⁶ After 1997, the reduction in gate length and half pitch reduced at a rate far greater than the node value. Node values are now no longer dependent on physical device dimensions, and no standard is maintained in the industry (Global Foundries has a 7 nm node process that is similar to Intel's 10 nm node process).²⁷

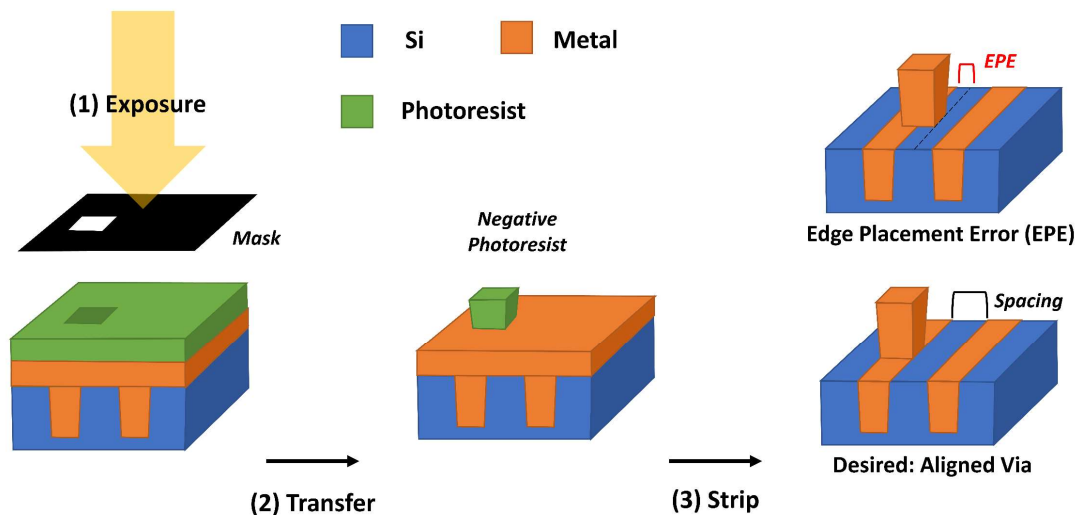


Figure 1.3: Schematic of a simplified photolithography process, using a negative photoresist. The desired end-result is shown, alongside the impact of an edge placement error.

Semiconductor device fabrication has relied on photolithography (optical lithography) in achieving ever diminishing feature sizes. Present IC fabrication can be summarized into film deposition, patterning and semiconductor doping, with patterning achieved through photolithography. The concept is shown in Figure 1.3. A material known as photoresist is placed on top of a chosen material. When exposed to ultraviolet (UV) light, this resist will either breakdown (positive resist) or become insoluble (negative resist). This exposure step will therefore require a series of masks, which dictate where the UV light will interact with the resist. The result is a surface that is partially covered by a resist, and various chemical stages can be implemented to create a patterned wafer – in the case of Figure 1.3, a metal contact is patterned onto a wafer through a transfer and strip step. The patterning process can be viewed as the ‘wiring’ of an IC, building the circuitry ‘top-down’ through a series of these steps.

The minimum device size (referred to as the critical dimension, CD) achievable from this process is dependent on the wavelength of the light (λ) used;

$$CD = k_1 \frac{\lambda}{NA} \quad (1.2)$$

Where k_1 is a coefficient that considers process related factors, and NA is the numerical aperture of the lens. Decreasing the wavelength or increasing the NA produces smaller devices. Blue wavelength light (436 nm) was initially used, followed by wavelength in the ultraviolet regime (UV, 365 nm) to deep-UV (248 – 193 nm).²⁸ With a numerical aperture of 1.35, the 193 nm wavelength achieved through ArF excimer lasers was seen as a saturation point in resolution for conventional optical lithography.²⁹ Single exposure processes at this wavelength achieved approximately 80 nm nodes, however this size was reduced to 22 nm and 14 nm through multiple patterning lithography (MPL) and litho-etch-litho-etch (LELE) processes.^{30,31} A perspective by Clark et al. in 2018 summarises that the minimum feature size of devices have become so small that single exposure

lithography is no longer possible in high volume manufacturing,²⁴ discussing that single metal interconnect layers can, at the time of writing, require three or more mask patterns to acquire the desired pattern, whereas historically, it would have taken one. This rise in processing steps increases fabrication time, with each additional mask step increasing the final chip cost. The addition of further mask steps also leads to a reduction in device yield due to the increased likelihood of edge placement errors (EPEs). EPEs describes the difference between intended and actual position of an IC feature, with the concept briefly shown in Figure 1.3. As node size continues to decrease, so does the margin for error in placement of IC components, with electrical shorting and chip failure possible if EPEs are not avoided.

Extreme ultraviolet lithography (EUV) has demonstrated the capability of achieving sub 10 nm nodes,³² while providing an alternative to the increase in mask steps needed for conventional lithography. EUV uses a wavelength range of what is known as extreme ultraviolet (13.5 nm) typically obtained from a plasma source. Despite achieving even smaller device sizes, EUV is still subject to EPE, is more energy demanding than its predecessors, while also requiring significant downtime due to the tools complexity.³³ The cost of EUV lithography is significant, the sole supplier ASML were reported in 2019 to have sold EUV machines for €120 million apiece,³⁴ with EUV also regarded as a higher cost tool to run than other lithography tools.³⁵

1.2 A New Way Forward

1.2.1 ‘Bottom-Up’ versus ‘Top-Down’

The success and associated challenges faced in terms of patterning due to ever diminishing device size and the resulting increase in cost has spurred significant research into alternatives to conventional semiconductor patterning methods. The top-down approach as described in section 1.1.3, whereby blanket films are deposited onto a substrate, followed by an etching step, can be combined with, or replaced by, a bottom-up approach.

A bottom-up approach implements chemical reactions to enable material growth, resulting in the formation of structures in an additive fashion. Unlike top-down, which require reductive steps to achieve patterning, a bottom-up process relies on self-assembly as seen in Figure 1.4. This example shows that film growth occurs on the underlying substrate, with certain regions of the surface being unsuitable for film growth to take place. These ‘active’ and ‘inactive’ surfaces facilitate or impede, respectively, the necessary chemical reactions for structure formation. By achieving this, relying on

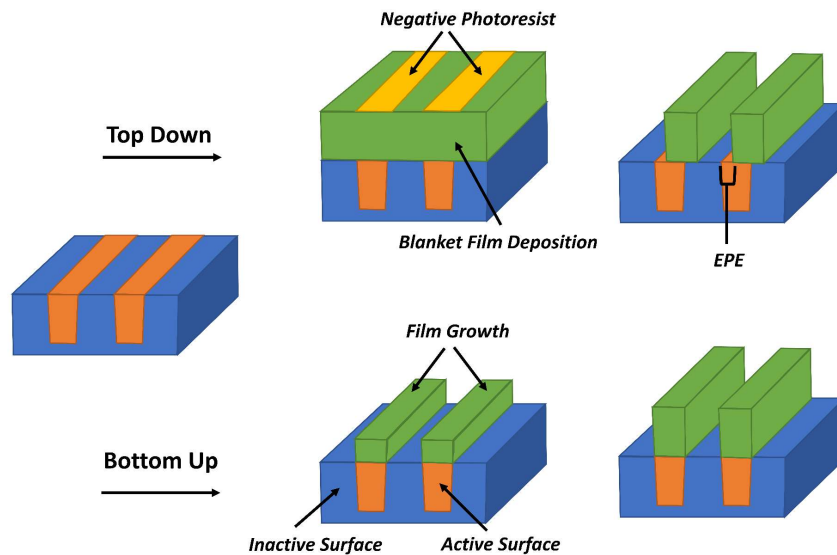


Figure 1.4: Schematic showing a top-down (conventional) and a bottom-up approach to achieving a patterned film. The top-down approach requires etching and stripping steps to achieve the desired result, with the aforementioned EPE arising if the mask alignment is incorrect. The bottom-up technique involves the selective growth on one surface only.³⁶

processes where resolution is determined by the wavelength of light as in photolithography can be avoided. The avoidance of masking stages for photoresist placement eliminates the risk of EPE,³⁶ and has the potential to greatly reduce the cost in patterning by replacing EUV lithography. A bottom-up approach may also not require an etch step, which can be impossible to perform on organic semiconductors and carbon-based material.

There are various approaches to achieving a bottom-up patterning approach,³⁷ however this chapter will focus on two areas that have particular importance to this study; polymer area selective deposition (ASD) and block copolymer (BCP) lithography. Both techniques often require the use of atomic layer deposition (ALD) and utilise polymers to achieve area activation and deactivation for patterning purposes.

1.2.2 Atomic Layer Deposition

1.2.2.1 Basic Theory

ALD is a versatile and popular technique in bottom up processing, first developed separately in the Soviet Union and Finland in the 1960s and 1970s and initially termed Atomic Layer Epitaxy (ALE) by T. Suntola and J. Antson.^{38,39} The technique is renowned for enabling the acquisition of pristine thin films, with the ability to fabricate materials – particularly metals and their associated oxides and nitrides – with atomic level control, in a ‘layer by layer’ fashion. This ability to accurately control the thickness of coherent films at the Ångstrom scale has led to the incorporation of ALD into fields such as microelectronics, photovoltaics and energy storage.^{37,40–42} ALD is particularly suited in CMOS and other IC component fabrication, such as high k dielectrics (section 1.1.2).⁴³ The technique is widely used in the semiconductor industry,^{44,45} with Intel introducing ALD processing into their production line in 2007.⁴⁶

ALD is a sub technique of Chemical Vapour Deposition (CVD). The CVD process involves the deposition of a solid material onto a surface from the gas phase by a chemical reaction occurring on a heated substrate.⁴⁷ The vapour that is fed into the reaction chamber is a reactive gas mixture, which contains the chemical components of the material to be deposited.

ALD is a relatively similar technique to CVD, however unlike the continuous film growth where all the reactants are present in a chamber at the same time, the ALD is a process divided into steps. The differences between CVD and ALD are evident in Figure 1.5. Both techniques involve the exposure of a substrate to reactant vapours/gases (precursors). The CVD process in Figure 1.5 (a) involves the exposure of a substrate to all the reactant gases at once, which results in a gas phase reaction and a continuous growth process. The ALD process in Figure 1.5 (b) has strict temporal confinements to ensure that the substrate is exposed to only 1 reactant vapor at a time, with the resultant growth process being self-limiting. While slower than CVD, the ALD process is a much more precise thin film growth technique.

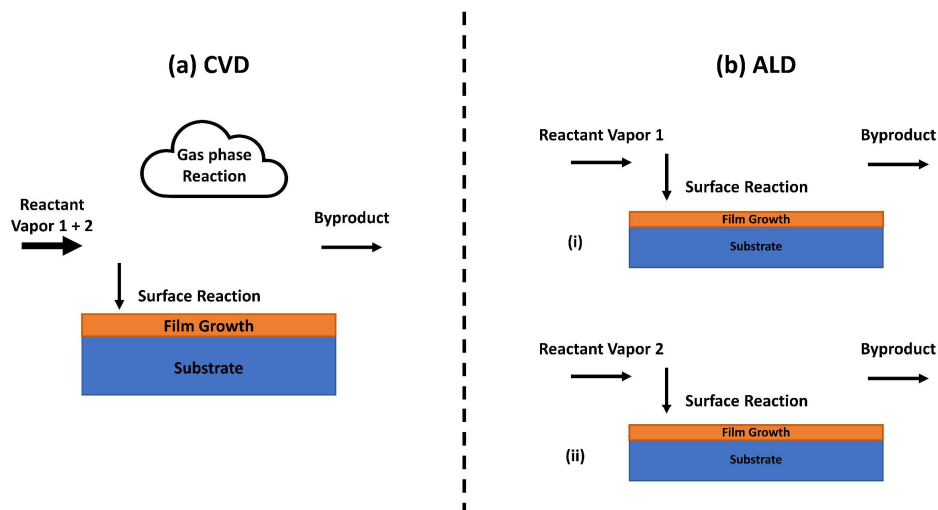
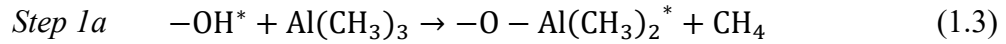


Figure 1.5: Simplified schematic of a CVD (a) and ALD (b) process. The CVD process consists of one stage where all gases necessary for film growth are present. The ALD process consists of different stages, with each stage containing different gases for a self-limiting growth process.

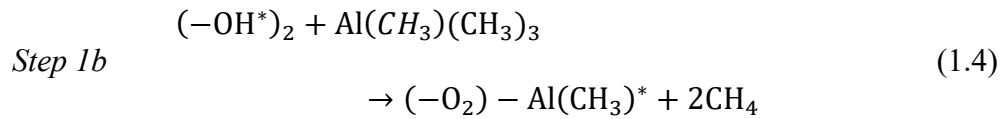
1.2.2.2 Thermal ALD

Thermal ALD achieves the step-by-step growth shown in Figure 1.5 (b) through surface reactions, which typically requires temperatures of above $\sim 150^\circ\text{C}$ to ensure that the desired reactions are energetically favourable. A classic example of thermal ALD is shown in Figure 1.6, which describes the growth of aluminium oxide through the precursors trimethylaluminum (TMA) and water – $\text{Al}(\text{CH}_3)_3$ and H_2O respectively. Al_2O_3 is a particularly important material for the semiconductor industry due to its role as a high-k dielectric material.^{48,49}

The process is made up of 4 different steps, each of which is self-limiting, thus offering the aforementioned precise control over the resulting films. The first step (i) involves exposing a substrate to a precursor which, as with CVD, reacts with the surface, however in ALD the surface ideally adsorbs 1 monolayer of the precursor's molecules onto the surface. In this specific case, the TMA interacts with the OH terminations on the substrate, with the production of methane gas as a by-product:

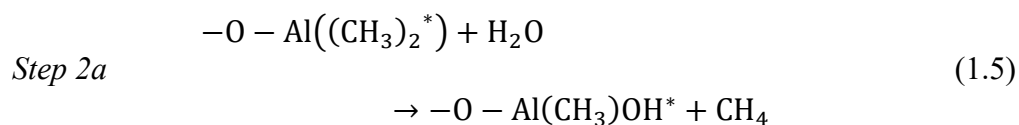


Where the asterisks denote the surface species for each process stage. In addition, another type of reaction occurs, where the TMA interacts with two hydroxyl groups:

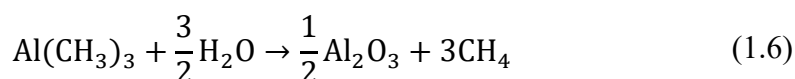


The excess precursor and resulting by-products are removed by a subsequent gas purge in the second step (ii). The third step (iii) involves the introduction of the second precursor, which, depending on the suitability of the surface and the two precursors, reacts with precursor 1. For the fabrication of oxides via thermal ALD, this second precursor (also referred to as the co-reactant) is commonly H_2O , as in this example. The pulse of water serves to oxidise the aluminium covered surface, resulting in the by-product of more

methane. The water reacts with the new surface species of the film, with the following reaction taking place if the previous reaction outlined in equation (1.3) had occurred:



The methane and excess co-reactant are then removed in another purge, completing the process of a cycle in this fourth step (iv), and leading to the eventual creation of a single atomic layer of aluminium oxide which is OH terminated. The total reaction can therefore be summarised as:^{50–53}



The number of times this cycle is repeated ultimately depends on the desired thickness, however it also depends on other parameters such as the chamber size and geometry, the temperature of the substrate and chamber, gas line valve size, precursor pulse time, purge time, temperature of precursor etc. Other universal ALD variables include precursor

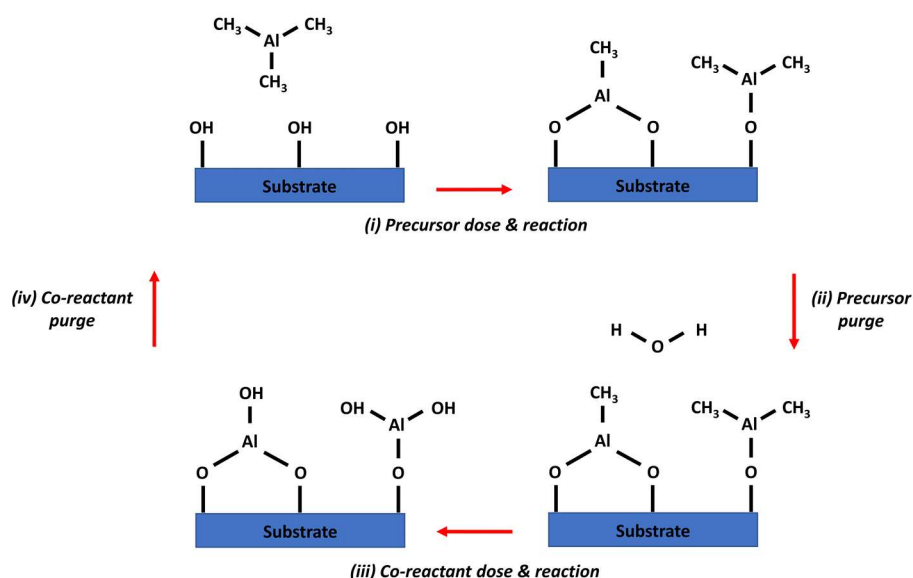
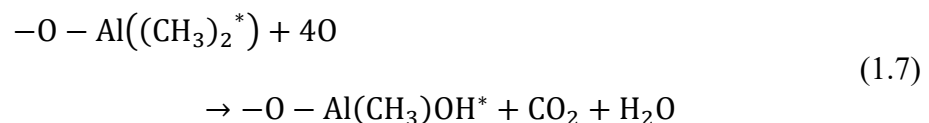


Figure 1.6: A chemical overview of a thermal TMA + H_2O ALD process, consisting of (i) a precursor dose and reaction with the substrate surface. This is followed by a (ii) precursor purge to remove excess precursor. The (iii) co-reactant dose occurs next, with a reaction occurring with the precursor on the substrate surface. The excess co-reactant is then removed in a (iv) co-reactant purge, and the cycle can then begin again.

choice (which includes the element being deposited and the form it is in) and the substrate that the deposition is taking place on. As seen in equation (1.3), the end termination of the surface plays a significant role in whether acceptable growth occurs. Killampalli et al. demonstrated the effect of depositing on different surfaces of a Self-Assembled-Monolayer (SAM) when using Tetrakis(dimethylamido)titanium – $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ – as a precursor.⁵⁴ The reaction probabilities for an -OH terminated SAM surface was greater than -NH₂ terminated surfaces, which in turn had a higher reaction probability than a SAM terminated with -CH₃ bonds, proving that significant amounts of study is required for perfecting specific ALD processes. This ability to grow ALD films on certain types of substrates due to their specific termination forms the basis of area selective ALD.^{36,37}

1.2.2.3 Plasma Enhanced ALD

Plasma enhanced ALD (PEALD) operates under the same self – limiting operational principles as thermal ALD, with the notable difference that the co-reactant is replaced with species generated via plasma. For the TMA example covered in section 1.2.2.2, the water dose is substituted by an oxygen plasma. The reaction process for this co-reactant stage as outlined in the thermal case in equation (1.5) becomes:⁵⁵



Where combustion-like reactions result in the creation of carbon dioxide and water as the by-product, instead of methane as in the thermal process.

One of the major advantages in PEALD is the ability to perform processes at lower temperatures than thermal ALD.^{56–58} This is because reactivity is obtained through the plasma co-reactant species, with a high temperature not necessary to induce the desired reaction as in thermal ALD. This reactivity stems from the presence of plasma radicals,

the kinetic energy of ions undergoing acceleration in the plasma sheath, the energy flux arising from the plasma and the surface recombination energy of the ions and other plasma species.⁵⁹ This increased reactivity also enables the incorporation of precursors unsuited for thermal ALD to be implemented effectively in PEALD.^{60,61} Owing to the presence of plasma radicals, PEALD is also a cleaner method of film growth than thermal ALD, with less impurities – such as carbon from incomplete precursor breakdown – present in the film.^{62,63} Other advantages of PEALD include reported improved electrical properties,^{64–66} film densities,^{66–68} and an increase in growth rates.^{69,70}

1.2.2.4 Area Selective ALD

Nanopatterning via area-selective ALD has attracted substantial interest as a route to achieving bottom-up fabrication of nanoelectronic components in the semiconductor industry.^{36,37} This can be achieved through several technical methods, involving the area activation and deactivation of different regions across a surface to promote or inhibit precursor interaction with the substrate, respectively. The most basic form of area deactivation involves terminating different regions of the same surface with functional groups that will enable or reject film deposition. An example of this involves performing metal oxide ALD on an OH and H terminated surface. Metal oxides readily develop on OH terminated films, whereas nucleation is prohibited initially on H terminated surfaces. This delay however is limited to the first few ALD cycles and applicable only to very thin films.⁷¹

The concept of ALD area deactivation led to the development of SAMs. SAMs are organic films of a single molecular thickness that can exhibit large scale ordering when deposited upon a surface. They consist of a head group, a hydrocarbon segment (backbone) and a terminal functional group or tail group, forming a stable monolayer film

across a surface due to a favourable interaction of the head group with the substrate.^{72,73} One example of a SAM is the structure octadecyltrichlorosilane (ODTS) with a chemical formula of $[\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3]$. ODTS can bond to an OH terminated SiO_2 substrate and once ordering is complete, the tail group of the SAM becomes the new surface termination group, which for ODTS, is CH_3 , changing the surface from hydrophilic to hydrophobic.⁷⁴ The role of the SAM is twofold – preventing the diffusion of ALD precursors to the substrate the SAM is covering, and providing a passivated surface that does not interact with the precursor and thus block growth. An extended, but finite exposure window exists for the SAM to block growth (decreasing with every ALD cycle) – with the SAM eventually allowing deposition if exposed to the precursor for a long enough duration. Despite this, the incorporation of SAMs into ASD ALD has been well documented and successful.^{75–77} More recently, polymer films such as polystyrene (PS) have been noted as an alternative to SAMs in area deactivation. The operational principles and advantages of these polymers, which can function in either area deactivation or activation ALD depending on the material, will be discussed in the section 1.2.3.

1.2.3 Polymers in Bottom Up Processing

1.2.3.1 Polymer Science – Basic Theory

A polymer is a large molecule (macromolecule) that consists of many smaller molecules (monomers). These monomers are structurally repeating, connected through covalent bonds.⁷⁸ A basic polymer consists of a backbone, which is the ‘chain’ that links the monomers together covalently. Additionally, pendant groups can attach to the backbone (such as the phenyl group attaching to the carbon backbone in polystyrene).

The covalent bonding and subsequent polymer creation is achieved through a process called polymerisation. The number of monomers in a polymer molecule is defined as the degree of polymerisation (N). The molar mass of a polymer (M) is defined as;

$$M = NM_{mon} \quad (1.8)$$

Where M_{mon} is the molar mass of the monomer or, repeating unit.

Most polymers are organic, with the backbone predominately made up of carbon and hydrogen, while potentially containing other elements such as oxygen and nitrogen. They can be found in nature such as cellulose (found in plants), or produced by humanity, such as PS and polyvinyl chloride (PVC) plastics. Inorganic polymers where the backbone does not contain carbon – such as polydimethylsiloxane – also exist.⁷⁹

1.2.3.2 Polymer Area Selective Deposition

ASD relies upon the modification of local surface properties, to allow for preferential deposition of a material on predefined areas of that surface. The basic concept of the polymer area selective approach is illustrated in Figure 1.7, showing the work of Cummins et al.⁸⁰ A patterned Cu/SiO₂ wafer was exposed to a solution containing thiol terminated poly-2-vinyl pyridine (P2VP-SH). Due to the termination of the polymer chain, the P2VP grafts to the Cu surface but not to the SiO₂, forming an area-selective polymer brush. A polymer brush describes a polymer with specific end-tethered chains (the chain termination), which has allowed it to graft – with a high density – to a surface.⁸¹ A subsequent cobalt nitrate (liquid) exposure results in the metal infiltrating and reacting with the P2VP. This is finally followed by a polymer removal step, achieved through an oxygen rich process such as O₂ plasma or UV/Ozone treatment, which also serves to convert the metal into a stoichiometric oxide, resulting in a patterned wafer where the Co is deposited on Cu regions only, without the need for any masking or etching steps. As

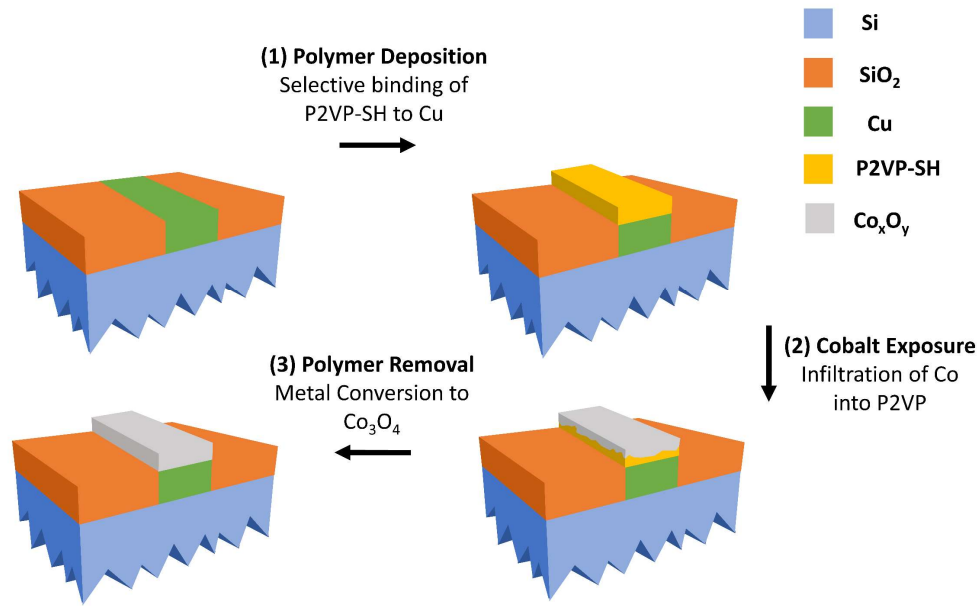


Figure 1.7: ASD of Co onto Cu through P2VP infiltration. P2VP selectivity bonds to Cu on a patterned Cu/ SiO_2 wafer due to the SH termination at the end of the polymer chain. Spin coating a Co Nitrate solution across the modified surface results in the Co interacting with the P2VP. Removing the polymer and oxidising the Co results in a layer of Co_3O_4 on top of the Cu regions of the wafer.

the metal grows where the polymer P2VP is placed, this ASD approach is referred to as an area activation method.

By adjusting the terminations on the surface or deposition material, ASD can allow for a variety of area selective possibilities. As described by the authors of the process in Figure 1.7, PS with amine terminations ($-\text{NH}_2$) selectively attach to the Cu region of the wafer much like the P2VP-SH. In vapor phase infiltration (VPI) processes using precursors such as TMA, PS rejects metal incorporation unlike P2VP,⁸² thereby making an area deactivation method. It should be noted that area selective deposition may be achieved through other enabling/inhibiting materials, most significantly, SAMs.⁷²

While polymer ASD represents a potentially cheaper alternative to achieving semiconductor patterning, unbound by lithography constraints and complex masking patterns, understanding the infiltration process into various polymer materials is lacking in the literature. Obtaining ultimate area selectivity remains a challenge, as areas that

were designed to reject material deposition often suffer from the depositing material forming ‘islands’ upon the surface. Achieving uniform infiltration and resulting metal films is also a difficulty. There are numerous vapor phase and liquid phase polymer infiltration techniques, each with parameters that need to be carefully studied for each specific substrate and deposition material.

1.2.3.3 Block Copolymer Lithography

BCPs contain dissimilar, covalently bonded polymer blocks, that exhibit microphase separation (self-assembly) into a range of morphologies, forming nanoscale patterns that have potential use for 2D and 3D fabrication processes.^{83,84} By implementing these different morphologies, it is anticipated that BCPs can be used to create a large array of future nano-electronic devices. Examples of the morphologies obtainable through BCP manipulation are shown in Figure 1.8 by Majewski and Yager.⁸⁵ The morphologies arising from BCPs that contain two (referred to as AB diblock copolymers) covalently bonded polymers are shown in Figure 1.8 (a) – spherical (S), cylindrical (C), gyroid (G) and lamellar (L). Electron microscope images are shown in Figure 1.8 (b - d). By adding a

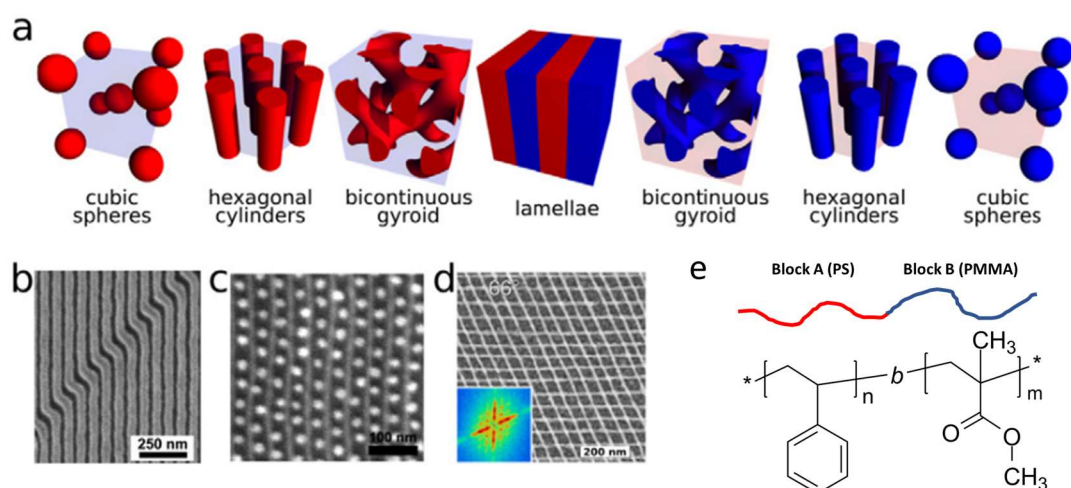


Figure 1.8 (a) Bulk equilibrium morphologies arising from AB diblock copolymers. (b-d) Electron microscope images of various BCP structures.⁸⁵ (e) Schematic of a linear AB diblock copolymer (PS-*b*-PMMA).

third polymer (ABC triblock copolymer), the range and complexity of available structures increases dramatically as outlined by Bates and Fredrickson.⁸⁶

The BCP structure is determined by several factors, which in the simplest form, can be considered for a linear AB diblock copolymer such as the structure in Figure 1.8 (e). Firstly, microphase separation – that prevents the two polymers from mixing – is a measure of how chemically incompatible the polymers are. Chemical and structural differences in an AB diblock copolymer provide enough excess free energy to ensure mixing does not occur. The ‘Flory-Huggins interaction parameter/energy’ (χ) for an AB diblock copolymer defines the free energy cost per monomer between A and B monomers, and it is defined as;⁸⁶

$$\chi_{AB} = \frac{Z}{k_B T} \left(\epsilon_{AB} - \frac{1}{2} \right) (\epsilon_{AA} + \epsilon_{BB}) \quad (1.9)$$

Where Z is the number of nearest neighbour monomers, $k_B T$ is thermal energy (Boltzmann constant multiplied by temperature) and ϵ_{AB} is the interaction energy per monomer between the monomers of A and B. If χ_{AB} is positive, there is net repulsion between the monomers A and B, however mixing occurs if χ_{AB} is negative.

The resulting morphology of the AB diblock copolymer is dependent on the degree of polymerization (N) and the composition, f_A , defined as;⁸⁶

$$f_A = \frac{N_A}{N} \quad (1.10)$$

Where N_A is the number of A monomers per molecule. The relationship between the combination parameter (interaction energy defined in equation (1.9) multiplied by the degree of polymerisation) and f_A is shown in Figure 1.9.^{86,87} Depending on the relationship, the AB diblock copolymer will exhibit the four phases as shown in Figure 1.8 – spherical (S), cylindrical (C), gyroid (G) and lamellar (L).

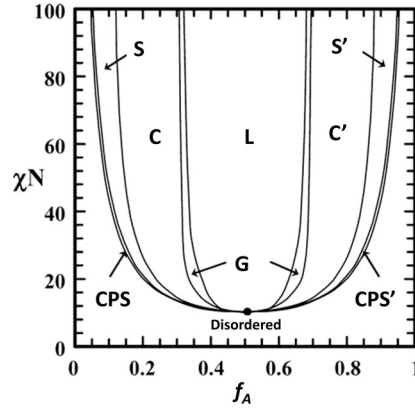


Figure 1.9: Self-consistent mean-field theory, showing the structural phase of a linear diblock copolymer, which is dependent on the composition f_A and the combination parameter χN . χ is the interaction energy between monomers and N degree of polymerisation.^{86,87}

Recent studies on BCPs have shown that nano-scale features can be developed—as illustrated by the work of Borah *et al* who have successfully implemented ion etching onto self-assembled polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) BCP patterns, thereby producing PS nanowires with the removal of the PMMA block.⁸⁸ PS-*b*-PMMA has also been used to create Al₂O₃ nanofeatures,⁸⁹ along with ZnO and TiO₂ nanopatterns.⁹⁰ Work by Cummins *et al* resulted in the creation of WO₃ nanowires by implementing a poly(styrene)-block-poly(4-vinylpyridine) (PS-*b*-P4VP) template,⁹¹ while self-assembled poly(styrene)-block -poly(ethyleneoxide) (PS-*b*-PEO) has been used to create lead zirconate titanate (PZT) nanodots by means of PEO infiltration.⁹²

An important consideration in BCP synthesis is the resolution of the resulting nanostructure, which is determined by χ and N . The higher the value of χ , the smaller BCP feature sizes can become.⁹³ Polymers that exhibit high χ values when bonded together are therefore of significant interest to research into alternatives to optical lithography. A table of room temperature χ values are displayed in Table 1.1. PS-*b*-PMMA domain sizes are limited to a low χ parameter, which is higher for systems such as PS-*b*-P4VP, PS-*b*-PDMS (poly(styrene)-block-polydimethylsiloxane) and PS-*b*-PDLA (poly(styrene)-block-poly(D-lactide)), allowing for the achievement of smaller features.

Table 1.1: Room temperature χ values for a selection of PS based BCP systems. A higher χ value leads to smaller domain size creation in the BCP structure. Feature sizes mostly tabulated in a review by Sinturel et al. is also shown.⁹⁴

BCP System	χ_{PS-X} parameter	BCP Lamellar Spacing (nm)	BCP Cylinder diameter (nm)
PS- <i>b</i> -PMMA	0.041 ⁹⁵	24 ⁹⁴	14 ⁹⁴
PS- <i>b</i> -PEO	0.077 ⁹⁶		17.4 ⁹⁴
PS- <i>b</i> -P2VP	0.11 ⁹⁷	13.8 ⁹⁸	
PS- <i>b</i> -P4VP	0.325 ⁹⁷	10.3 ⁹⁴	
PS- <i>b</i> -PDMS	0.191 ⁹⁹	20 ⁹⁴	8 ⁹⁴
PS- <i>b</i> -PDLA	0.233 ¹⁰⁰	17.7 ¹⁰¹	

When used for the nanopatterning metal/metal oxides, both BCP lithography and polymer ASD can be categorised into three steps. The first step is concerned with polymer fabrication. As previously described, the pattern of the BCP structure is impacted by the type and amount of polymers that make up the block, while the critical parameters in a polymer ASD approach is impacted by the substrate surface and terminations of the surface and polymer chain. The second step involves area selective metal infiltration into the material. For a diblock BCP structure, the metal will ideally infiltrate one of the polymers while avoiding the other, ‘inactive’ polymer. The ASD approach necessitates that different regions across the surface will either enable or inhibit infiltration and/or deposition. The final step involves the conversion of the infiltrated metal to a stoichiometric metal/metal oxide, with the removal of the polymer. In a successful process, the patterning of the metal is in the same morphology as the original BCP or ASD-polymer structure.

1.2.3.4 Comparing Polymers and Self Assembled Monolayers for Area Selective Deposition

As mentioned in section 1.2.2.4, SAMs operate in a similar capacity to end-tethered polymer brushes in that they can be selectively bonded to different surfaces, and provide ASD capability through their tail group, particularly in the field of ALD.^{75,102–104} Unlike polymer brushes, SAMs are typically used to mask areas of a substrate from unwanted growth, whereas different polymers can be used to either promote or inhibit growth on the surface they are deposited upon. Infiltration of receptive polymer films has a unique advantage over SAMs, being able to determine the resulting deposited materials thickness/density by varying the polymer film thickness. The production of a SAM monolayer can be a time consuming process due to the necessity of ensuring proper ordering (where the tail group is at the surface), potentially taking days to process.¹⁰⁵ It will be discussed in chapter 2 that the fabrication process for the polymer brushes used in this work can be synthesized to a point where film formation takes seconds.¹⁰⁶ However, the success of SAMs as an ALD blocker has been significantly reported on in comparison to polymer brushes to the author's knowledge.

1.2.3.5 Polymer Infiltration Through ALD Based Processes

Area-selective nanopatterning through the selective reaction and infiltration of patterned polymer films is a growing field of research, enabled through area selective grafting of polymer brushes to substrates or BCP patterning.^{80,107–109} The process involves the use of active polymers as an infiltration media for metal interaction, alongside inactive polymers that undergo minimal interaction when exposed to the metal precursor. Precursor exposure and subsequent polymer infiltration/rejection can be achieved using precursors in either liquid or vapor phase, the latter of which is employed in the case of area selective

ALD. Once this exposure step is completed, the polymer film can be easily removed with an oxidizing process, leaving a patterned metal oxide, located in the regions where only the active polymer was present.

The use of polymers in area selective ALD provides the potential to develop nano-patterned, conformal films, with thickness and composition of the resulting oxide layer controlled by the ALD process parameters, in addition to the polymer fabrication parameters. Conventional ALD-like processes have been used to study the effect of precursor interaction with polymer films,^{110,111} although alternative techniques with similarity to ALD have emerged, with vapor phase infiltration (VPI) being a promising technique in achieving successful, area-selective infiltration and rejection of metal precursors into certain polymer materials.¹¹²

VPI has been defined as a process designed to maximise the sorption, infiltration and entrapment of a precursor into an active polymer film.¹¹³ The process has similarities to ALD, and is compatible with typical commercial ALD reactors which are already employed in large-scale processing. Both VPI and ALD require the use of chemical precursors that are introduced to a reaction chamber (under rough vacuum, roughly 0.1 – 10 mbar) containing a sample, with which the precursor reacts if the chemistry between precursor and sample is favourable. The differences between the two techniques arise at this point – while ALD is focused on the deposition of a material atop the sample, VPI is concerned with the infiltration of that material into the sample. A ‘typical’ VPI process involves the exposure of a material, usually heated, to several ALD-like cycles. One VPI cycle consists of the following: **(1)** A designated amount of precursor enters the chamber. This step is referred to as the *dose step* and can be controlled by carrier gas flow (N₂ or Ar), chamber pressure, precursor temperature and the time the precursor valve is open (*dose time*). **(2)** After the dose step the chamber is immediately placed under static

vacuum (*hold step*) for a period ranging from seconds to tens of minutes (*hold time*). Static vacuum is achieved by ceasing pumping, with the goal of maximising precursor – sample interaction. **(3)** The chamber is then purged (*purge step*), and the cycle can commence again. A co-reactant is often used in such a process, meaning the addition of **(4)** a co-reactant dose step, **(5)** a co-reactant hold step and **(6)** a co reactant purge. Various alterations in this cycle sequence have resulted in VPI being subcategorised further into semi-static-mode/flow-mode sequential infiltration synthesis (SIS), multiple pulsed infiltration (MPI), and sequential vapor infiltration (SVI). Semi-static-mode SIS includes a precursor and co-reactant hold and purge step, with the chamber fully evacuated and then purged after each hold step.⁸² Flow-mode SIS and MPI employ a similar procedure, however the chamber is not fully evacuated after each hold step.^{114,115} SVI consists of several consecutively occurring precursor dose, hold and purge steps. This is followed by a similar sequence but for the co-reactant.¹¹⁶ It should be noted that the addition of the co-reactant is, in an ideal case, not necessary, as unlike in conventional ALD, the precursor should react with the polymer film without the need for the addition of a co-reactant.

1.3 Overview of Results Presented

The data and results presented in this thesis have arisen from an active collaboration project between the author's own affiliation, the School of Physical Sciences at Dublin City University (DCU), and the Centre for Advanced Materials and BioEngineering Research (AMBER) at Trinity College Dublin (TCD). The project was supported by Intel and Science Foundation Ireland (SFI).

The AMBER centre was focused on the development of a rapid polymer brush process as described in section 1.2.3.2, as well as the infiltration of metal into these polymers via a *liquid phase* approach. Polymer removal and conversion of the infiltrated metal to oxide could then be achieved. The research objective of DCU and hence this thesis was to characterise these resulting films at each stage of the process (polymer pre and post metal exposure, and the ensuing metal-based films post polymer removal). This was achieved predominately using techniques available at DCU but was complemented by resources at Intel and synchrotron laboratories. A description of these experimental techniques is presented in chapter 2. Additionally, using ALD infrastructure, infiltration into polymer brushes via a *vapor phase* (section 1.2.3.5) route was investigated in this work as an alternative to the *liquid phase* method. The use of plasma for polymer removal and conversion of infiltrated metal was also examined.

The main results arising from this thesis are thus split into 3 chapters, each with the overall objective of developing an understanding into the characteristics of metals/metal oxides that have been developed through an area selective process that relies on the infiltration of metal ions into certain polymer materials.

The experimental work focuses predominately upon four covalently grafted polymer brushes developed at TCD: P2VP, poly-4-vinyl pyridine (P4VP), PS and PMMA. The molecular diagrams of these polymers are displayed in Figure 1.10. The method of brush fabrication means the polymers are ASD compatible and can be patterned via conventional lithographic masking or by tailoring selective polymer brush end groups to bind to site specific wafer regions. This approach may have significant relevance for silicon device technologies, particularly in monolithic integration due to the low temperature ceiling (<500 °C) required for CMOS compatibility.

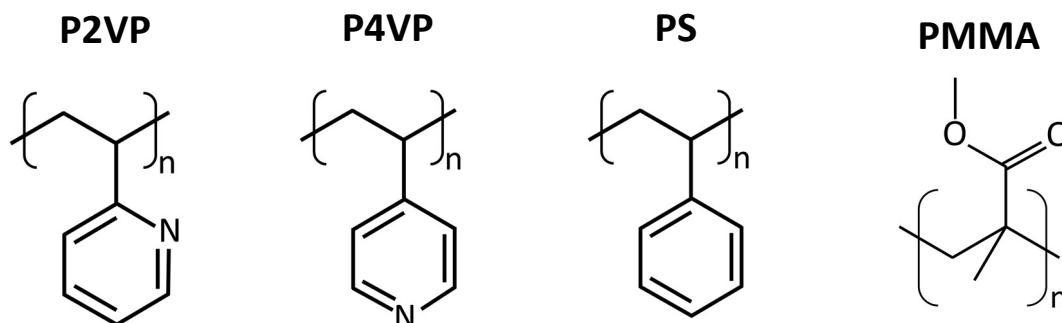


Figure 1.10: Schematics of the main polymers analysed throughout this body of experimental work; poly-2-vinyl pyridine (P2VP), poly-4-vinyl pyridine (P4VP) polystyrene (PS) and polymethyl methacrylate (PMMA).

PS is a well-established material for achieving area deactivation – preventing metal growth in ASD/BCP processes in ALD and other infiltration methods.^{82,106,117} Similarly, the use of PMMA as an infiltration medium in both ASD and BCP processes has been significantly studied – the carbonyl group in PMMA serves as a focal point for metal – polymer interactions.¹¹⁴

A particular emphasis was therefore placed on the characterisation of pyridines for use as the infiltration receptive polymer due to the less reported but promising architecture of these polymers. The capability of the unique brush fabrication method (discussed in chapter 2) is scrutinised in detail. Both P2VP and P4VP have favourable characteristics for use as area activation media in ASD and BCP lithography.^{106,118–121} Due to the

nitrogen lone pair located in the pyridine ring, both poly-vinylpyridines (PVPs) can facilitate metal coordination bonding.¹²² Additional reactions such as protonation and quaternisation can also occur, providing a number of possible routes by which the material can facilitate infiltration.^{123–125} As observed in Table 1.1, when placed in BCP formations with PS (P2VP-*b*-PS, P4VP-*b*-PS), both PVPs display the capability to pattern at sub 10 nm dimensions due to the high χ values obtained from these systems, giving PVPs a distinct advantage over the well understood PMMA-*b*-PS systems.⁹⁴ It is worth noting the position of the nitrogen contained in the pyridine ring is a critical aspect of PVPs, with the geometry of P4VP more suited to facilitating chemical interactions due to the proximity that the nitrogen in P2VP has to the polymer backbone. This proximity can result in steric hindrance, preventing optimal interaction conditions between a metal and P4VP.¹²⁶

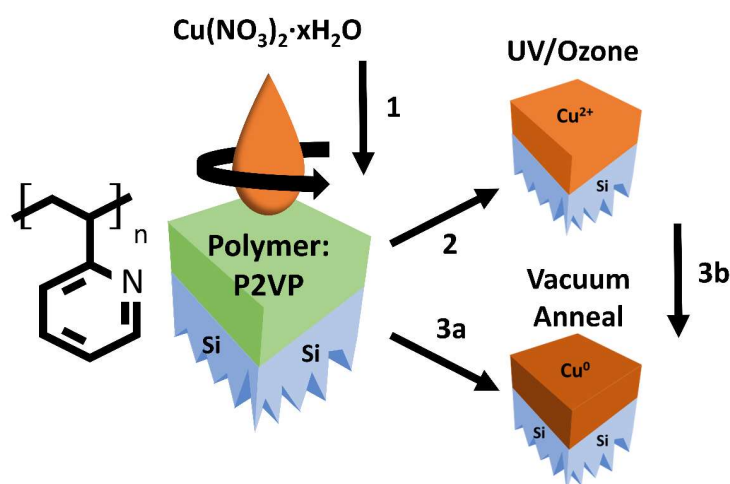


Figure 1.11: Graphical abstract of the experiment outlined in section 3. A P2VP brush is exposed to a Cu salt containing solution, before being exposed to a UV/Ozone and vacuum anneal to highlight the ability of the technique to generate metal oxides and metals respectively.

The first experimental results in chapter 3 (Figure 1.11) evaluate the ability to create metal oxides and metals (specifically copper) through the exposure of P2VP-OH brushes to a metal salt containing solution. This unique *liquid phase* polymer infiltration route has many benefits, including cost effectiveness, speed, and ease to perform. Both copper

oxide and metal were successfully fabricated through a UV/Ozone treatment and vacuum anneal respectively, highlighting the versatility of the technique to create a variety of semiconductor devices such as dielectric and interconnect materials. The chapter serves as a proof of principle experiment, validating PVP brushes and the liquid phase approach as viable process candidates in polymer ASD/BCP processing.

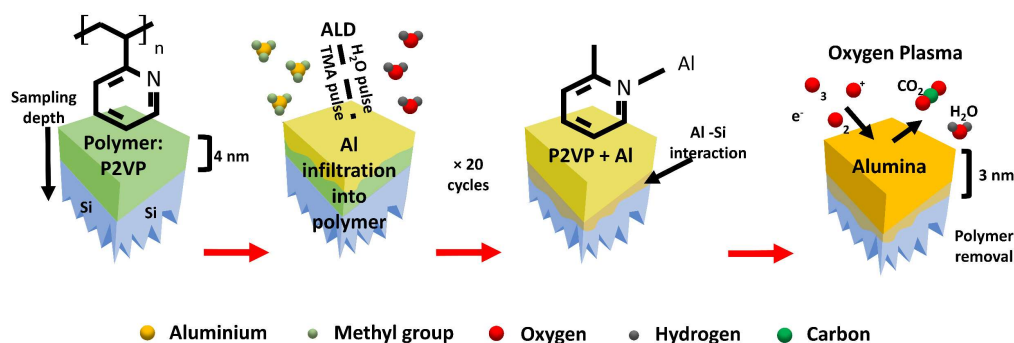


Figure 1.12: Schematic outlining the experimental procedure used in the initial part of section 4. P2VP infiltration was achieved through a conventional ALD process, with aluminium being the desired infiltration element.

Chapter 4 is split into three parts, all of which focus on characterising metal oxides that have been fabricated by a *vapor phase* infiltration approach. Instead of spin coating a solution onto the brush films as in chapter 3, the polymers of interest were exposed to metal vapor precursors in the gas phase. Vapor phase area selective infiltration techniques such as ALD are desirable for the tuneability and control the user has in dictating the resulting oxide's properties, with successful implementation also meaning this polymer infiltration technique would be compatible with the increasing use of ALD in advanced semiconductor device manufacturing. The first part of this section is concerned with assessing P2VP-OH brushes as in chapter 3, but with applying conventional ALD recipes to assess how the polymer performs (Figure 1.12). TMA was used as the precursor for infiltration, and an in-situ oxygen plasma was used to convert the polymer – metal blend into a thin film of alumina. Complete infiltration of aluminium into the polymer film was

observed, and rapid removal of the polymer and conversion to alumina was successful through oxygen plasma processing.

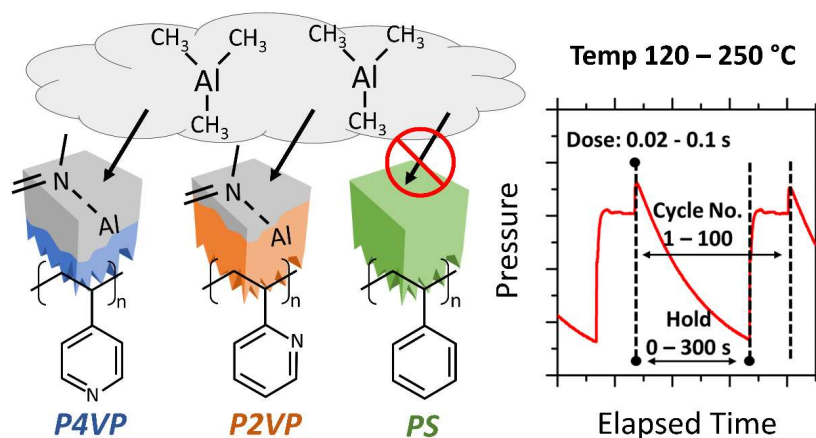


Figure 1.13: Graphical abstract concerning the experiment reported on the latter half of section 4. A VPI process was developed to ensure maximum or minimum Al incorporation into the PVP and PS brushes, respectively. A typical pressure versus time plot used for the experiment is shown on the right.

With the P2VP-OH brush showing capacity for both vapor and liquid phase infiltration, the next sections of chapter 4 cover a detailed, TMA vapor phase infiltration study on a range of polymer brushes (P2VP, P4VP, PS and PMMA). Unlike the earlier work in chapters 3 and 4, which were proof of principle experiments designed to investigate the suitability of pyridine containing polymers for ASD infiltration, these results build upon internal and external findings, providing evidence of an industrial scalable ALD-type process that culminates with a comprehensive report on the effect of editing parameters in a VPI process (Figure 1.13). Additionally, the experiment introduces the approach to comparing different infiltration receptive polymers to allow for direct comparative studies. An emphasis was placed on developing an area selective, ‘SIS’-like process that demonstrated the capability of PVP brushes as an infiltration receptive polymer to be used alongside the traditional blocker polymer, PS. The section identifies several important factors when developing a VPI process to ensure area selectivity, characterises the interaction that takes place between TMA and P2VP/P4VP and notes the distinct

advantages in the use of P4VP, arising from the difference in position of the pyridinic nitrogen.

With the advantages and limitations of both the polymer liquid phase and VPI methods learned from chapters 3 and 4, the electrical performance of the metal oxides produced by both methods is examined in chapter 5 (Figure 1.14). Aluminium oxide films designed by the VPI recipe developed in chapter 4 is compared to an ALD film, using the same precursor (TMA) and in the same temperature range. This is followed by a study into hafnium oxide films designed via liquid phase infiltration. As both films are high-k dielectrics, analysis of these materials were of significant interest to Intel, and the results in this chapter provide more insight into the quality of the films designed via polymer infiltration, and whether integration into applications such as gate dielectrics can be realised. Key issues in how to improve the films are also identified.

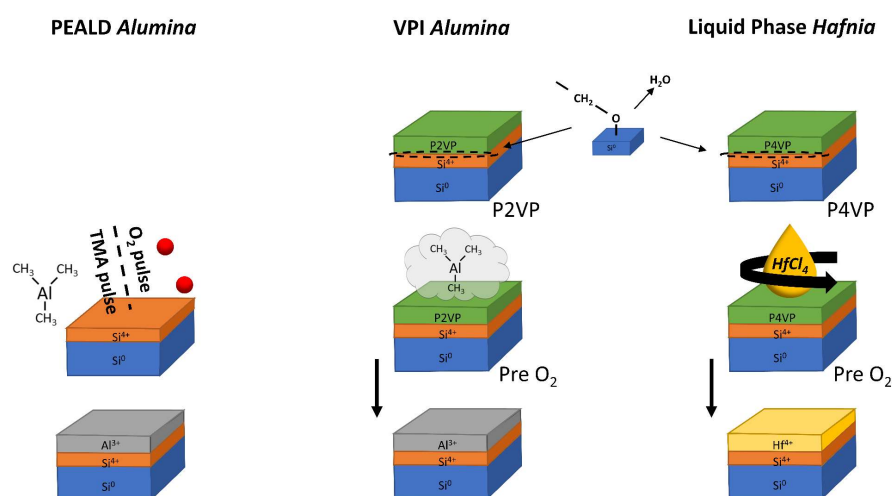


Figure 1.14: Films analysed through a combined surface and electrical characterisation approach in chapter 5. Alumina films process via PEALD and VPI were compared. A liquid phase methodology of creating hafnia was also assessed.

Chapter 6 concludes with a summation of the main findings arising from the results in this work, with a discussion on possible future research areas to focus on in infiltration studies for polymer brushes of relevance to ASD/BCP fields.

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2 Principles of Experimental Techniques

The results presented in this thesis involves the use of a large array of different experimental equipment, and the following chapter outlines the theoretical principles of each major technique employed.

When concerned with the chemical properties of films – such as chemical bonding, stoichiometry, elemental makeup and depth profiles, the photoemission techniques X-ray photoelectron spectroscopy (XPS) and hard X-ray photoelectron spectroscopy (HAXPES) were used. These techniques provide information about the properties and quality of a film growth/deposition process and were vital for determining the success of polymer growth, whether a polymer had incorporated or rejected a metal, and the assessment of the quality of various films post processing. This was complemented by grazing angle, attenuated total reflectance Fourier transform infrared spectroscopy (GA-FTIR) for accurate assessment of organic bonding.

Film thickness determinations were achieved using ellipsometry and transmission electron microscopy (TEM) cross section imaging. TEM was also used to provide greater information concerning the uniformity of samples. Energy dispersive X-ray spectroscopy (EDX) was used in conjunction with TEM cross sectioning for the easy discernment of the different layers in the film as well as being another method for ensuring uniformity. Assessing the surface roughness and whether the topography of films was of high quality was done using atomic force microscopy (AFM).

Metal oxides for application as dielectrics were electrically characterised using current – voltage (IV) sweeps and capacitance – voltage (CV) measurements to provide breakdown field and dielectric constant value measurements, respectively. These measurements provided a perspective on the electrical quality of the films.

The chapter concludes with an overview of the method used for polymer brush fabrication. This rapid, grafting-to method developed by collaborators at the AMBER institute forms the basis of all polymers analysed in this work.

2.1 X-ray Photoelectron Spectroscopy

2.1.1 Overview

XPS is a surface characterisation technique that allows one to determine chemical information of solid materials. The technique is based on the principle of the photoelectric effect - that an X-ray photon can ionize an atom, producing an ejected free electron (the photoelectron) with a kinetic energy K_E :

$$K_E = h\nu - B_E - \phi_S \quad (2.1)$$

Where $h\nu$ is the incident X-ray energy (the photon energy, the product of Planck's constant h , and the frequency of the photon, ν). Conventional XPS systems typically use Al $K\alpha$ ($h\nu = 1486.7$ eV) or Mg $K\alpha$ ($h\nu = 1253.6$ eV) X-rays. B_E is the binding energy of the

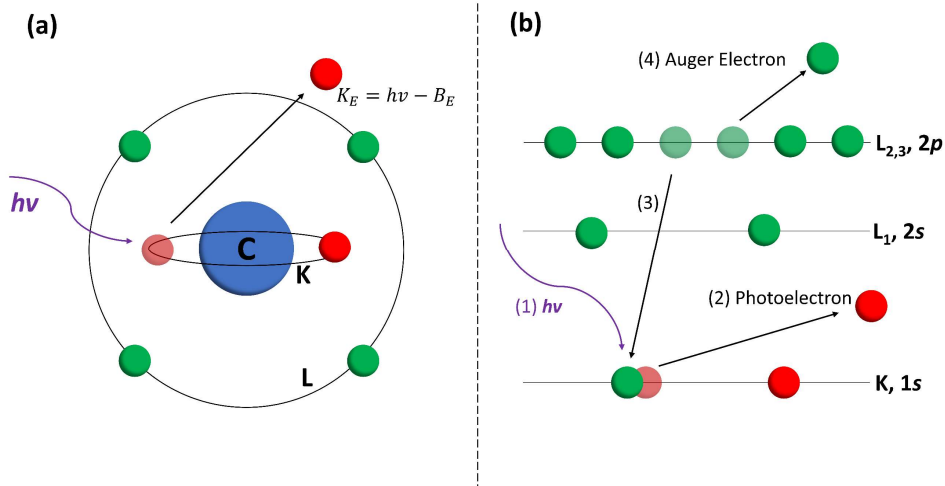


Figure 2.1: (a) basic principle of XPS. An atom (in this case, carbon) is exposed to a photon of energy $h\nu$. This results in the emission of a photoelectron from a core level with a kinetic energy equal to the difference between the photon energy and electron binding energy. (b) The auger electron emission process. The photoelectron process due to incident X-rays (step 1-2) can lead to a relaxation process (3), where an electron from an upper shell drops to fill the new vacancy. This can lead to an emission of a photon or, the emission of another electron (4), referred to as an auger electron.

emitted photoelectron, and Φ_s is the work function of the spectrometer. A brief schematic of this process is shown in Figure 2.1 (a).

2.1.2 Technical Details

2.1.2.1 Theoretical Basics

Every electron in an atom has a binding energy, determined by many factors, which are now briefly discussed. Firstly, the electron energy depends on the energy level it is located in. For example, the binding energies of the Al 2*p* and Al 1*s* electrons are approximately 73 eV and 1560 eV, respectively.¹ The closer the electron is to the nucleus, the higher its binding energy. Secondly, the electron binding energy is determined by the element that the atom ‘belongs to’. The Al 2*p* electron binding energy of 73 eV is much smaller when compared to the Cu 2*p* binding energy 933 eV.¹ The higher the atomic number, the greater the resulting binding energy.

XPS can provide much information regarding the material under analysis by virtue of the detailed elemental and chemical information available from the binding energy spectra of core level electrons. Equation (2.1) shows that by irradiating a sample with sufficiently high photon X-rays, photoelectrons of a K_E range from 0 eV to the incident $h\nu$ are ejected from the surface, which can easily be converted to a spectrum of binding energy. By additionally considering sensitivity due to electron scattering (discussed in section 2.1.3.2), the user can determine the material elemental composition and chemical analysis of those elements.

Another important factor that effects the resulting binding energy of the orbiting electrons is the chemical environment. The electron binding energy for Si 2*p* electrons, where the silicon atoms are covalently bonded to other silicon atoms in a crystal (Si-Si), is 99.4 eV. However, the binding energy of electrons in the Si 2*p* core level when the Si atom is

bonded to oxygen (e.g. in SiO_2) is approximately 103.5 eV.² The valence electrons in the silicon atoms for a Si-Si crystal are shared equally, but the incorporation of oxygen, which has a higher electronegativity than silicon (it attracts more electrons due to its less occupied valence shell), causes a shift in electron density away from the silicon atom towards the oxygen atom. This effect results in photoelectrons from the Si core level in an Si-O system containing a greater positive charge than the Si-Si environment, causing a reduction in the K_E (and thus increase in B_E) of the silicon photoelectrons from the Si-O part of the film when compared to the Si-Si crystal. The dependence of binding energy on chemical environment is known as the *chemical shift*.

By considering the chemical shift associated with each element present in a thin film, XPS can provide detailed information regarding the material under analysis.

2.1.2.2 Experimental Setup

XPS systems typically require at least high vacuum (HV) to operate (although ambient pressure XPS where this is not a requirement is growing in popularity),³ meaning that analysis takes place in a vacuum chamber of pressures around or below 1×10^{-8} mbar. Performing XPS in HV is required as the measurement is reliant on electron counting, and pressures above this could hinder the measurement, as there would be a reduction in electron mean free path, λ_e . At ultra-high vacuum (UHV) and HV pressures, atoms commonly found in the ambient (N, O, C, H) are present in small enough quantities so as to not affect the measurement. Effects due to sample interaction with the ambient are undesired since the user wishes to extract information only about the uncontaminated surface of the sample. In addition to this, the equipment that makes up a standard XPS tool – such as the X-ray source, analyser, ion gauge – often require HV to work.

The basic elements that make up a typical XPS system are shown in Figure 2.2. X-rays are generated by bombarding a metal target – usually Al or Mg – with electrons that have been accelerated onto it by a high potential (often above 10 kV). These X-rays are focused onto the sample under analysis, with the resulting emission of photoelectrons with energies as stated in equation (2.1).

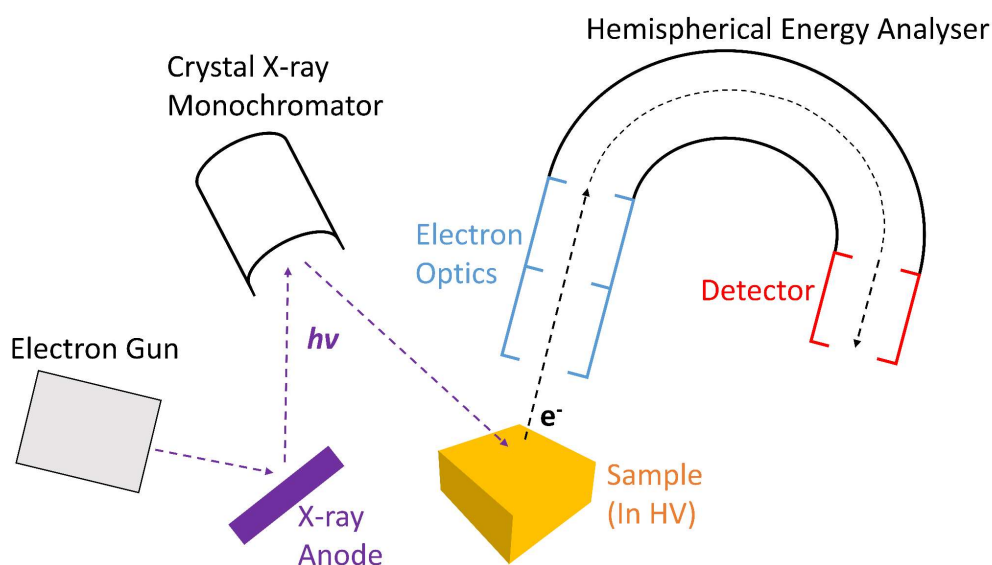


Figure 2.2: A typical, monochromatic XPS system. The analyser displayed here is hemispherical, although other variations exist.

Photoelectrons emitted from the sample then travel into and through the electron energy analyser. The analyser is made up of 3 main parts; the collection lens (electron optics), the energy analyser and the detector.⁴

The collection lens is the first part that the photoelectron travels through in the analyser. The lens controls the area of analysis, while also defining the acceptance angle between the sample and the analyser – the larger the analysis area and acceptance angle, the more electrons are gathered. The lens also retards the K_E of the photoelectron down to the set pass energy of the energy analyser.

A typical hemispherical electron analyser consists of two semi-circular electrodes – one inner, one outer (with a radius of R_1 and R_2 respectively) – with a path between them

through which the photoelectron will pass (with a radius of R_0). A potential difference of V_1 and V_2 is applied across the inner and outer electrode respectively. Photoelectrons arriving at the energy analyser will only reach the detector if their energy (eV) is defined as:

$$E_0 = e\Delta V \left(\frac{R_1 R_2}{R_2^2 - R_1^2} \right) \quad (2.2)$$

Where e is the electron charge and ΔV is the potential energy difference between V_1 and V_2 .⁵ Electrons with an energy slightly above or below this expression can also reach the output of the detector. These electrons can also be counted at the same time, provided there are enough channels located on the analyser, allowing for a quicker measurement.⁵ The electron analyser typically has two modes of operation; constant analyser energy (CAE) and constant retard ratio (CRR). In CAE mode, the photoelectrons are accelerated or retarded to a user defined energy which is the energy the photoelectron has when it travels through the analyser (the pass energy). As the pass energy is reduced, the resolution increases at the expense of electron counts. CRR mode operates by retarding the photoelectrons to a user defined fraction, where the pass energy is proportional to the K_E of the photoelectron. CAE mode is typically used due to the constant resolution, and as the XPS results acquired in this work are all from CAE mode, CRR will be discussed no further.

It should be noted that since the sample is being exposed to X-rays, photoelectrons of different K_E are being emitted from the surface. The analyser therefore operates by means 'sweeping' the accepted K_E across the user defined range.

2.1.3 Analysis of XPS data

Standard XPS spectra consists of the binding energy versus photoelectron counts, as shown in Figure 2.3. The main factors that are encountered in every XPS dataset are now discussed.

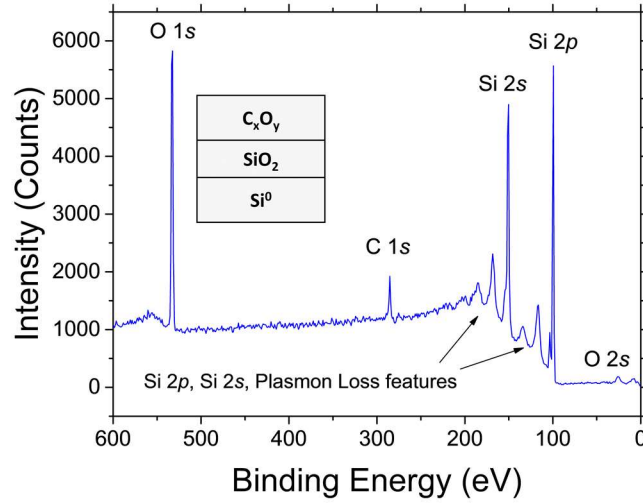


Figure 2.3: A typical XPS survey spectra, showing the results of a scan completed on silicon. Silicon from the underlying substrate is observed, as well as silicon oxide. Carbon is also observed and is usually attributed to a thin contamination layer that on top of the sample.

2.1.3.1 Analysis Depth

Despite photons near Al and Mg K α energies having a penetration depth of 1000 nm or more in most materials,⁴ XPS is a strongly surface sensitive technique, limited to acquiring information from approximately the first 10 nm of a film. This limit is imposed by the inelastic mean free path (IMFP) of the photoelectrons, which states how far an electron travels in a solid before undergoing an inelastic scattering event. This is represented in the Beer Law equation:

$$I_k = I_0 e^{(-d/\lambda_{IMFP} \cos \theta)} \quad (2.3)$$

Where I_k and I_0 are the final and initial intensity of the photoemission signal respectively, d is the distance the photoelectrons travel, λ_{IMFP} is the IMFP and θ is the angle of emission with respect to the normal.

In the general case, X-rays are incident on a sample surface. At a depth d in the sample, they generate a flux of photoelectrons travelling towards the surface (referred to as I_0). These electrons must travel a distance d to escape the sample without being scattered and undergoing an energy change, leading to a final intensity of unscattered electrons, I_k . As stated, the final intensity is also affected by the IMFP (λ), and the take-off angle θ . This angle refers to the angle the electrons emerge from the surface with respect to the normal. This is shown in Figure 2.4. Varying this angle leads to the development of angular resolved XPS (ARXPS). A large take-off angle results in an XPS spectra that is more dominated by signals near the surface, whereas low take-off angle spectra show greater intensities from material deeper below the surface (which will be referred to as bulk signal). The IMFP depends on the element and core level that the photoelectron has been ejected from, and also on the material that the electron is travelling through and the kinetic energy of emitted photoelectron (itself in part influenced by the incident photon beam). When d is large enough, I_k becomes too small to measure. This value of d is the detection depth limit of the XPS, and as mentioned, is typically below 10 nm.

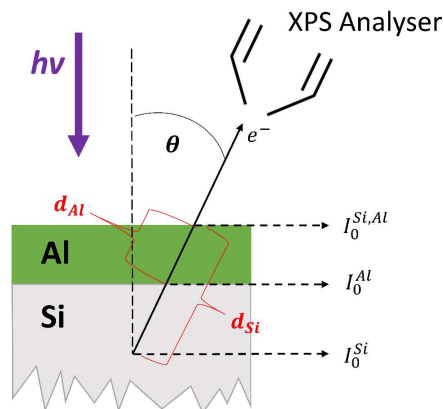


Figure 2.4: A simple schematic highlighting the parameters observed in the Beer equation.

2.1.3.2 Elemental Sensitivity

XPS is a quantitative technique, meaning that the more there is of a certain element in the X-ray beam at a certain depth, the greater the photoemission intensity from that element at that depth will be (thus ensuring stronger photoemission peaks associated with that element will be obtained). This allows for the determination of a material's stoichiometry.

When considering a homogenous material, the intensity (I_p) of a photoemission peak can be given in simplified form as:

$$I_p = J\rho\sigma K\lambda_{IMFP} \quad (2.4)$$

Where J is the photon flux, ρ is the concentration of the atom (associated with the peak) in the material, σ is the cross-section for that photoelectron, K is a constant that accounts for instrumental factors, and λ_{IMFP} is the IMFP of the associated photoelectron.⁵ The intensity is obtained from a core level peak – from the peak height or, more accurately, area under the curve calculations.

The electron cross section is referred to as the probability of achieving photoelectron emission. Every core level of every element has a cross section – the smaller the value, the less probable that photoemission occurs.^{5,6} The cross section also depends on the incident photon energy.⁷

By assuming the photon flux is constant, the σ , λ_{IMFP} and K terms in equation (2.4) can be incorporated into an experimentally determined sensitivity factor (F), with each core level of every element subsequently containing a unique value. The sensitivity factors used in this work are obtained from data originally published by Wagner et al.⁸

The assumption allows for the determination of the concentration of all atoms present:

$$\%(A) = \left\{ \frac{I_A/F_A}{\sum I/F} \right\} \times 100 \quad (2.5)$$

In this case, $\%(A)$ is the percentage of element A in the sample, and I_A is the intensity of a photoemission peak associated with that element. F_A is thus the sensitivity factor associated with that core level. Calculating the percentage for all elements present thus allows for the determination of the stoichiometry of the material. This is dependent on the photon flux maintaining a constant value, as well as the film being homogenous.

2.1.3.3 Peak Fitting

The shape of XPS core level spectra can be affected by a variety of factors such as multiple chemical states (e.g. Si^{1+} - Si^{4+}), spin orbit splitting and charging effects. To accurately analyse these spectra, it can be necessary to deconvolute them into single peaks for correct interpretation of data. A ‘peak’ represents a photoemission signal in one chemical state – such as Si-Si or SiO_2 .

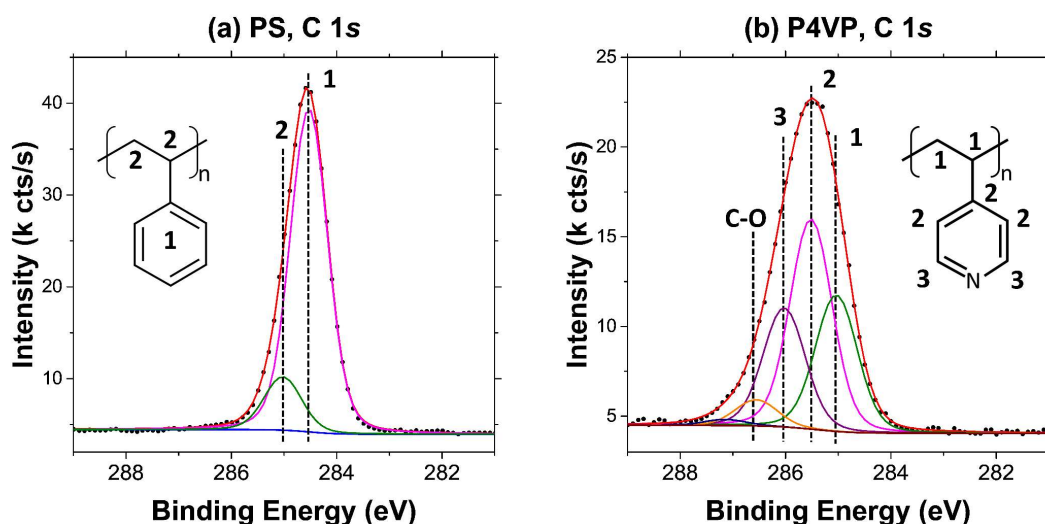


Figure 2.5: XPS spectra of the C 1s core level for two polymer samples – (a) PS and (b) P4VP. The carbon in both polymers is known to exist in different chemical states, requiring deconvolution to separate the spectra into separate peaks. Each peak represents a different chemical state attributed to the specific polymer.

An example of peak fitting is shown in Figure 2.5, which displays an acquired C 1s spectra for a PS (a) and P4VP (b) film. The chemical structure of each polymer is also shown. Carbon in PS is present in the polymer backbone, and in the benzene ring, requiring the fitting of two peaks into the spectra. The P4VP structure is however greater in complexity, requiring peaks attributed to the carbon backbone, as well as carbon – carbon bonds and carbon – nitrogen bonds occurring in the pyridine ring. By accurately fitting the spectra with correct parameters such as peak widths and binding energy positions, features like anomalies and different chemical states can be observed, such as the presence of carbon – oxygen bonds occurring in the P4VP spectra in Figure 2.5 (b).

2.1.3.3.1 Line Shape and Peak Width

Every peak in an XPS spectrum has a specific lineshape. This lineshape can be expressed mathematically as a combination of a Lorentzian and Gaussian functions, known as a Voigt curve. The Voigt curve has a final peak width of:^{9,10}

$$\Gamma_V = \sqrt{\Gamma_{Gaussian}^2 + \Gamma_{Lorentzian}^2} \quad (2.6)$$

Where Γ is the peak width – or full width half maximum (FWHM) of the peak. Both the Gaussian and Lorentzian peak width values contain important information concerning a specific XPS peak.

Lorentzian: From Heisenberg’s uncertainty principle, the creation of a core-hole during the photoemission process results in a Lorentzian broadening of the photoemission peak. Each core-hole has a finite lifetime, which is dependent on how quickly the hole is filled by an electron from another shell:⁴

$$\Gamma_{Lorentzian} = \frac{h}{\tau} \quad (2.7)$$

Where $\Gamma_{Lorentzian}$ is the peak width (in eV), h is Planck's constant and τ represents the core-hole lifetime (in seconds). Inner shell orbitals (e.g. 4s) have a much shorter core-hole lifetime and therefore a larger peak width than outer shells (e.g. 4f). Additionally, atoms with higher atomic numbers also have larger peak widths due to the abundance of electrons. It should be noted that the Lorentzian width is dependent on the intrinsic properties of the specific core level under analysis, and therefore should theoretically be consistent across a range of XPS systems.

Gaussian: This broadening is determined by many factors, which includes the limits of resolution from the photoemission analyser. Phonon broadening effects also contribute to the Gaussian broadening.¹¹ Since the Gaussian is determined by tool specific parameters, it is ultimately dependent on the system under use. The final width of the Gaussian component can be expressed as follows:

$$\Gamma_{Gaussian} = \sqrt{\Gamma_c^2 + \Gamma_a^2 + \Gamma_p^2} \quad (2.8)$$

Where the Γ_c , Γ_a and Γ_p are the peak widths accounting for chemical effects such as phonon broadening.¹¹ Γ_a accounts for the non-perfect resolution realities from the photoemission analyser, and is dependent on the analyser pass energy and slit width. Γ_p represent the spectral line width of the incident X-rays.¹²

The X-ray line width for conventional XPS depends on the X-ray source used, and whether the light is passed through a crystal monochromator. A monochromatic X-ray source reduces the X-ray line width to enhance the resolution of photoemission peaks. This is facilitated by diffracting X-rays using a quartz crystal, as described by the Bragg equation:

$$n\lambda = 2d \sin \theta \quad (2.9)$$

Where n is the diffraction order, λ is the X-ray wavelength, d is the crystal lattice spacing, and θ is the angle of diffraction. X-rays diffracting from the crystal will either interfere constructively or destructively; if the path difference ($2d \sin \theta$) is an integer multiple of $n\lambda$, then constructive interference occurs.

The goal of the X-ray monochromator is to therefore produce spectrally narrow X-ray lines. The line width of Al X-rays decreases from 0.90 eV to 0.25 eV after passing through the quartz crystal, greatly improving the resulting photoemission resolution. In addition to this, the quartz crystal also removes unwanted aspects of the X-ray spectrum, such as satellite peaks and the bremsstrahlung continuum. The monochromator also reduces the spot size of the X-rays incident on the sample.⁵ An example of data taken from a monochromatic and non-monochromatic X-ray source can be seen in Figure 2.6, and an increase in resolution is seen.

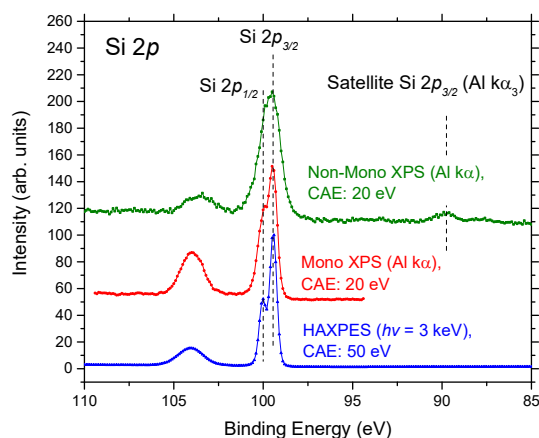


Figure 2.6: Comparison of Si 2p spectra taken from a non-monochromatic X-ray source (DCU, green), a monochromatic X-ray source (DCU, red), and from a HAXPES beamline at a synchrotron light source (SOLEIL Synchrotron, blue). Being the only system where X-rays are not passed through a crystal, satellite X-ray peaks can be seen in the non-monochromatic X-ray spectra.

The instrumental resolution over a small energy range is assumed to be constant, therefore, unless a known chemical phenomenon exists, it is expected that the FWHM of peaks making up an XPS core-level spectra are equal.

2.1.3.3.2 *Spin Orbit Splitting*

In quantum mechanics, the total angular momentum vector (J) is defined as:

$$J = L + S \quad (2.10)$$

Where L is the total orbital angular momentum vector and S is the total spin angular momentum vector, which has a value of $\pm\frac{1}{2}$. There are two possible J values unless $L = 0$.

Every subshell has two possible J values, apart from s-orbitals, which do not have orbital angular momentum ($L=0$). This variance in J results in photoelectrons having two different binding energy values if emitted from a subshell other than s . These two different binding energies are referred to as a doublet. An example of which can be clearly seen in the HAXPES Si $2p$ spectra in Figure 2.6. As this is a $2p$ peak, it is made up of $p_{3/2}$ and $p_{1/2}$ components.

Depending on the subshell, and hence J value, the area ratio of the two peaks will vary, displayed in Table 2.1. In addition, the binding energy difference between the doublet components also changes, however this is not a constant with each subshell. (E.g. The Si $2p$ doublet splitting distance is 0.6 eV, whereas it is approximately 0.4 eV for the Al $2p$ core level).

It should be noted that the two doublet components should not be considered as separate peaks in the fitting process. As the doublet components arise from the same core level and from the same chemical state, the FWHM values and area ratios should be equal across the doublet components unless other factors affect them, such as the Coster-Kronig transition (Auger process occurring within the same shell as the initial vacancy – affects the core-hole electron lifetime and thus the peak linewidth).¹³ Additionally, the binding energy difference between the doublets should be the same for each peak associated with the core level in question.

Table 2.1: Spin-orbit splitting j values and peak area ratios.¹⁴

Subshell	J value	Area Ratio
s	$1/2$	Na
p	$1/2 \quad 3/2$	1:2
d	$3/2 \quad 5/2$	2:3
f	$5/2 \quad 7/2$	3:4

2.1.3.3.3 Background

The ‘background’ in XPS spectra refers to the regions of binding energy where no photoemission peak is present. The counts are non-exhaustively attributed to photo and Auger electrons which have lost kinetic energy from inelastic scattering events. The effect can be seen in Figure 2.3 – the intensity of the background has increased on the higher binding energy side of all major photoemission peaks. This is because inelastic scattered electrons from the excited core level are now contributing to the spectra.¹⁵

This background must be accounted for to ensure accurate peak fitting, with a poor choice of model resulting in incorrect peak areas. Peak fitting software usually incorporate a certain mathematical function which represents the background, with common options including the linear, Shirley and Tougaard background.

The linear background is a horizontal or sloped straight line that spans the two endpoints of an entire peak fit. The method is easily applicable in non-specialist peak fitting software, however it is uncommon for XPS spectra to have a flat background. Both the Shirley and Tougaard background are favoured due to the over simplification of the linear model.¹⁶

The Shirley background assumes that the background at any binding energy in the region of a photoelectron peak is proportional to the integrated intensity of the peak at lower binding energies.^{15,17} The background thus increases as with the area of the peak. This

approach was developed further by performing iterations of the fitting process to further increase its accuracy, referred to as the Shirley – Sherwood background.¹⁸

The Tougaard background is an algorithm that is modelled by considering the inelastic electron scattering. It is reported to be successful over large binding energy regions, however the Shirley – Sherwood background is preferred in narrower zones.^{19–21}

2.2 Hard X-ray Photoelectron Spectroscopy

2.2.1 Overview

Hard X-ray Photoelectron Spectroscopy (HAXPES) uses synchrotron radiation photons in the hard X-ray regime for the excitation of photoelectrons.

Like XPS, HAXPES is a surface analysis and characterisation technique that relies on the photoelectric effect, with the considerations in XPS analysis discussed in section 2.1.3 also applicable to HAXPES analysis. Several key differences are evident between the two techniques however, since HAXPES generates photons from an electron beam in a storage ring, rather than via conventional generation in an X-ray tube. ‘Hard’ X-rays are defined as an X-ray beam with a photon energy of above 2 keV, with the range 2 – 10 keV often defined as a sub section, the ‘tender’ X-ray regime.²² The main differences resulting from this are now discussed.

2.2.2 Technical Details

2.2.2.1 *Synchrotron Radiation*

The fundamental principle in synchrotron radiation was first discovered by Heinrich Hertz, who reported that charged particles emit electromagnetic radiation when accelerated. This radiation can be used for multiple purposes, which includes generation of photons with energy in the hard X-ray regime. A typical synchrotron source will accelerate electrons to relativistic speeds, with this ‘beam’ of electrons kept in a storage ring. This ring will produce radiation by means of transverse acceleration of the electron beam – produced using magnets.

An example of a synchrotron (SOLEIL Synchrotron) is shown in Figure 2.7.²³ An electron gun produces high energy (100 MeV) electrons (1), which are then brought up to 2.75 GeV in a booster ring (2). These electrons then enter the synchrotron ring (3),

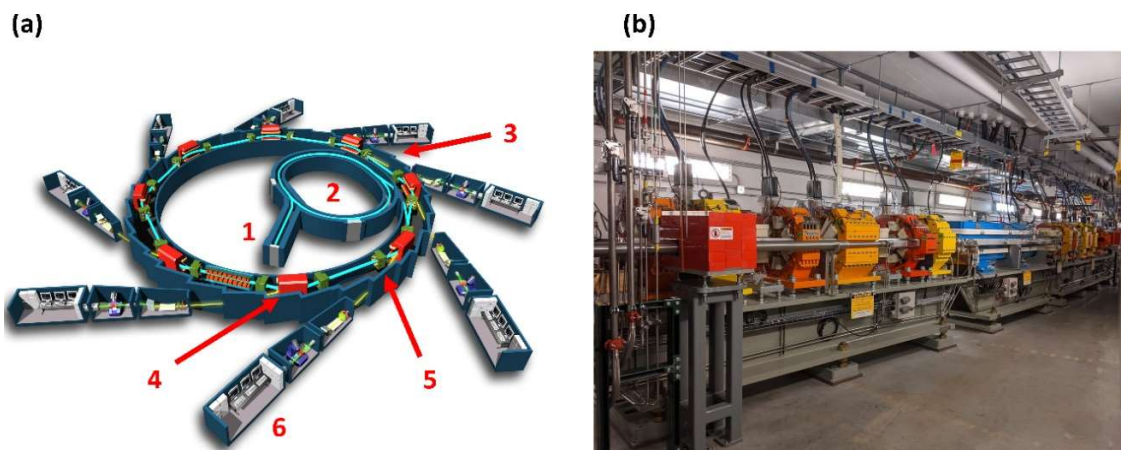


Figure 2.7: (a) Overview of synchrotron SOLEIL. (b) A picture of the beamline inside Brookhaven National Light Source. The brightly coloured blocks are the magnets used for the controlling and bending of the magnetic beam.

where magnets are employed to control the trajectory and oscillation of the beam (4), shown in Figure 2.7 (b). The synchrotron radiation is produced by these bending magnets and undulators. The energy loss experienced by the beam is compensated by radiofrequency cavities (5).

Several beamlines (6) are located around the ring. These beamlines make use of the synchrotron radiation in a variety of techniques including HAXPES.^{23,24}

2.2.2.2 HAXPES Beamline

A significant limiting factor in XPS is the analysis depth of the measurement, limited to approximately 10 nm and below. Furthermore, due to the attenuation of photoelectrons, most of the information arising from an XPS spectrum is concerned with the first few nanometres of the film under analysis. This limitation spurred the progression of HAXPES beamlines, which implement synchrotron radiation to achieve photoemission with light in the X-ray regime as with a conventional XPS system. Unlike in laboratory based XPS systems, which rely upon the strongest X-ray line ($K\alpha$) for the acquisition of photoemission peaks, a HAXPES beamline can optimise the synchrotron radiation to

produce an incident beam over a range of energies. This range varies between beamlines, but typically covers a keV range from soft to hard (SOLEIL $h\nu = 2.3 - 12$ keV; Diamond $h\nu = 0.1 - 20$ keV; Brookhaven $h\nu = 2.0 - 7.5$ keV),^{25–27} allowing for the acquisition of more core level signals that would be unobtainable in conventional XPS. The major difference between HAXPES and XPS is therefore the K_E of the emitted photoelectrons, with the basic analysis concepts explained in section 2.1.3 remaining applicable due to the same fundamentals.

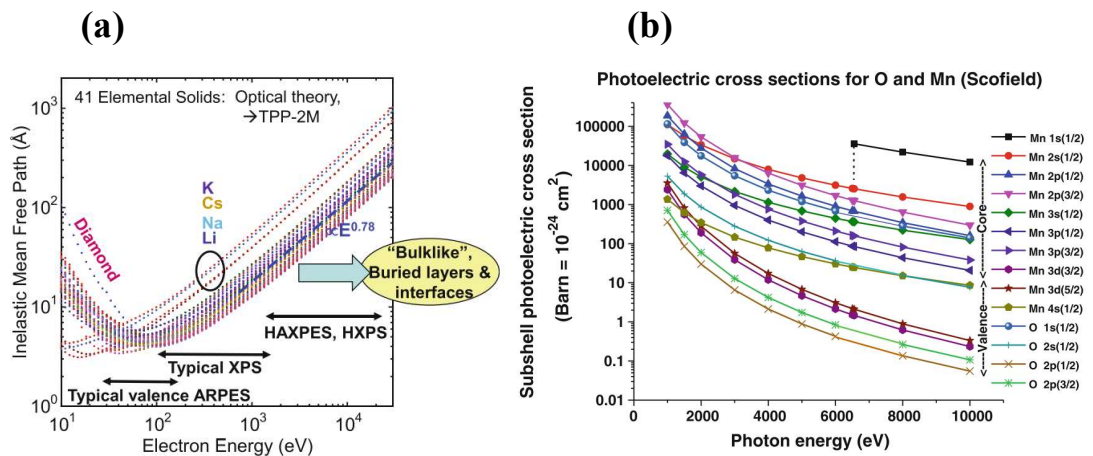


Figure 2.8: (a) Relationship of the IMFP with electron energy.²⁸ (b) Dependence of photoelectron cross section with photon energy.

The Beer law, as discussed in equation (2.3), showed that a photoemission signal is dependent on how far the emitted photoelectron must travel through the material to reach the analyser, as well as the IMFP. This IMFP is directly correlated with the photon energy (and thus K_E of the photoelectron) that resulted in photoemission, with the relationship shown in Figure 2.8 (a).²⁸ HAXPES typically uses a photon energy of above 2 keV, with the resulting photoelectrons therefore having a much higher K_E than conventional XPS. This greatly increases the IMFP, thus allowing for signals from a greater depth to be observed in a photoemission spectrum. This provides several advantages over conventional XPS, as the sample material below the initial few nanometres can be studied

more easily due to higher signal intensities, and interfaces below the limits of conventional XPS detection can also be studied. Historically, HAXPES analysis was hindered by the photoelectron cross section, which decreases with increasing photon energy as Figure 2.8 (b) implies.⁷ This behaviour resulted in a low photoemission intensity and a poor signal to noise ratio. However, ‘third generation’ synchrotrons overcame this intensity issue, increasing the brilliance (photon flux per unit area) sufficiently through the installation of undulators.^{1,22,29,30}

As mentioned, the higher photon energy allows for the extraction of more bulk sensitive information of a film when comparing HAXPES spectra to XPS, with the analysis of deeper interfaces unobtainable in conventional XPS photon energies possible. Furthermore, the ability to increase the photon energy also facilitates the acquisition of more core levels possessing a binding energy that is too high for conventional X-ray sources to induce photoemission. This can have several advantages. Core levels that are complex to analyse can be complemented with the acquisition of other strong core line signals. An example of this is the acquisition of the Al 1s (unobtainable via XPS), which eliminates the need to analyse the Al 2p, which is difficult to study accurately due to the small spin orbit splitting value of approximately 0.4 eV, and the low sensitivity factors associated with it.^{8,31} Additionally, core levels of a higher binding energy can be obtained in the case where an element with a strong core level overlaps with another element’s core level signal, such as the Ruthenium, where the Ru 3d peak overlaps with C 1s.³²

The ability to tune the photon energy provides additional advantages of HAXPES over XPS. Firstly, a varying photon energy results in the elimination of core level and Auger peak overlapping. An example of this is the Co 2p, where there is a strong overlap between the Co 2p and the Co LMM Auger line when using a Al K α X-ray source.³² The ability to analyse the same spot on a sample at a ‘high’ and ‘low’ HAXPES photon energy

also allows for an accurate depth profiling measurement – XPS requires rigorous optimisation for an accurate depth profiling ARXPS measurement.³³ The higher, tuneable photon energy of HAXPES also makes it a much more favourable depth profiling measurement to XPS – which is limited in analysis depth as discussed, and TEM, Ar sputtering and secondary-ion mass spectrometry (SIMS) – which are destructive techniques.

Other advantages of the HAXPES measurement include,^{22,34}

- Increasing of the effective electron attenuation length (EAL) alongside the IMFP with rising photon energy. The EAL is similar to the IMFP, except that the EAL also takes into account elastic scattering events.^{35,36} Like the IMFP, it changes depending on the photoelectron kinetic energy, the elemental core level the photoelectron was emitted from and the material(s) that the photoelectron is travelling through to escape the sample.
- High resolution photoemission spectra that is greater than monochromated X-ray sources.³⁷
- High brightness and photoemission intensity, orders of magnitude higher than conventional XPS.
- The reduction in inelastic background, allowing for less ambiguity in spectra analysis and fitting.
- HAXPES beamlines are typically equipped with highly sophisticated photoemission analysers for optimal resolution.

2.3 Ellipsometry

2.3.1 Overview

Ellipsometry measures a change in the polarisation of light as it is reflected or transmitted through a material. By monitoring this change, optical and film thickness properties (as well as other characteristics such as composition, crystallinity, roughness and doping concentration) of the material can be obtained.³⁸

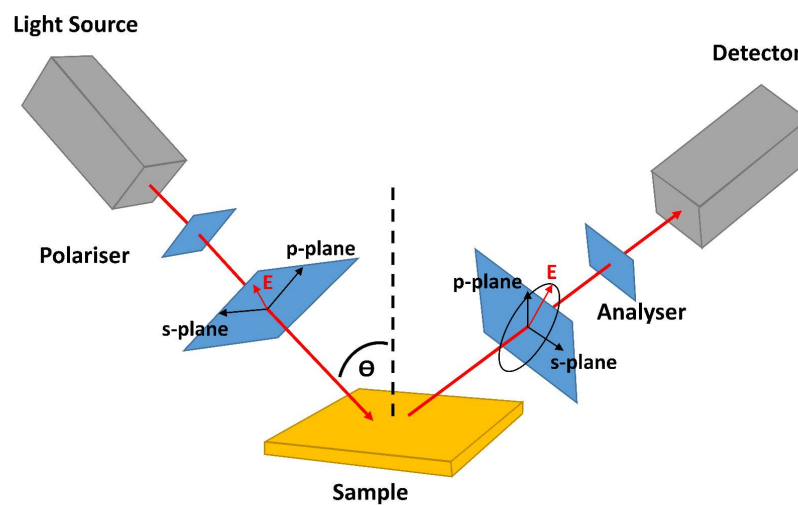


Figure 2.9: Schematic of an ellipsometry setup. Polarized light is made incident upon a sample, with changes in the polarization after material interaction picked up by the analyser/detector setup.

The basic operating principle of an ellipsometer setup is demonstrated in Figure 2.9. Light from a source is passed through a polarizer, and thus becomes linearly polarised light. Once reflected off the sample surface, this light becomes elliptically polarised, with the changes in polarisation dependent on the material it has interacted with. The elliptically polarised light then travels through a continuously rotating polarizer (the analyser), with the detector subsequently determining the reflected polarization and compares this to the initial, linearly polarised light.

2.3.2 Technical Details

2.3.2.1 Theoretical Basics

Linearly polarised light consists of two orthogonal waves that are in phase – with one oscillating perpendicular (*s* component) and the other parallel (*p* component) to the plane of incidence. Once elliptically polarised, the two orthogonal waves have a different relative amplitude and phase. It is this difference between the linear and elliptically polarised light that the ellipsometry measurement takes advantage of. The change in polarization is expressed mathematically as follows:

$$\rho_r = \frac{r_s}{r_p} = \tan \psi e^{i\Delta_p} \quad (2.11)$$

Where the amplitude component ψ and the phase difference Δ_p are the measured ellipsometry parameters. These parameters are related to the amplitudes of the *s* and *p* components after sample interaction (and normalized to the incident light), referred to as r_s and r_p respectively. The term ρ_r is stated as the complex reflectance ratio, and is dependent on several parameters, which includes the thickness of the film under analysis (*t*), the refractive indices of the ambient, film and substrate (N_a , N_f , N_s , respectively) the angle of incidence (Θ) and the wavelength of the source (λ). Generally, the refractive indices of the ambient and substrate, the angle of incidence and the source wavelength are known, which allows for the determination of the film's thickness and refractive indices from the measurement of ψ and Δ_p .^{39,40}

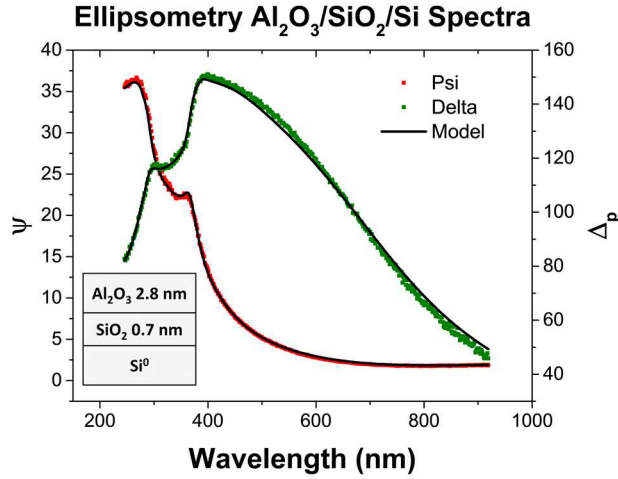


Figure 2.10: Example spectra of ψ and Δ_p values recorded from $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ stack. A Cauchy model was applied to the spectra, with the best fit determining the Al_2O_3 thickness as 2.8 nm. The SiO_2 thickness was known prior to measurement.

Using measured data of ψ and Δ_p to obtain t and N_f values require the use of dispersion equations, which compare the experimental data to mathematical models. By applying Fresnel's equations, the chosen model can determine t and N_f values which yield a best fit, with an estimator such as the mean squared error (MSE) typically used to track the quality of the fit. There are a number of mathematical models for which this is possible, such as Cauchy, Sellmeier, general oscillators such as Drude/Lorentz and B-Spline.⁴¹ These models implement dispersion equations, which take into account the optical constants of a material and how they vary with wavelength. A typical sample ellipsometry spectra from this work and the model employed is shown in Figure 2.10. To obtain a thickness value for the Al_2O_3 film, a reference Cauchy model was implemented over the chosen wavelength range. The Cauchy model can be used for optically transparent materials and was exclusively used in this work as all films under analysis were no thicker than ~ 10 nm.

2.4 Fourier Transform Infrared Spectroscopy

2.4.1 Overview

The frequency dependent interaction of infrared (IR) radiation with matter forms the basis of IR spectroscopy. When passed through a sample, IR is absorbed at specific frequencies by the molecules present in the material. The frequency that the absorption occurs at is determined by the structural characteristics of the molecule, including the mass of the atoms in the molecule, the strength of the bond and the environment around the molecule. An IR absorbance/transmission spectrum is made up of various peaks/troughs where a molecule has absorbed a certain frequency of IR light. At this absorption point, the incoming IR is of the same frequency as one of the fundamental modes of vibration of that molecule. These vibrations are associated with a change in the dipole moment of the molecule and are commonly classified into stretching or bending vibrations. Stretching represents the continuous change of distance between two bonded atoms, whereas bending describes a change in angle between the bonds in the molecule. Bonds in the molecule can stretch in-phase (symmetric stretching) or out-of-phase (asymmetric stretching).^{42,43}

2.4.2 Technical Details

2.4.2.1 Theoretical Basics

For a molecule to interact with IR radiation, it must have a dipole moment. This is due to the vibrations that cause the absorption attributed to changes in a molecule's dipole moment. Nonpolar molecules with no net electrical charge such as N_2 , therefore cannot be detected by IR spectroscopy. Additionally, molecules with a large dipole moment, such as $\text{C}=\text{O}$, where a large electronegativity difference exists between the carbon and oxygen, will lead to a strong absorption band.

The frequency of a vibrational mode (ν) at which absorption occurs is represented by:⁴⁴

$$\nu = \frac{1}{2\pi} \sqrt{\left(\frac{k}{\mu}\right)} \quad (2.12)$$

Where c is the speed of light and k is the force constant, derived from Hooke's Law, relating to the stiffness of the bond. The parameter μ is defined as the reduced mass:

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} \quad (2.13)$$

Where m_1 and m_2 are the masses of the atoms at each end of the bond.

Initial IR spectroscopy devices operated by using two independent IR beams, with one beam travelling through the sample and the other passing through a reference species. Upon passing through the sample, the beam is dispersed by a grating monochromator into its component frequencies. Each frequency is measured independently and compared to the reference beam.⁴⁵ This classic, 'dispersive' IR spectrometer was eventually replaced by the more powerful FTIR spectrometer.

2.4.2.2 FTIR

The FTIR setup involves the use of an interferometer, with the oldest and most common type, the Michelson interferometer, shown in Figure 2.11. IR radiation generated at the source, is passed through a collimating mirror (to make the light parallel) and made incident upon a beamsplitter. The beamsplitter either reflects or transmits this incident light, creating two separate beams of different paths. The two beams travel a certain distance before being reflected back to the beamsplitter – one via a fixed mirror, the other by a moving mirror as Figure 2.11 implies. This allows for the beams to recombine and interfere with each other depending on the path difference, before travelling as a single wave through the sample and to the detector. Continually altering the moveable mirrors position thus ensures the recombined wave has an intensity profile that matches a cosine

wave when plotted against the path length difference (which is directly related to the position of the mirrors).

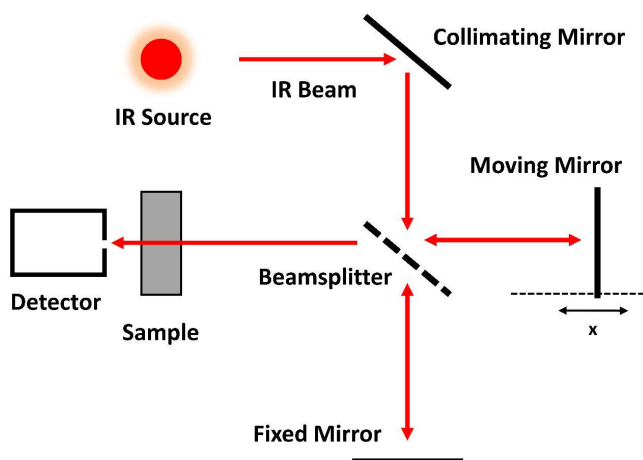


Figure 2.11: Fundamental components of a Michelson interferometer in a FTIR setup.

A plot of this intensity versus optical path difference at a specific wavelength is referred to as an interferogram. For an FTIR spectra, IR light across a range of wavelengths is required, resulting in the production of multiple interferograms. The detector measures the sum of all these interferograms, with the effect of placing a sample in the path of the recombined beam reducing the intensity of the absorption. To convert the measured interferogram summation to an absorption spectra, a Fourier transform is used.⁴⁶

2.4.2.3 Attenuated Total Reflection

Difficulties arise in FTIR spectroscopy where it is necessary to analyse thin films. The resultant absorption signals are very weak due to the low intensity arising from limited interaction of the IR beam with the absorbing molecules of the film. An adaptation to the conventional ‘single pass’ FTIR setup is referred to as attenuated total reflectance FTIR (ATR-FTIR), which overcomes this issue by increasing the distance IR light travels through the film of interest many times compared to what is achievable through a standard FTIR setup. This is achieved by utilizing total internal reflection and evanescent waves.

The total internal reflection of light at a boundary between two mediums forms the principle of ATR-FTIR. Total internal reflection occurs when light is propagating through an optically dense medium towards an optically rare medium at an angle of incidence greater (θ_i) than the critical angle (θ_c). The refractive index of medium 1 (n_1) is therefore greater than medium 2 (n_2). At the point of internal reflectance, the incoming and outgoing beams undergo constructive interference, and an evanescent wave is formed in the medium of lower refractive index.

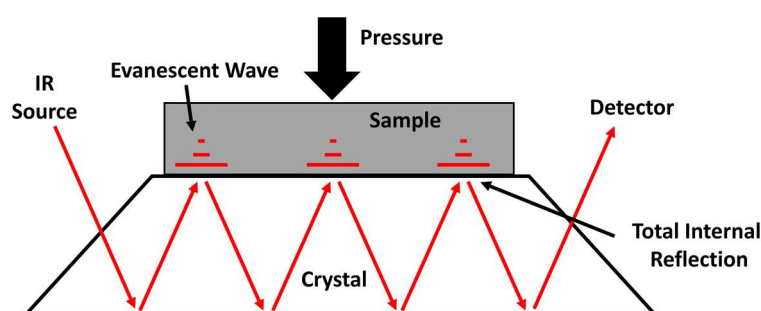


Figure 2.12: GA-FTIR sample setup. Due to the higher refractive index of the crystal compared to the sample, total internal reflection occurs at the interface. An evanescent wave enters the sample and is attenuated depending on the chemical structure present. To ensure good contact between the sample and crystal, pressure is maintained on the backside of the sample.

While the setup is like a conventional FTIR, the key difference in ATR-FTIR is how the light beam interacts with the sample, which is shown in Figure 2.12. A sample is placed in contact to a material with a high refractive index, such as a germanium crystal, with the IR light directed to propagate through this crystal. Total internal reflection is made occur within the crystal at its interface with the sample. As discussed, the refractive index of the sample must be lower than that of the crystal, and the angle of incidence must exceed the critical angle. An evanescent wave is formed in the sample, decaying exponentially before recombining with the beam in the crystal. The evanescent wave may be partially absorbed by molecules within the sample, based on the basic principles of IR spectroscopy covered in section 2.3.2.1. The depth of penetration of the evanescent wave

into the sample ranges from a maximum of approximately 10 μm to sub-1 μm . The resulting absorption within the sample leads to the attenuation of the totally reflected beam, which can then be compared to a background spectrum taken by the instrument when no sample was placed on the crystal. As Figure 2.12 implies, due to the repeating nature of the total internal reflection, a greater amount of absorption from the thin film can occur due to repeated evanescent wave interaction, as opposed to the once-off pass in conventional FTIR setups.⁴⁶

The ability to analyse films of thickness in the nanometre scale regime is made possible by the grazing angle ATR-FTIR setup (GA-ATR-FTIR – or GA-FTIR for shorthand). The operation principle is the same as in ATR-FTIR, however it is important that the substrate of the sample has a higher refractive index than the thin film under analysis. The evanescent field thus remains in the film sandwiched between the crystal and substrate, and does not interact appreciably with the substrate.

2.5 Atomic Force Microscopy

2.5.1 Overview

Atomic force microscopy (AFM) is a surface sensitive technique that analyses the surface topography of a material, providing 3D profiles of the surface with nanoscale sensitivity. Figure 2.13 shows the basic principle of a modern AFM. A laser shines onto a flexible cantilever, with the light then being reflected into a four-quadrant photodetector. The cantilever contains a probe (tip radius < 10 nm), which traces over the surface of the sample using a raster scanning process. As the cantilever moves across the surface, it will move up or down depending on the surface topography that the probe tip is mapping due to the force experienced between the tip and the surface, thus altering the reflected laser light on the photodetector. This force is described using Hooke's Law:

$$F = -kx \quad (2.14)$$

Where F is the force, k is the spring constant and x is the cantilever deflection. This force is measured by monitoring the change in the reflected laser light, producing a 3D image – with nanometre detail – of the scanned area.

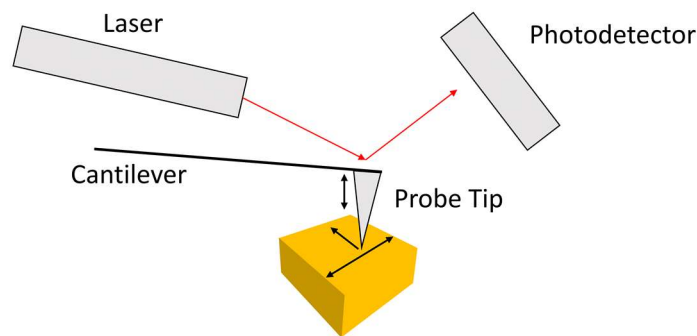


Figure 2.13: Basic AFM diagram. A probe tip scans a designated area across the sample. The cantilever will bend, depending on the roughness/surface topography

AFM was first reported by G. Binnig and C.F. Quate.⁴⁷ In their work, the AFM probe was shown to require a high resonant frequency to isolate the system from external vibrations.

The resonant frequency (f_0), of the probe is given by:

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m_0}} \quad (2.15)$$

Where m_0 is the mass of the cantilever. Considering equation (2.14) and (2.15), a large resonant frequency can be obtained from a tip with a small spring constant, providing the mass of the probe is small enough. Additionally, G. Binnig and C.F. Quate showed that small deflections in the cantilever allowed the detection of very small forces (10^{-11} N).

2.5.2 Technical Details

2.5.2.1 Modes of Operation

There are three common modes of operating and acquiring data with an AFM, contact mode, intermittent contact and non-contact mode.⁴⁸

2.5.2.1.1 Contact Mode

The operational distance between the probe tip and the surface of the sample is below 0.5 nm in contact mode. The force between the cantilever and the surface is repulsive, deflecting the cantilever, and kept as a constant for the experiment, resulting in an image of the surface being obtained. This mode results in fast scanning time however can lead to damage to probes. Because the probe is in contact constantly with the surface, hard surfaces are usually best suited for this mode of operation.

2.5.2.1.2 Intermittent/Tapping Mode

This mode involves the cantilever making intermittent contact with the sample while vibrating with a resonant frequency of hundreds of kHz. An oscillation frequency is applied to the tip, close to the resonant frequency, and this is kept constant for the experiment by adjusting the height of the tip above the sample surface, which generates the imaging data. Lateral forces are reduced due to minimal contact time between the probe and the sample.

In addition to basic height images obtained from tapping mode, two other images are obtained from this mode of operation, amplitude and phase imaging. Amplitude imaging displays the voltage needed to keep the amplitude of the cantilever constant, while phase imaging maps the phase difference between the driven oscillations of the cantilever. Amplitude imaging can provide high contrast between surface features, while phase imaging can provide information such as chemical composition, adhesion and friction.⁴⁸

2.5.2.1.3 *Non-Contact Mode*

The probe – sample separation is usually in the range 0.1 – 10 nm in this mode. Very low forces are therefore exerted on the sample, albeit at a cost to the spatial resolution, and this mode is often used to image delicate/deformable surfaces, e.g. with liquid upon the surface.

2.5.2.2 *Roughness Calculations*

An important measurement AFM data provides for this work is the acquisition of surface roughness – obtained through AFM height images. This is particularly important for analysing the quality of polymer brush layers and resulting films of metal oxides. The software used for roughness calculations was Gwyddion.⁴⁹

The roughness average (R_a) measures the deviation in height, and is defined as:

$$R_a = \frac{1}{N} \sum_{j=1}^N |r_j| \quad (2.16)$$

The root mean square (RMS) roughness (R_{RMS}) is another way of performing roughness calculations, yielding the standard deviation of surface heights:

$$R_{RMS} = \sqrt{\frac{1}{N} \sum_{j=1}^N r_j^2} \quad (2.17)$$

It is the average of the measured height deviations taken within the evaluation length and measured from the mean line. This provides a measurement more sensitive to peaks and valleys compared to R_a .^{48,50,51}

2.6 Electron Microscopy

2.6.1 Overview

The Rayleigh criterion of a light microscope, defines the maximum (diffraction limited) resolution, δ :

$$\delta = \frac{0.61\lambda}{\mu \sin \beta} \approx \frac{\lambda}{2} \quad (2.18)$$

Where λ is the wavelength of the photons being used to probe the object under investigation, and the term $\mu \sin \beta$ is defined as the numerical aperture. Considering the wavelength range of visible light (380-750 nm), the resulting minimum resolvable feature size is approximately 160 nm.

This limitation in resolution can be addressed by considering the wave/particle duality – that there is a wavelength associated with a particle that has mass. This is defined as the deBroglie wavelength:

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2meU}} \quad (2.19)$$

Where h is the Planck constant. With p , v , m , e and U representing the momentum, velocity, mass, charge and accelerating voltage of the particle respectively.

The electron has a small enough mass to yield a wavelength comparable, or less than, the interatomic distances in solids when accelerated to kV levels. Additionally, electrons with a substantial accelerating voltage will be able to penetrate materials to depths of the order of micrometres.

By accelerating electrons closer to the speed of light (c), the wavelength of the electron according to the deBroglie equation must be revised to account for relativistic effects:

$$\lambda = \frac{h}{\sqrt{2m_0eU \left(1 + \frac{eU}{2m_0c^2}\right)}} \quad (2.20)$$

Where m_0 is the rest mass of the electron.

By using electron-based instead of light-based microscopes, the traditional diffraction limitations associated with the visible wavelength of light can be overcome due to the smaller wavelength of accelerated electrons. However the quality of electron lenses is generally much poorer than optical lens for off-axis rays, thus reducing the numerical aperture of electron lens. However, the net result is still a substantial increase in the resolution possible in an electron microscope compared to a light microscope. The use of electron microscopes has allowed features as small as 0.5 Å to be resolved.⁵² Both the scanning electron microscope (SEM) and transmission electron microscope (TEM) have been used extensively in material science, with the TEM being used predominately in this work. It should be noted that all TEM (and corresponding EDX) imaging and sample preparation discussed in this work was performed by collaborators at Intel Ireland in the Leixlip plant (A. Bell, D. Bird, C. O'Neill and J. McKenna) or at the Center for Research in Advanced Materials – Centro de Investigación en Materiales Avanzados (Cimav), Mexico.

2.6.2 Transmission Electron Spectroscopy

2.6.2.1 Theoretical Basics

TEM is a technique whereby high energy electrons pass through a thin sample, resulting in electron – sample interactions that produce sub-nanometre resolution images with magnifications of up to 1,500,000. Despite taking considerably more time for sample preparation and data acquisition, compared to SEM, the TEM is far superior in terms of resolution and magnification.

A schematic of a TEM is shown in Figure 2.14. Electrons produced by a tungsten filament or field emission gun are accelerated to a high voltage (80 – 200 kV). The TEM is under vacuum to allow for a greater electron mean free path. These electrons are collimated into a small coherent beam by the condenser lens of the system. The beam will then pass through a sample, which has usually been prepared for analysis via Focused Ion Beam (FIB). FIB preparation is necessary to thin the sample so that the accelerated electrons can travel through it. The objective lenses are then used to focus the transmitted beam, and the projector lens provides final magnification before the electron beam reaches the fluorescent screen. The intermediate lens serves to change the operating mode of the TEM.

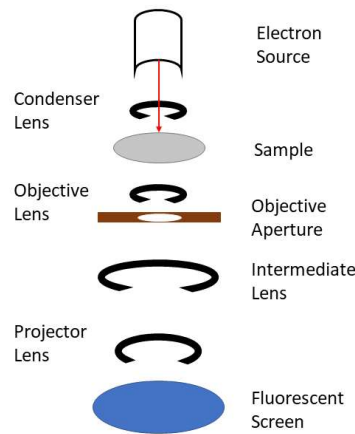


Figure 2.14: Schematic of a typical TEM setup.

There are two basic modes of operating a TEM: imaging and diffraction modes. The imaging mode requires the objective aperture to be placed in the back focal plane of the objective lens. The objective aperture can be used to select only the central beam, where only non-diffracted electrons pass, referred to as bright field imaging. Dark field imaging by contrast selects diffracted beams (from different lattice planes) to pass through the aperture and form the image. Diffraction mode is achieved by using the sample as a diffraction grating, resulting in the beam forming a diffraction pattern. This mode of

operation can be useful in determining which parts of a sample are crystalline and also the crystal type and orientation.

Plan view and cross-sectional images of a sample can be achieved through TEM analysis. TEM is used predominately in this work for thin film thickness and quality observations, thus cross-sectional images are solely used for this report.

2.6.3 Energy Dispersive X-ray Spectroscopy

2.6.3.1 Theoretical Basics

The schematic in Figure 2.15 (a) shows the interactions that occur when a sample of ‘infinite depth’ is subjected to e-beam bombardment. One important emission process that occurs from e-beam bombardment is the generation of characteristic X-rays, shown in Figure 2.15 (b).

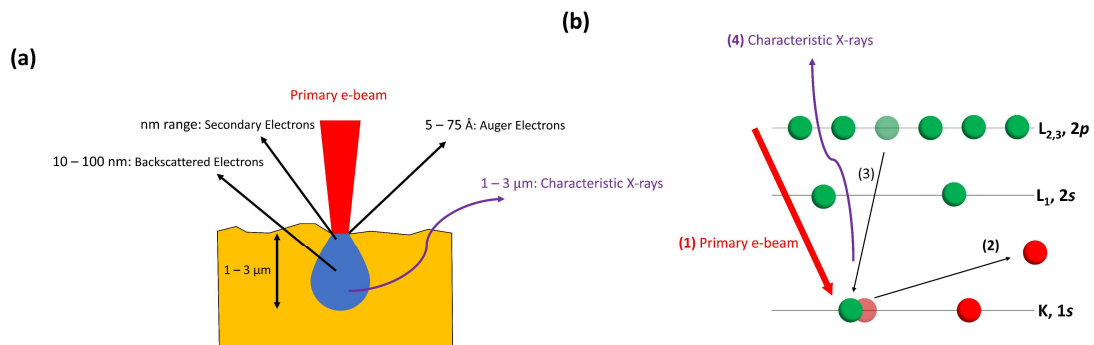


Figure 2.15: (a) Resulting information arising from a sample under e-beam bombardment. (b) Process of characteristic X-ray generation from e-beam bombardment.

When the electron beam is incident on an atom (1), the energy loss experienced by the beam is transferred to the atom, resulting in orbiting electrons to move to higher energy core level shells or escaping the atom entirely (2). The vacant hole left behind the escaped electron will then be filled by another electron in the atom from a higher energy shell (3). The subsequent relaxation process that occurs in the atom can result in an auger process as seen in Figure 2.15 (b), or the production in a characteristic X-ray (4) from the electron moving from a higher energy position to the lower, vacant position. The energy difference between these two states is the resulting energy of the emitted X-ray.

As discussed in section 2.1, the energy of each specific core level electrons is unique to every element. This means that the characteristic X-rays produced by the e-beam tell the user what the surface under analysis is made up of elementally. This resulting technique of EDX thus provides spatially resolved chemical information, and is a complementary technique to both SEM and TEM that use secondary/backscattered and transmitted electrons respectively to provide surface and topography information. As the work presented here is concerned with thin films (sub 20 nm), all EDX imaging used in this work are cross section images, because using EDX for plan view TEM imaging is not possible due to the very small sample thickness along the electron beam path (samples for TEM are thinned via FIB to ~ 100 nm).

2.7 Electrical Characterisation

2.7.1 Overview

It was discussed in chapter 1 that many of the materials fabricated in this work are designed for implementation into the semiconductor industry, most notably, as metal oxides to function as gate oxides. Electrical measurements of metal oxides through IV and CV sweeps, allow for the characterisation of arguably the most important aspects of the film's properties.

All IV and CV measurements in this work are made on devices that resemble a metal oxide semiconductor capacitor (MOSCAP). The MOSCAP is a simplified device that mimics part of the MOSFET, consisting of a metal (M), oxide (O) and semiconductor (S) layer. An example of a p-type MOSFET and MOSCAP are shown in Figure 2.16 (a) and (b) respectively.

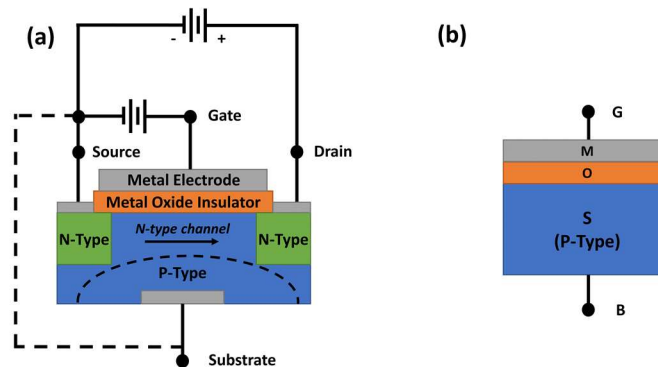


Figure 2.16: Diagram of a p-Type (a) MOSFET and (b) MOSCAP. The MOSCAP is simplified into 3 parts, the metal (M), oxide (O) and semiconductor (S).

2.7.2 Current – Voltage Sweeps

2.7.2.1 Theoretical Basics

A perfect gate oxide would result in no current flow between the gate electrode and semiconductor under all biasing conditions of the MOSFET operation, while still allowing for high capacitance devices. However, due to the quantum mechanical behaviour of electrons, the gate dielectrics found in MOSFETS are not perfect insulators, with leakage current observable when a voltage is applied to the gate of the device. Eventually, as the applied voltage increases, breakdown of the insulating properties of the oxide film will occur when the voltage across the gate reaches a certain value. At and above this breakdown voltage (V_B), the gate oxide is no longer an insulator, allowing the flow of current through it. It also remains permanently damaged as a result.

The oxide's V_B can be converted to its breakdown field (E_B) if the thickness of the oxide is known, which is dependent on the material used, but also other parameters such as the growth mechanism and thickness of the film (Table 2.2).

Table 2.2: Overview of breakdown field for several materials with the capacity of functioning as a gate oxide. The resulting E_B is dependent upon the metal oxide, the growth method used and the thickness of the film.

Material	Growth Mechanism	Thickness (nm)	E_B (MV/cm)
SiO ₂	Thermal Oxide	3	23 ⁵³
Al ₂ O ₃	ALD	5 – 6	10 ⁵⁴
HfO ₂	ALD	4	4 ⁵³
ZrO ₂	ALD	8	6 ⁵⁵

Electrical (or avalanche) breakdown refers to the phenomena where free electrons are accelerated by the applied electric field, eventually ionising other atoms and creating

more free electrons when the voltage reaches a critical point. Thermal breakdown results from tiny currents present in weak parts in the dielectric (such as a non-stoichiometric region that leads to local free charge carriers) that increase, along with the associated generated heat, as the voltage across the insulator increases. The localised temperature increase will eventually get so high that failure occurs.

It is therefore desirable to obtain devices with a high breakdown field – however a trade off in regard to the relative dielectric constant, k , is witnessed (the materials in Table 2.2, ranked in terms of their breakdown field, follows an inverted ranking order when listed against the material k value).⁵⁶

Both the leakage current and breakdown field of the gate oxide is of significant interest in this study and can be measured by performing voltage ramps across MOSCAP structures. By electrically stressing and ultimately breaking down dielectric films, information about the integrity and lifetime of gate oxides can be obtained. Comparing novel metal oxide fabrication methods to state-of-art techniques such as ALD, will also validate new processes for industry integration.

Prior to breakdown, the predominant current flowing through the dielectric is associated with quantum mechanical electron tunnelling. Two main gate current mechanisms are associated with this tunnelling current; the direct tunnel (DT) current J_{DT} and the Fowler-Nordheim tunnel (FNT) current J_{FNT} .⁵⁷

For dielectrics with a thickness of approximately 3 nm and below, the DT current must be considered. The DT current becomes dominant in these films at gate voltages (V_G) satisfying the condition $V_G < \phi_B/q$, where ϕ_B is the tunnelling barrier height and q is the electron charge. Electron tunnelling occurs through the entire oxide layer as shown in the energy band diagram of a p-type MOSCAP in Figure 2.17 (a), where tunnelling

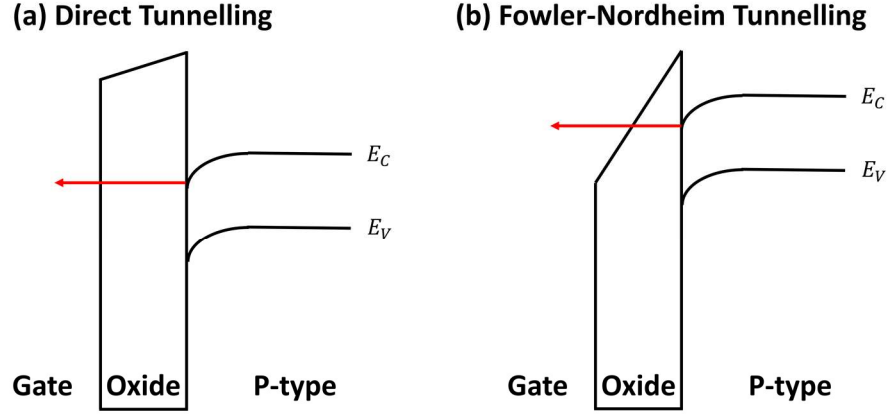


Figure 2.17: Band diagrams for a MOSCAP, showing the case where direct tunnelling (a) and Fowler-Nordheim tunnelling (b) occurs.

electrons do not enter the conduction band of the oxide. Charge carriers ‘see’ the full oxide thickness in the DT current case. The mathematical expression for the DT situation is complex, with several versions existing.⁵⁸ The expression for J_{DT} using the Wentzel-Kramers- Brillouin (WKB) approximation is:⁵⁹

$$\begin{aligned}
 J_{DT} \approx & \left(\frac{q^2}{2\pi h T_{ox}^2} \right) \times \left(\phi_B - V_{ox}/2 \right) \\
 & \times \exp \left(\frac{-4\pi(2qm_{DT})^{\frac{1}{2}} T_{ox} (\phi_B - V_{ox}/2)^{\frac{1}{2}}}{h} \right) \\
 & - \left(\frac{q^2}{2\pi h T_{ox}^2} \right) \\
 & \times \phi_B \exp \left(\frac{-4\pi(2qm_{DT})^{\frac{1}{2}} T_{ox} \phi_B^{\frac{1}{2}}}{h} \right)
 \end{aligned} \tag{2.21}$$

If the gate voltage satisfies $V_G > \phi_B/q$, a FNT current occurs. Unlike DT, FNT currents typically occurs in films of thicknesses above 4 nm and are generally not significant for dielectrics below such a thickness. The energy band diagram for a p-type MOSCAP is visible in Figure 2.17 (b). Charge carriers in the FNT case ‘see’ a triangular barrier. The mathematical expression for FNT current is,⁶⁰

$$J_{FNT} = \left(\frac{q^3 V_{OX}^2}{8\pi h \phi_B T_{OX}^2} \right) \times \exp \left(\frac{-8\pi (2m_{FNT})^{\frac{1}{2}} \phi_B^{\frac{3}{2}} T_{OX}}{3hqV_{OX}} \right) \quad (2.22)$$

Where h is Planck's constant, T_{ox} is the thickness of the metal oxide, and V_{OX} is the oxide voltage. The terms m_{DT} and m_{FNT} are the tunnelling electron effective mass associated with DT or FNT current, respectively.⁶¹

2.7.2.2 Weibull Statistics

Testing identical devices with electrical measurements, such as IV sweeps, will reveal a range of breakdown voltages. To quantify this spread of results, the Weibull distribution is commonly employed in the electrical characterisation of dielectrics.^{62,63} This statistical distribution function employs a 'weakest link process', and is particularly suited for reliability analysis of dielectric breakdown, where failure tends to be dominated by the weakest point in the dielectric – localised regions that degrade and cause the entire system to fail.⁶⁴

For current voltage sweeping, the Weibull distribution for V_B is expressed as;

$$F(V_B) = 1 - \exp \left[- \left(\frac{V_B - \gamma}{\eta} \right)^\beta \right] \quad (2.23)$$

With β representing the shape parameter or Weibull slope, and η representing the scale parameter or 63% value, which is the voltage value when 63% of the sample set have undergone dielectric breakdown. The γ value is the delay or burn-in time, usually 0 in most experiments.

Taking the natural log of both sides, and assuming $\gamma = 0$, equation (2.28) can be expressed as;

$$\ln[-\ln(1 - F(V_B))] = \beta \ln(V_B) - \beta \ln(\eta) \quad (2.24)$$

A plot of $\ln[-\ln(1 - F(V_B))]$ versus $\ln(V_B)$ would therefore provide a straight-line graph where β is the slope. Similarly, the V_B value at the y-intercept represents η , the voltage at which 63% of the devices will have failed.

The cumulative distribution function (V_B) in equation (2.24) is estimated by firstly sorting the measured breakdowns from smallest to largest, followed by the application of a ranking algorithm. In this work, a median ranking was employed, through the use of the Benard approximation;

$$F(i) = \frac{i - 0.3}{n + 0.4} \quad (2.25)$$

Where i is the failed device number and n is the total number of tested devices.⁶⁵

The Weibull distribution is a useful analysis method for dielectric breakdown, not only supplying a statistically informed V_B (and hence E_B) that considers weakest link processes, but also providing an outlook into the reliability of the device. A low β value indicates a device with a wide range of V_B values, whereas a high β suggests a more reliable device with a narrower expected breakdown range.^{61,66}

2.7.3 Capacitance – Voltage Sweeps

2.7.3.1 Theoretical Basics

Measuring the capacitance of a MOSCAP device provides a direct assessment of an oxide film quality for the integration into MOSFET devices. It was discussed in chapter 1 that a fundamental operating principle of a MOSFET is the capacitor-like behaviour between the metal electrode and semiconductor region. When a bias is applied to the gate of the device, the capacitance effect results in current flow between the drain and source. Equation 1.1 showed that this capacitance can be increased by decreasing the thickness of the oxide in the MOSFET – which can create issues of leakage current due to electron tunnelling, or by selecting materials of a higher k value.

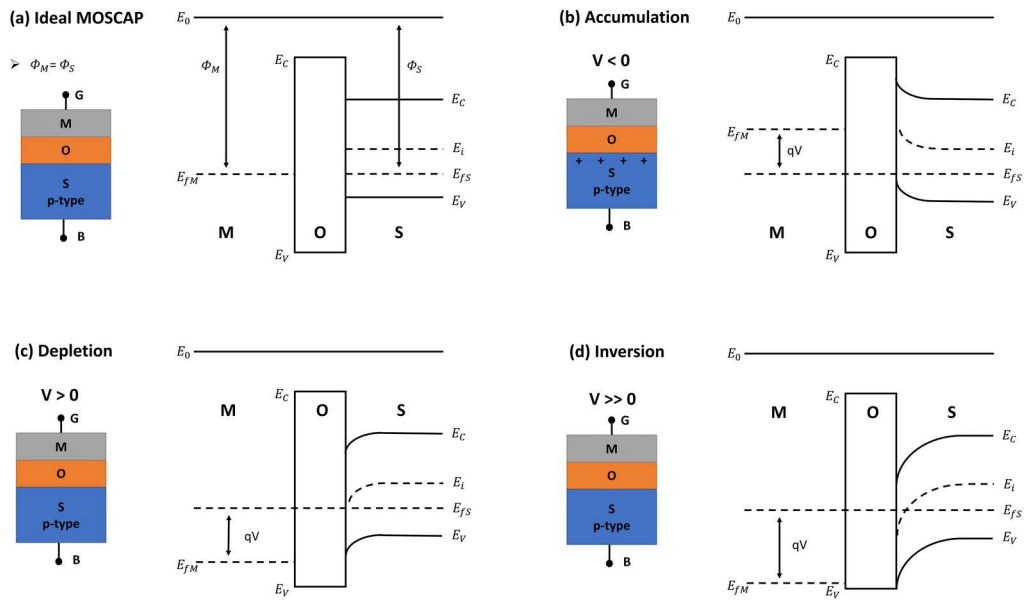


Figure 2.18: Band energy diagrams for an ideal p-type MOSCAP. The non biasing case is shown in (a). Accumulation, depletion and inversion are shown in figure (b – c) respectively.

The MOSCAP CV measurements involve the connecting of the gate and base of the structure to a capacitance meter, with the resulting voltage sweep across the accumulation, depletion and inversion regions of the structure. The band energy diagrams of a p-type MOSCAP for each condition are shown in Figure 2.18.

The ideal case for a p-type MOSCAP under zero bias is shown in Figure 2.18 (a). It is assumed that the work function of the metal (Φ_M) and the semiconductor (Φ_S) are equal. As the semiconductor is p-type, the Fermi level of the semiconductor (E_{fs}) lies below the intrinsic level (E_i).

Once a negative bias is applied to the gate of the p-type MOSCAP, the device is operating in accumulation mode, shown in Figure 2.18 (b). The negative biasing on the gate causes the metal's Fermi level to increase, and results in the accumulation of holes in the p-type semiconductor to accumulate near the semiconductor – oxide interface. This effectively causes the semiconductor near the oxide interface to become more doped with holes, and resultant band bending occurs in the band energy diagram to reflect this.

If the voltage is now increased, the MOSCAP will enter the depletion stage as is observed in Figure 2.18 (c). A positive bias will also impact the shifting of the metal's Fermi level, but in the opposite direction. This causes a reverse effect within the semiconductor near the oxide interface – less holes are located in this region due to the abundance of positive charge from the metal region. This creates a larger depletion zone in the semiconductor device, as electrons drawn towards the semiconductor – oxide interface are countered by the holes in the p-type device.

Figure 2.18 (d) shows the outcome of a further increase in positive biasing to the gate region. Band bending caused from the positive charge on the metal has become so extreme that there now is a region where the semiconductor's intrinsic level lies below its Fermi level. Significant amounts of electrons are now present at the semiconductor – oxide interface, with the new electrons no longer depleting the p-type semiconductor more deeply, but becoming mobile near the interface. This effectively creates a n-type semiconductor near the oxide interface, known as the N-channel and represents when current can flow between source and drain in a p-type MOSFET.

2.7.3.2 Analysis of CV Data

The CV data in this work was obtained through the use of an AC impedance meter (LCR meter), which allows for the acquisition of CV sweeps at a range of frequencies (typically in the range of kHz – MHz). AC impedance is measured by applying an AC voltage across a device and measuring the resultant current and voltage across the device.⁶⁷ The capacitance is dependent on the change of charge due to the change in voltage:

$$C = \frac{dq}{dV} \quad (2.26)$$

To understand the resultant CV plot, the charge distributions for the accumulation, depletion and inversion regions are drawn up in Figure 2.19. The AC voltage results in a charge variation in the device, causing a rise in capacitance. In accumulation mode, there is a build-up of negative and positive charge at the metal-oxide and semiconductor-oxide interface respectively, where the total capacitance (C) is only dependent upon the insulating oxide (C_{ox}):

$$C = C_{ox} \quad (2.27)$$

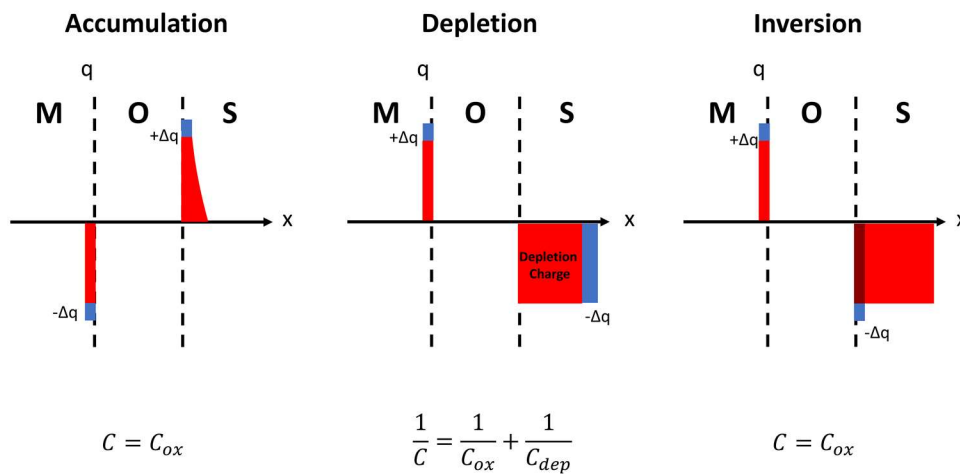


Figure 2.19: Charge distribution for a p-type MOSCAP under accumulation depletion and inversion conditions.

In depletion mode, the creation of a depletion zone in the semiconductor creates a scenario where there are two capacitors in series, one dependent on the oxide as in accumulation mode (C_{ox}), and the other dependent on the capacitance arising from the depletion region (C_{dep}):

$$\frac{1}{C} = \frac{1}{C_{ox}} + \frac{1}{C_{dep}} \quad (2.28)$$

As discussed from Figure 2.18, inversion mode occurs when there is an abundance of mobile charge carriers (electrons for p-type) in the semiconductor near the semiconductor – oxide interface, meaning the capacitance across the device is now only dependent on C_{ox} as in accumulation.

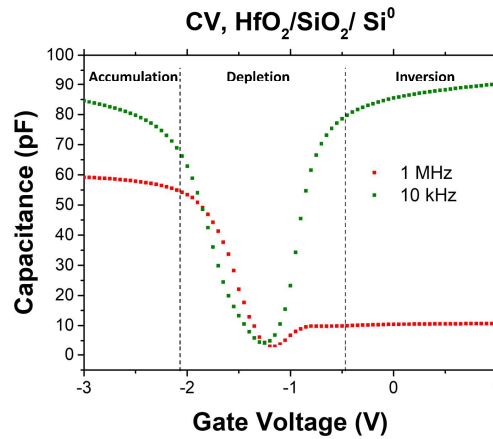


Figure 2.20: Sample CV plot of a p-type MOSCAP for a high (1 MHz) and low (10 kHz) frequency condition.

An example of a CV plot that incorporate accumulation, depletion and inversion regions for a p-type MOSCAP is shown in Figure 2.20. In accumulation mode, capacitance is stable in accordance with equation (2.27). In the depletion mode, a drop off in total capacitance is observed with increasing voltage. This increase in voltage increases the depletion region of the p-type semiconductor, reducing the value of C_{dep} and resulting in an overall reduction in capacitance across the MOSCAP as equation (2.28) implies.

At low frequency measurements, the capacitance value for the inversion region of the plot is expected to be equal to the capacitance in accumulation. This condition does not hold true for high frequency measurements, where the inversion charge is unable to follow the applied AC voltage. Electron hole pairs are not generated fast enough for the semiconductor charge to match the gate charge, resulting in lower values of inversion capacitance compared to the value obtained in accumulation.⁵⁸ It should be noted that, as is typical for CV measurements in literature, a frequency range of 1 MHz – 1 kHz was used for this work. High frequency CV measurements can lead to a reduction in measured capacitance and a decrease in the capacitive reactance, as the MOSCAP behaves more like a conductor (this effect can be seen in Figure 2.20, where a lower capacitance reading is observed in the accumulation region for the higher frequency measurement). Lower frequency measurements however lead to an increase in the capacitive reactance, with the MOSCAP behaving more like a resistor.

Considerable amounts of this work targeted the fabrication of high- k materials from the polymer infiltration approach, with the measurement of the dielectric constant for the processed metal oxides desired. Calculation of the dielectric constant was obtained by measuring C_{ox} , based on equation 1.1 from chapter 1;⁶⁸

$$C_{ox} = \frac{\epsilon_0 k_{ox} A}{t_{ox}} \quad (2.29)$$

Due to the sample preparation requirements, most MOSCAP structures consisted of a SiO₂ interlayer between the silicon and metal oxide, resulting in C_{ox} representing two capacitors in series;

$$\frac{1}{C_{ox}} = \frac{1}{C_{SiO_2}} + \frac{1}{C_{MO}} \quad (2.30)$$

Where C_{SiO_2} is the capacitance arising from the SiO₂ interlayer (calculated using theoretical values), and C_{MO} is the capacitance of the metal oxide.

2.7.3.2.1 Non ideal behaviour

Up to this point, all CV measurements described are concerning an ideal MOSCAP, with the following assumptions:

Band bending does not occur under zero bias conditions, such that $\Phi_M = \Phi_S$. This assumption led to the idealised energy band diagram for Figure 2.18 (a). The flatband condition, where no band bending takes place at the semiconductor – oxide interface, occurs at a bias of 0 V for an ideal MOSCAP, due to the identical work functions of the semiconductor and metal. In practice, work function differences between the metal and semiconductor can exist, resulting in the occurrence of band bending even before a bias is applied. To allow for the alignment of bands and thus reach a flatband condition for a non-idealised case, a flatband voltage (V_{FB}) must be applied that is equal to the difference between the metal and semiconductor work functions:

$$V_{FB} = \Phi_{MS} = \Phi_M - \Phi_S \quad (2.31)$$

No charges present in the oxide. In a non-idealised case, four types of oxide charges are found in the oxide layer;

- i. *Interface trapped charge (D_{it})* are positive or negative charges that occur from defects such as structural, oxidation induced or metal impurities. Such charges can be neutralised by annealing the device ($>400^\circ\text{C}$) in a H_2 environment.⁶⁹
- ii. *Fixed oxide charge (Q_f)* is a positive charge that occurs near the semiconductor – oxide interface, and is dependent on the growth process of the oxide, such as oxidation ambient and temperature, cooling conditions, and crystal orientation. High oxidation temperatures can reduce the amount of fixed oxide charge, with annealing in an Ar or N_2 ambient after oxidation also possible if high oxidation temperatures are not desired.⁵⁸

- iii. *Oxide trapped charge* (Q_{ot}) arises from holes and electrons trapped within the oxide and like interface trapped charges, may be removed through annealing in a H_2 environment.
- iv. *Mobile oxide charges* (Q_m) ionic impurities such as Na^+ , Li^+ , or K^+ that can occur during the fabrication process.

The latter three charges do not vary with applied gate bias, meaning, the *effective oxide charge* (Q_{eff}) be expressed as a summation of the three:

$$Q_{eff} = Q_f + Q_{ot} + Q_m \quad (2.32)$$

The presence of charge also effects the V_{FB} , meaning, in the presence of charge, equation (2.31) becomes:

$$V_{FB} = \frac{Q_{eff} + D_{it}}{C_{ox}} + \Phi_{MS} \quad (2.33)$$

Where D_{it} represents the interface charge density at the flatband voltage condition. The $Q_{eff}/C_{ox} + \Phi_{MS}$ term of the equation are an additive constant to the flatband voltage, causing a parallel shift in the CV curve to be observed. The D_{it}/C_{ox} term causes changes to the CV distribution, although this is not a simplistic parallel shift as Q_{it} changes with applied voltage.⁷⁰

The effect of charge in the oxide can be visible in CV plots by applying a voltage sweep across the device followed by an immediate secondary sweep in the reverse direction. This is often referred to as the ‘trace’ and ‘retrace’ of the CV plot, respectively. During the first sweep, charges within the oxide are either pushed towards or away from the semiconductor – oxide interface. The second sweep (retrace) then pushes the charges in the opposite direction to the first. This effect causes a difference in the V_{FB} for the trace and retrace, as Figure 2.21 represents.

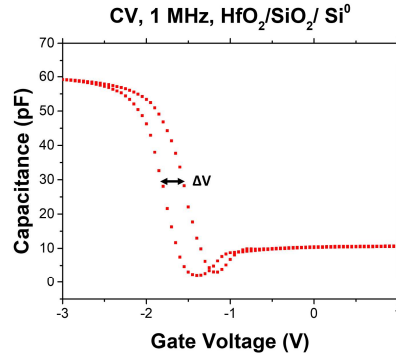


Figure 2.21: Example plot of a typical CV sweep. Sweeping voltage from positive to negative (trace) and then back (retrace) reveals a hysteresis in the voltage (ΔV), which can be related to charges occurring within the MOSCAP structure.

Exact determination of charge distribution in MOSCAPs is complex, and the CV analysis contained in this body of work uses the simplified equation for the determination of the density of trapped oxide charge (N_{OT} , in cm^{-2}):

$$N_{OT} = \frac{C_{ox}\Delta V}{qA} \quad (2.34)$$

Where ΔV is the voltage hysteresis, taken at the flat-band capacitance (C_{FB}) or at half the maximum capacitance in accumulation ($C_{ox}/2$), q is the electron charge and A is the electrode area.^{71,72}

2.8 Polymer Brush Fabrication

The research presented in this work exclusively focuses on studying the process of metal/metal oxide production through the infiltration of covalently grafted polymer brushes, which have the potential to be integrated into patterning applications through ASD and BCP type processes.

The fabrication process for these brushes was based upon the work of our collaborators R. Lundy et al.⁷³ Polymer powders with a hydroxyl (-OH) termination were purchased from Polymer Source Inc. Canada and used as received. This specific termination was required for attachment to corresponding, -OH terminated silicon substrates. As discussed in chapter 1 (section 1.2.3) however, the end termination of the polymer material can be altered for attachment to a variety of surfaces.

The initial step involved dissolving the polymer powder into a solution by stirring overnight at room temperature. The chosen solvent was dependent on the polymer powder used. Determining whether a solution will dissolve the chosen polymer powder was achieved through the Hansen solubility approach to obtain a χ value;⁷⁴

$$\chi_{AB} = \frac{V_s}{4RT} \left[4(\partial_{d,A} - \partial_{d,B})^2 + (\partial_{p,A} - \partial_{p,B})^2 + (\partial_{h,A} - \partial_{h,B})^2 \right] \quad (2.35)$$

Where V_s is the molecular volume, R is the gas constant, T is the temperature. ∂_d , ∂_p and ∂_h represent the nonspecific dispersive, specific polar and specific hydrogen interactions respectively.

This solution was then spin-coated at 3000 rpm for 30 s onto the -OH terminated silicon wafers. The blanket silicon with native oxide was provided by our collaborators at Intel. Preparation for polymer spin coating involved the cleaving and resultant washing of the silicon through ultrasonication in isopropyl alcohol (IPA) for a minimum of 15 minutes. The silicon surface was then -OH terminated via piranha⁷⁵ or O_2 plasma treatment. Both

techniques have unique trade-offs that must be considered for the end application – piranha treatment requires extreme caution (corrosive and explosive risks) and is time consuming, while the O_2 plasma process results in the growth of a SiO_2 interlayer that is thicker than the native oxide layer of < 1 nm.

Immediately after spin-coating, the samples were annealed for covalent grafting onto the silicon via condensation reactions.⁷⁶ Samples were then placed into a solvent (of the same type that was used to dissolve the powder) and ultrasonicated for 10 minutes. This step was repeated at least once, with the purpose of removing physisorbed ungrafted polymer material. A graphical representation of the process is shown in Figure 2.22.

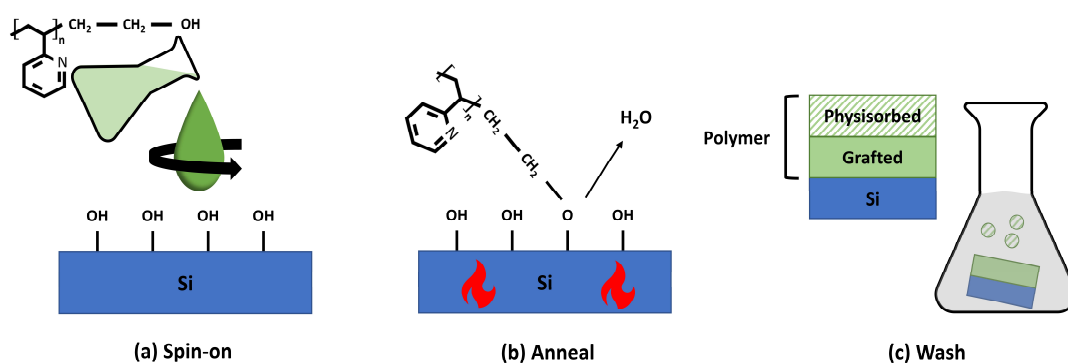


Figure 2.22: Schematic overview of the polymer brush fabrication process as developed by R. Lundy *et al.*⁷³ A solution containing a dissolved polymer is spin-coated onto a functionalised substrate. A subsequent anneal (b) produces a polymer film consisting of grafted and ungrafted material. This physisorbed part of the film is removed by ultrasonication washing.

Referred as the *grafting-to* method, this process was observed to produce highly coherent and uniform polymer films, with careful optimisation that saw the annealing time/polymer grafting reduced to seconds (cutting the entire process time to under 30 minutes).⁷⁷ The rapid aspect of the approach gives the grafting-to method a unique advantage over SAMs – where fabrication time typically lasts at least several hours.⁷⁸

2.9 References

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3 Characterising Liquid Phase Metal Infiltration into Polymer Brushes

3.1 Introduction

This chapter presents the results of a HAXPES study on the creation of metallic copper layers via metal-salt infiltration into a P2VP polymer film. Metal salt inclusion is a wet chemistry, liquid phase process which allows for the fabrication of both metal and metal oxide films. This is achieved by infiltrating a receptive polymer through exposure to a liquid containing metal salt precursors.

Prior to examining the infiltrated polymer brushes, a P2VP brush film was assessed to understand the quality and characteristics of the film fabricated via the grafting-to method as described in chapter 2 section 2.8. This was achieved through GA-FTIR, TEM, EDX and AFM measurements.

As discussed in chapter 1, P2VP is an attractive polymer for ASD and BCP integration, and proof of its capability in a liquid phase infiltration process is a desirable objective. A copper infiltrated P2VP film was subject to UV/Ozone treatment to form copper oxide and annealed in-vacuum to reduce the film to metallic copper. HAXPES and TEM measurements were used to study the polymer film before and after metal salt infiltration, along with analysis of the copper oxide created after UV/Ozone treatment. The results show successful infiltration of the metal salt into the polymer film, as well as complete conversion to copper oxide following UV/Ozone treatment and reduction to metallic copper with a subsequent in situ anneal, which demonstrates the ability of the technique for the creation of several key integrated circuit features.^{1,2}

3.2 Experimental Details

3.2.1 Polymer Brush Fabrication

P2VP-OH – $M_w = 6.2 \text{ kg mol}^{-1}$, polydispersity index (PDI) = 1.05 – was dissolved in tetrahydrofuran (THF, inhibitor-free, CHROMASOLV Plus, for HPLC, $\geq 99.9\%$) to form a 0.2 wt% solution. Polymer brushes covalently grafted to piranha treated silicon were prepared as outlined in section 2.8, with a 30 minute 190°C anneal implemented for polymer grafting.

3.2.2 Liquid Phase Infiltration

Copper(II) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, 99.999%) was purchased from Sigma Aldrich and dissolved in ethanol (anhydrous, for HPLC $\geq 99.9\%$) to form a 0.5 wt% solution. The solution was spin-coated at 3000 rpm for 30 s onto polymer films to attain metal – polymer interaction.

Polymer removal and simultaneous copper oxidation was performed by exposing the samples to UV/Ozone for 3 hours using a Novascan PDSP-UV4.

3.2.3 Characterisation

HAXPES analysis was performed at SOLEIL Synchrotron at the Galaxies Beamline.³ Spectra were acquired at pressures of 1×10^{-9} mbar with photon beam energies of 3 keV and 10 keV, which allows for probing of deep core levels of all elements present, as well as the acquisition of more bulk sensitive (10 keV) and more surface sensitive (3 keV) spectra. Si(1 1 1) and Si(3 3 3) monochromators were used for the 3 keV and 10 keV beams respectively. The effect of an in situ anneal on both infiltrated salt and UV/Ozone treated polymer samples was also investigated. All anneals were performed at a

temperature of 400 °C for 30 min in the preparation chamber (adjacent to the analysis chamber) with a base pressure of 1×10^{-9} mbar.

All peak fitting analysis of the HAXPES spectra was performed using the AAnalyzer software.⁴ The spectra were fitted by using a Voigt function, and the Gaussian and Lorentzian values for each core level are tabulated in Table 3.1. Each core level was assigned a single Gaussian and Lorentzian value for all its components, with the exceptions being one component in the O 1s and several components in the Cu core levels, due to significant differences in the chemical environment. Shirley-type and slope backgrounds were used for all the core levels, with the exception of the Cu 2p, where a static Shirley background was implemented. The spectra were not normalised, however an offset was applied so that the background of each photoemission plot occurred at 0 intensity (counts).

Table 3.1: Gaussian and Lorentzian values used for the fits determined via AAnalyzer.

Core Level	Chemical	$h\nu$	Spin Orbit	Gaussian	Lorentzian	Binding
Peak	Environment	(eV)	Splitting (eV)	(eV)	(eV)	Energy (eV)
Si 2p	Bulk	3000	0.6	-	-	99.4
C 1s	Pyridine	3000	-	1.04	0.2	285.7
N 1s	Pyridine	3000	-	1.13	0.51	399.8
O 1s	P2VP/SiO ₂	3000	-	1.13	0.25	532.6
O 1s	Cu ⁰	3000	-	0.58	0.25	530.2
Cu 2p	Cu ⁺²	3000	19.7	1.28	0.05	934.5
Cu 2p	Cu ⁺¹	3000	19.7	1.28	0.05	933.4
Cu 2p	Cu ⁰	3000	19.7	0.84	0.05	932.4

Cu 1s	Cu ⁺²	10000	-	2.58	1.04	8982.4
Cu 1s	Cu ⁺¹	10000	-	1.46	1.04	8981.1
Cu 1s	Cu ⁰	10000	-	1.48	1.04	8979.9
Al 1s	Al _x O _y	3000	-	1.32	0.33	1559.6

Sample preparation for the TEM was performed in a FEI Helios Nanolab 450 S. Substrates were imaged to locate a clean, defect free area. This area was subsequently platinum capped. Pt was deposited via a gas injection system (GIS) technique. Low accelerating voltage was used to construct a protective layer, initially a 500 V electron beam was used to deposit Pt, thereafter a 2 kV and finally a 30 kV ion beam. Cross section lamella was lifted out using standard focused ion beam procedures. This lamella was platinum welded to the molybdenum grid and stored in a vacuum sample holder prior to TEM imaging. TEM imaging was performed in a FEI OSIRIS TEM. All imaging was performed at 200 kV.

Both bright field and scanning transmission electron microscope (STEM) modes were used. For STEM imaging, detector lengths of 220, 550 and 770 mm were used. EDX mapping was used to perform elemental analysis of samples. All EDX maps were acquired during a sampling duration of 20 min.

GA-FTIR spectroscopy was performed using a Harrick VariGATR accessory on a Nicolet iS50 spectrometer (unpolarized, angle of incidence is 65°, 32 scans, resolution 8 cm⁻¹). AFM was used to analyse the P2VP-OH surface roughness on a Bruker Dimension 3100 AFM.

3.2.4 Acknowledgements

GA-FTIR data acquisition was obtained by Mr. Mark Croke and Dr. David James from Thermo Fisher Scientific, with the analysis performed by Ms. Clara Zehe.

3.3 Results

3.3.1 Surface & Interface Characterisation of Poly(2-vinylpyridine) Brushes

GA-FTIR spectroscopy allowed the acquisition of IR spectra even from the ultrathin P2VP-OH film used in this work, after subtracting the silicon background signal. The resulting spectrum is shown in Figure 3.1 (a). The bands at 2927 and 2854 cm^{-1} correspond to the vibrational mode of the aliphatic polymer backbone. Deformations in the free backbone lead to the signals at 1473 and 1436 cm^{-1} . The stretching modes of the pyridine ring are located at 1592 and 1570 cm^{-1} with an additional ring deformation band at 987 cm^{-1} .⁵ The feature at 787 cm^{-1} corresponds to out-of-plane deformations of the hydrogen atoms of the pyridine ring. It is shifted to slightly higher frequencies compared to 1,2-substituted aromatic rings due to the higher electronegativity of the nitrogen atom. The signals at 1233 and 1153 cm^{-1} correspond to C—O—C and C—OH vibrations, respectively, resulting from the terminating hydroxy groups of the polymer. These data

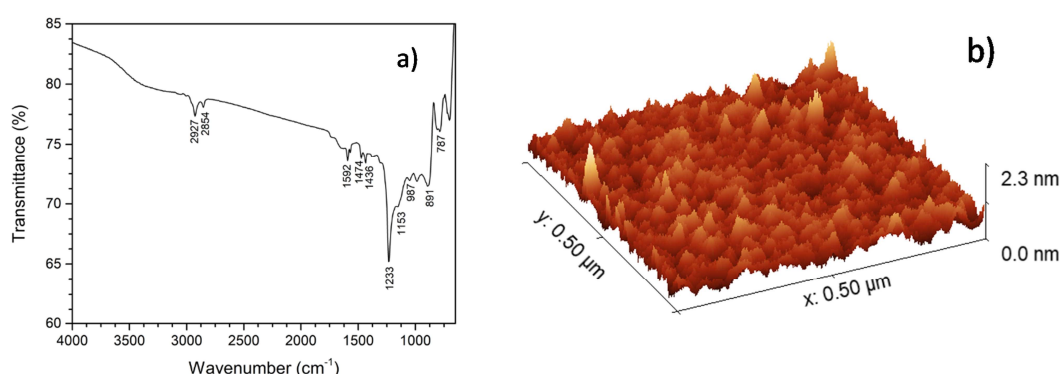


Figure 3.1: (a) Grazing-angle ATR IR spectrum of a thin P2VP film. (b) AFM 3D height image of P2VP surface.

indicate that partial condensation of the hydroxy group with the hydroxy functionalized silicon substrate may occur during film deposition. This hypothesis agrees with the observation of a visible band at 891 cm^{-1} corresponding to a Si—C bond vibration.⁶

AFM measurements were also performed on the analysed P2VP-OH samples to assess the physical surface profile of the spun-on polymer film, with a 3D height image shown in Figure 3.1 (b). The average root-mean-square surface roughness of the P2VP-OH according to AFM analysis was approximately 0.21 nm, which indicates the presence of a very smooth film that is similar to values obtained for the Si substrate.

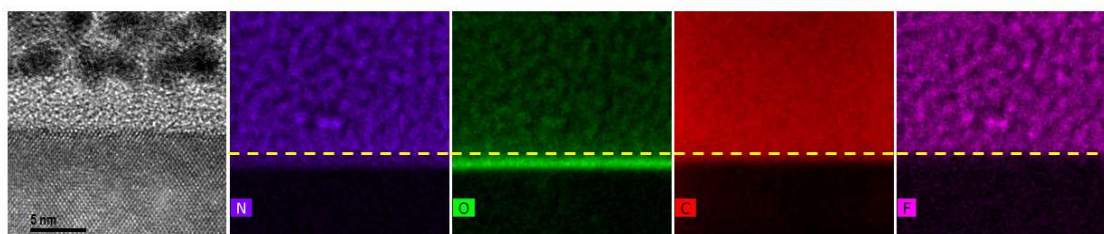


Figure 3.2: TEM and EDX cross sectional images of a P2VP brush film. From left to right: TEM image highlighting a film of 5 nm in thickness above the silicon bulk, nitrogen, oxygen, carbon and fluorine EDX images. The EDX confirms that the constituents of P2VP (carbon and nitrogen) are present in a thin layer on top of silicon. The yellow line indicates where the polymer ends and the platinum resist begins. This was observed by detecting fluorine in the resist.

TEM and EDX cross section images of the polymer films are shown in Figure 3.2. The TEM imaging reveals the presence of an approximately 5 nm film on top of the silicon bulk. It is assumed that this measurement encompasses both the SiO₂ and P2VP film, however, as the SiO₂ is native, the P2VP film is expected to account for ≥ 4 nm of the film. The presence of carbon and nitrogen in this film – the main components of the P2VP film – is confirmed through EDX. These results complement the GA-FTIR and AFM results in that the P2VP brush has grafted to the silicon surface and is uniform across the surface.

3.3.2 Hard X-ray photoelectron spectroscopy study of copper formation by metal salt inclusion in a polymer film

3.3.2.1 P2VP film

Wide energy range survey scans of the P2VP thin films were undertaken using a photon beam energy of 3 keV, and C *1s*, N *1s*, O *1s* and Si *2p* signals were acquired. Figure 3.3 (a) shows the Si *2p* signal for all experimental steps, which consists of two photoemission components separated by a binding energy of 3.9 eV.

The lower binding energy component represents Si⁰ (silicon bulk), while the higher binding energy peak represents Si⁴⁺ (SiO₂), attributed to the native silicon oxide substrate onto which the polymer was grafted.⁷ All spectra were adjusted for charging such that the position of the 2*p*_{3/2} bulk component was fixed at 99.4 eV.^{8,9} This compensation was applied to all core levels in this work.

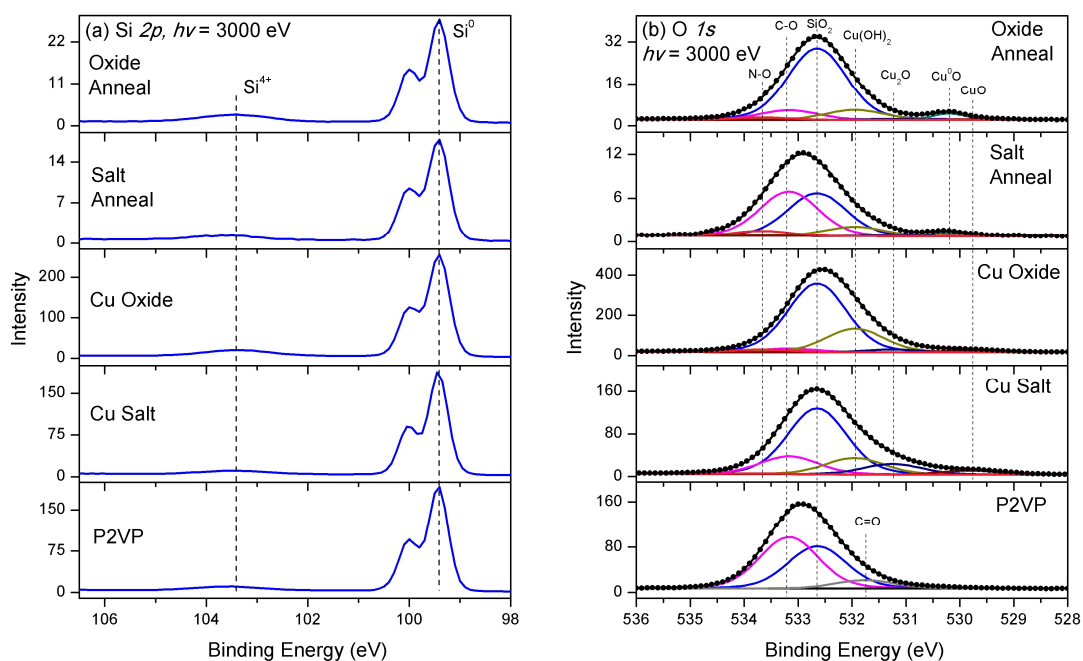


Figure 3.3: (a) Si *2p* peak data at $h\nu = 3$ keV for all the experimental steps. The data has been shifted so that the bulk signal occurs at 99.4 eV. The composition of each peak remains unchanged throughout all the samples analysed, however the counts are reduced significantly after both anneal steps (associated with the formation of metallic copper). (b) Fit of the O *1s* peak for all the experimental steps. A significant shoulder develops on the spectra at the lower binding energies after the infiltration step, attributed to the copper oxide components.

The signal is dominated by the Si bulk signal due to the large sampling depth of the 3 keV photon beam, however SiO₂ is evident clearly at 103.3 eV. There is also evidence of low concentrations of Si³⁺, Si²⁺ and Si¹⁺ signals in the spectra, representing sub-stoichiometric silicon oxides at the interface between the oxide and the silicon bulk and where the polymer grafts to the SiO₂ layer.

The O 1s in Figure 3.3 (b) for the P2VP is dominated by C-O and SiO₂ bonds, occurring at 533.2 eV and 532.6 eV, respectively.¹⁰⁻¹³ The minor peak at 531.8 eV resembles carbon oxygen bonds arising from atmosphere exposure.

The C 1s spectra for each experimental step ($h\nu = 3$ keV) are shown in Figure 3.4 (a). The P2VP signal contains C-C bonds at 285.0 eV,¹⁴⁻¹⁶ which are associated with the carbon chain in the polymer. The peak at 285.7 eV represents a combination of all carbon signals present in the pyridine ring.^{17,18} The C 1s signal for the P2VP is dominated by this (C-Pyridine) component. The peaks at 286.5 eV and 287.6 eV are associated with C-O and C=O bonds respectively, while the final peak at 288.7 eV is attributed to carboxyl groups (O-C=O), based on reports in the literature.^{14,16,19} The C-O bonds are attributed to the interface where the polymer bonds to the SiO₂, as well as contributions from the top surface oxidation due to atmosphere exposure. The other O components in the spectra (C=O and O-C=O) can also be attributed to this top layer.

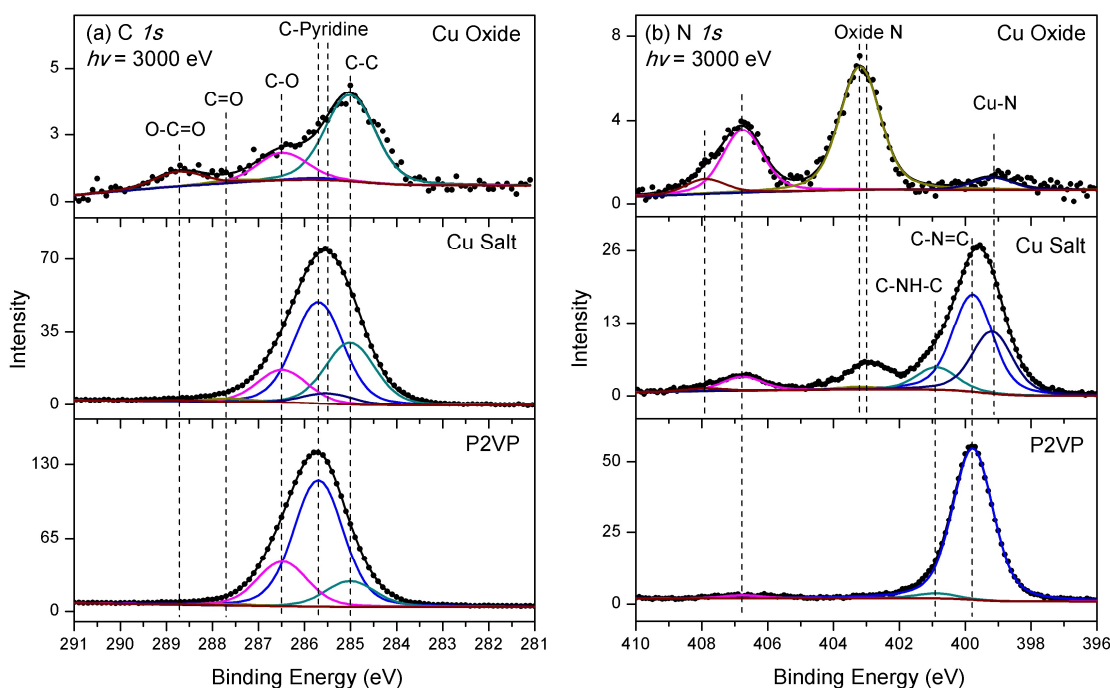


Figure 3.4: (a) C 1s core level fit for the polymer pre and post infiltration. C-Pyridine bonds dominate the P2VP, while being almost completely removed after the oxidation step. (b) Fit of the N 1s peak for the polymer, salt and copper oxide. A lower binding energy component is attributed to Cu interaction with the pyridinic N after the infiltration step. A small signal attributed to oxidised nitrogen is the only significant remainder of the element after the UV/Ozone treatment. Physiosorbed nitrogen is also evident with the addition of a higher binding energy component.

Figure 3.4 (b) shows the spectra and fit of the N 1s for the polymer pre- and post-infiltration as well as post-UV/Ozone treatment. For the as-deposited P2VP, three component peaks are apparent, with the major component located at 399.8 eV. However trace signals are also found at 400.9 eV and 406.8 eV. The peak at 399.8 eV is attributed to pyridinic (C-N=C) nitrogen, while the component at 400.9 eV can be attributed to C-NH-C bonds (pyrrolic nitrogen),^{20,21} or alternatively, represent the protonation of pyridinic nitrogen. This is discussed in further detail in chapter 4. The small component at 406.8 eV is associated with physiosorbed nitrogen.

3.3.2.2 *P2VP post liquid salt exposure*

HAXPES survey scans of the 'Cu salt' samples reveal peaks associated with Cu in addition to the polymer and Si components, indicating that the process has incorporated Cu into the polymer (the presence of Cu is also confirmed by EDX analysis). Spectra for the infiltrated polymer samples were acquired at $h\nu = 3$ keV. The Cu 1s spectrum was also obtained, using a photon beam energy of 10 keV, however caution must be applied for the fits of the Cu 1s due to lack of literature references, and the spectra is meant for comparative purposes only.

When compared to the P2VP sample, the Si 2p spectrum in Figure 3.3 (a) for the Cu salt sample reveals little has changed in the profile of the peak, showing that the Cu salt has not chemically interacted with the silicon substrate or native oxide layer.

The O 1s spectrum in Figure 3.3 (b) undergoes a significant change in profile after the infiltration step, which is explained by the addition of peak components attributed to oxidised copper bonds, with Cu(OH)₂, Cu₂O and CuO identified at 531.9 eV, 531.2 eV and 529.8 eV respectively, similar to what has been reported by Biesinger and others.^{22,23} SiO₂ is the most prominent component, with the surface C-O bonds decreasing in intensity due to the introduction of the metal salt.

Once the infiltration step has been completed, the profile of the C 1s in Figure 3.4 (a) undergoes some changes. The peak maximum experiences a shift, resulting from the addition of a component at 285.5 eV, 0.2eV lower in binding energy when compared to the C-pyridine peak at 285.7 eV. This suggests a strong interaction between the infiltrated Cu and the pyridine ring is occurring.

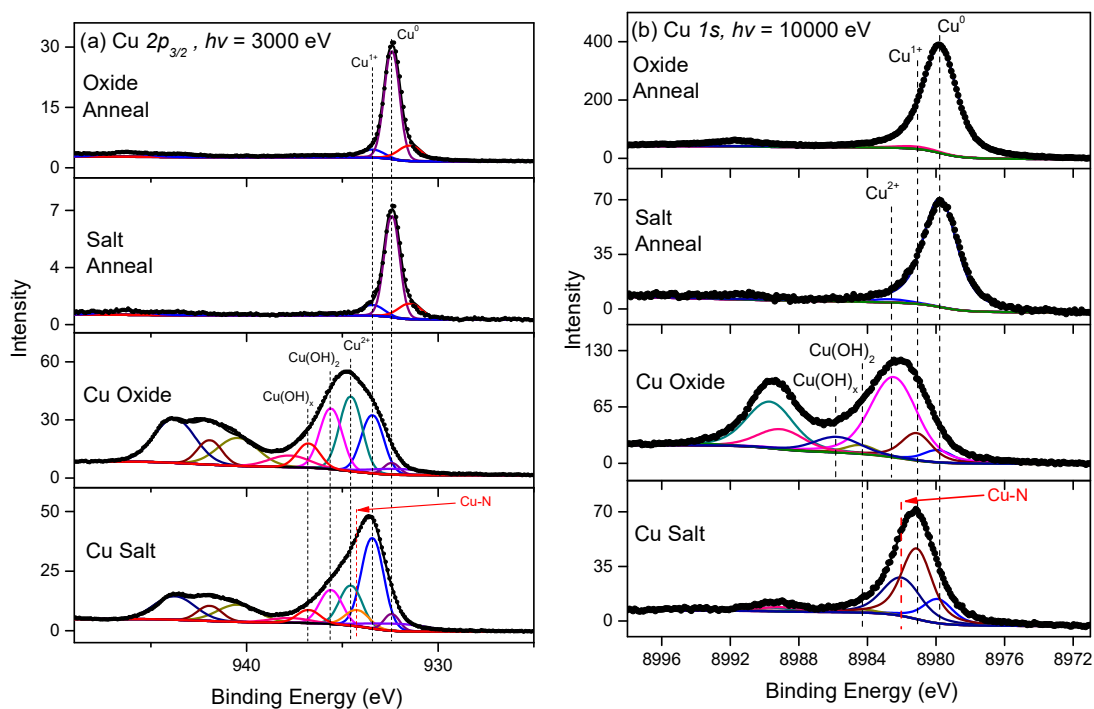


Figure 3.5: (a) HAXPES spectra of Cu $2p_{3/2}$, $h\nu = 3$ keV. The spectra for the infiltrated salt sample shows a strong Cu^{1+} contribution, while the subsequent UV/Ozone treatment results in Cu^{2+} becoming the most significant component. Annealing both these samples results in the formation of a film dominated by a metallic Cu^0 contribution. The metallic signal is significantly stronger on the annealed, UV/Ozone sample. (b) XPS spectra of Cu $1s$, $h\nu = 10$ keV, which are broadly consistent with the Cu $2p_{3/2}$ data in (a). The intensities of the spectra are not normalised to any reference, however an offset has been applied so that the background of each plot occurs at 0 intensity.

The infiltration step causes a shift in the maximum peak position of the N $1s$ signal in Figure 3.4 (b). This is caused by a new component in the peak profile at a lower binding energy than the pyridinic N. This peak is attributed to Cu-N bonds, and it is centred around 399.2eV, at a binding energy of 0.6 eV lower than the C-N=C bonds.²⁴⁻²⁶ A small peak located at 403.2eV is assigned to oxidised nitrogen.^{21,27} This is attributed to the nitrate salt used during the spin-on process.

The Cu $2p_{3/2}$ spectra can be deconvoluted into its constituent components as shown in Figure 3.5 (a). The salt-infiltrated sample has major components at 933.4, 934.5, 935.6 and 934.2 eV, with the first three representing Cu^{1+} , Cu^{2+} , $\text{Cu}(\text{OH})_2$ respectively,²² while the latter is attributed to Cu-N bonds. A sub oxide component $\text{Cu}(\text{OH})_x$ attributed to the environment is located at 936.7 eV, while a component at 932.1 eV was also added to the

fit. Unattributed low binding energy features have been observed in a variety of core levels from XPS analysis,^{28–30} and it is possible that this feature has arisen from surface defects arising from strains in the film.^{31,32} A small peak at 932.4 eV was associated with metallic copper (Cu^0). The components at 937.7, 940.4, 941.9 and 943.7 eV were associated with shake up satellite features for each Cu oxidation state for the Cu 2p.²² Therefore the salt-infiltrated film consists of Cu in a number of oxidation states, including $\text{Cu}(\text{OH})_2$ as well as $\text{Cu}(\text{OH})_x$, with the most prominent being Cu^{1+} .

The Cu 1s spectra, acquired at $h\nu = 10$ keV, and shown in Figure 3.5 (b), is correlated with the Cu 2p fit. Peaks at 8979.9, 8981.1 and 8982.0 eV are attributed to Cu^0 , Cu^{1+} and Cu-N bonds. $\text{Cu}(\text{OH})_2$ can also be seen at 8984.4 eV, while the components at around 8989.5 eV are attributed to satellite features. Consistent with the Cu 2p data in Figure 3.5 (a), the most prominent oxidation state appears to be Cu^{1+} .

EDX mapping data of the infiltrated polymer, shown in Figure 3.6 (a), reveals a thin layer of Cu that resides atop of a layer containing Si and O signals. The proximity that the Cu signal has to the Si_xO_y film demonstrates that the Cu salt has successfully penetrated the P2VP layer.

3.3.2.3 *Effects of UV/Ozone exposure to infiltrated P2VP*

The copper oxide samples (labelled as ‘Cu Oxide’ in the relevant figures) prepared via a three-hour UV/Ozone treatment were analysed in a similar manner to the Cu salt samples, with $h\nu = 3$ keV spectra obtained for the Si 2p, C 1s, N 1s, O 1s and Cu 2p peaks, along with $h\nu = 10$ keV spectra of the Cu 1s. The Si 2p spectrum in Figure 3.3 (a) remains unchanged in profile following the UV/Ozone treatment.

The O 1s spectra in Figure 3.3 (b) for the copper oxide sample is similar to the Cu salt sample, however there is an increase in the intensity of the signal. There is a reduction in

C-O bonds, correlating with the C 1s spectra, while the SiO₂, Cu(OH)₂ and CuO components increase. The oxidation state of the copper changes during the treatment, as there is an increase in CuO and a decrease in Cu₂O after the UV/Ozone treatment, consistent with the Cu peak fit in Figure 3.5 (a) and (b).

The oxidation step reveals a noisy C 1s spectrum in Figure 3.4 (a), with C-C bonds representing the majority of the peak profile. The reduction of the C-pyridine signals correlates with the N 1s spectra in Figure 3.4 (b). C-O bonds remain and are attributed to the surface of the material due to atmosphere exposure. The N 1s spectrum in Figure 3.4 (b) shows that the oxidation step leaves only trace Cu-N bonds, while the oxidised nitrogen peak becomes the most prominent. The C-N=C bonds are no longer visible, indicating that UV/Ozone treatment has successfully removed the P2VP.

The Cu 2p_{3/2} spectrum in Figure 3.5 (a) for the copper oxide sample is similar to the copper salt profile, with a few notable differences. The Cu-N component that was observed in the salt at 934.2 eV is no longer present, consistent with the N 1s spectra. There is also a change in the most prevalent oxidation state of the Cu signal, as the most intense oxidation state of copper transitions from Cu¹⁺ to Cu²⁺, correlating with the O 1s peak. A significant increase in the hydroxyl groups associated with the copper is also noted. It can therefore be concluded that, before the oxidation step, the spun-on copper salt solution exists in the polymer film in a mixed oxidation state, with Cu¹⁺ being the most prominent. After UV/Ozone treatment however, the copper nitrogen bonds are removed, and the overall oxidation of the copper becomes dominated by Cu²⁺ and Cu(OH)₂.

The differences between the salt and oxide samples are even clearer in the Cu 1s spectra, with the major component now being Cu^{2+} instead of Cu^{1+} as discussed above in the Cu 2p spectra, with the increase in $\text{Cu}(\text{OH})_2$ also correlating with the Cu 2p fit. The oxidized Cu signal is significantly more intense here, with the two satellite features also being major components now due to the increase in Cu^{2+} .

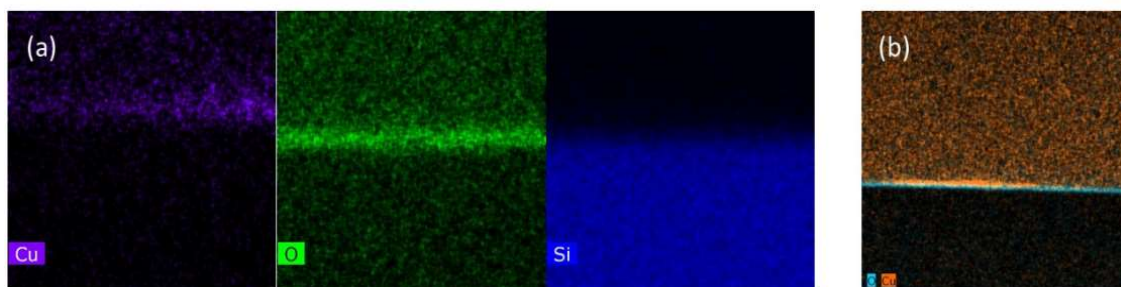


Figure 3.6: (a) EDX mapping data from TEM measurements of the polymer film infiltrated by the Cu salt sample which display evidence of the incorporation of Cu into the film in a thin layer above the SiO_2 . (b) EDX overlaid image of copper and oxygen for the UV/Ozone treated sample. The result shows the successful formation of copper oxide on the surface, however the layer is uneven and not continuous across the surface.

EDX mapping data of the copper oxide sample supports these conclusions from the XPS data, showing a thin layer containing Cu and O on top of a SiO_2 thin layer. The film is incomplete in regions, as shown in Figure 3.6 (b), highlighting the need for further work to perfect the fabrication process to achieve continuous films.

3.3.2.4 Reductive Anneals

It was outlined previously that both the Cu salt and the Cu Oxide samples were annealed at 400°C for 30 minutes (labelled ‘salt anneal’ and ‘oxide anneal’, respectively). The Si 2p spectrum in Figure 3.3 (a) shows a notable drop in signal after the annealing step of both the annealed salt-infiltrated and oxide samples when comparing it to the pre-anneal copper oxide spectrum (as well as the Cu salt and P2VP samples). This is consistent with the formation of Cu^0 and the associated reduction in the electron mean free path in Cu^0 when compared to oxidised Cu.³³

Following anneal the O 1s peak in Figure 3.3 (b) for both samples is significantly reduced in intensity. As Figure 3.3 (b) shows, annealing results in the formation of metallic Cu, which explains the reduction in not only the copper oxide O 1s components, but also the SiO₂, due to a metal layer being present above the material. For the salt annealed sample, C-O bonds make up a significant portion of the fit, suggesting that carbon remains on the sample. The oxide annealed sample is dominated by the SiO₂ signal, and unlike the salt annealed sample, there is little evidence of C-O bonding, as most of the C had been removed prior to the oxidation step. Another aspect of the fit is the component located at 530.2 eV. This was fitted with a narrower Gaussian contribution than the other oxygen components, and is attributed to Cu-O bonding, despite the reduction to metallic copper evident in the subsequent Cu 2p and Cu 1s analysis (labelled Cu⁰O for simplicity). This feature becomes evident in the annealed salt-infiltrated sample due to the presence of Cu⁰, and rises in intensity in the annealed oxide sample, which has a more clearly defined Cu⁰ signal. Despite the anneal, there remains some oxygen within the film, with a higher temperature and/or longer exposure time required for a more robust reduction procedure. A significant decrease in intensity of the C 1s is observed when annealing the Cu salt sample, with only small signals of C-C and C-O bonds. This fact, combined with the removal of all N signals, shows that the polymer layer has been removed by the anneal. The analysis in the previous section for the Cu oxide sample revealed that only small signals in the C 1s signal remained after the oxidation step. Following the anneal however, these trace elements are desorbed. The small signals from the N 1s signal were also no longer observed after the anneal.

Annealing both samples resulted in the Cu 2p_{3/2} spectra of Figure 3.5 (a) losing the shake-up features seen in the spectra of both the Cu salt and Cu oxide samples, with the maxima of the doublets shifting to a lower binding energy. The fit shows that the anneal has

converted both samples from oxide into metallic copper, with only a small component of Cu^{1+} remaining.³⁴ It should be noted however that the intensity of the Cu^0 signal is significantly larger in the annealed copper oxide sample. This is significant, since it potentially shows that, although annealing both the salt-infiltrated and the oxidised samples yields the same result, a greater amount of Cu^0 remains on the annealed Cu oxide sample, indicating the importance of the oxidation step. This increase in intensity is also seen in the annealed Cu 1s spectra on Figure 3.5 (b), supporting the conclusions drawn from Figure 3.5 (a).

3.4 Conclusion

The photoemission and EDX data provide important information regarding the chemical interactions that occur in the metal salt inclusion process. Every critical core level at each stage of the process has been fitted robustly, with the peak fitting parameters carefully obtained. The HAXPES data shows that, once the metal salt solution is spun onto the polymer, the Cu undergoes a strong chemical interaction with the N in the pyridine ring, with the detection of an N-Cu bonding component in the N 1s, Cu 2p and Cu 1s core levels. The EDX mapping data supports these conclusions, showing that thin films of the polymer pre- and post-metal salt infiltration can be acquired. The UV/Ozone process converts the salt-infiltrated film into a pure copper oxide layer. The removal of the polymer is evident from EDX mapping and the lack of C 1s and N 1s core levels in the photoemission spectra. Annealing the copper oxide layer produces Cu^0 on the surface, demonstrating that both insulating dielectric materials and conducting films can be fabricated using this approach.

Significant progress is being made in developing future polymer ASD processes for nanoelectronic device fabrication. The study reported here provides a detailed

understanding of a novel ASD process. A starting polymer has been analysed, successfully infiltrated and subsequently fabricated to copper oxide and metallic copper respectively. The work has proven that by using this wet chemistry technique, P2VP polymer films can be created, infiltrated with metal salts, and used to create metals and metal oxides. This demonstrates that P2VP can be used for high-k dielectrics and metallic nanoelectronics device fabrication via ASD for large scale CMOS using several processing steps. For further advancements in ASD, it is essential to assess the chemical environment of fabricated materials. The HAXPES measurements have shown that it is possible to analyse in detail the chemical environment of each species present throughout the range of experimental steps, thereby obtaining a full understanding of the surface chemistry that underpins the infiltration, oxidation, and reduction processes of the technique. In addition, the study is beneficial for technologies that utilise pyridine containing BCP's.

The characterisation methodology presented herein has been used to understand the infiltration properties of a range of liquid phase precursors, which, alongside Cu, was

Liquid Phase Infiltration into PVP Brushes

Successful infiltration/metal formation: Nitrate Salt

Successful infiltration/metal formation: Chloride Salt

Degradation of metal oxide after polymer ashing

Figure 3.7: Periodic table of elements tested on PVP brushes for liquid phase metal salt infiltration. The AMBER institute showed that a large array of metal salts can be successfully infiltrated into the PVP brushes.

expanded to include infiltration and area selective studies into metal containing salts such as Al, Ti and Hf.^{35–38} It was subsequently determined that regions covered by either no polymer (bare substrate), or by PS brushes (inactive polymer) prevented metal deposition in those areas, proving the area selective compatibility of the process in this chapter. The full range of metal salts that were successfully infiltrated in the aftermath of this work into either P2VP or P4VP by collaborators at AMBER is shown in Figure 3.7. It is apparent that a large number of metals can be infiltrated through liquid phase infiltration. Hafnium and zirconium are of particular interest as these high-*k*-based materials are currently employed as the gate dielectric in advanced CMOS processes and as such, a route to area selective deposition of these metal oxides is desirable.

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4 Characterising Vapor Phase Metal Infiltration into Polymer Brushes

The results presented in this chapter focus on the mechanics of metal infiltration into polymer brushes via vapor phase techniques. These processes were performed in specialist vacuum chambers, which allowed for specific quantities of gases to be admitted to the chamber containing the polymer film.

The chapter is split into 3 sections, based on the different experimental methodologies used. The initial investigation reported in section 4.1 applies a conventional ALD recipe to P2VP films to gauge precursor – polymer reactions and whether infiltration can be achieved in the vapor phase with pyridinic based brushes. This was facilitated through a research collaboration between DCU and Tampere University Finland, where the ALD process was performed.

Section 4.2 applies SIS – like processes to a variety of polymers, with the objective of providing experimental evidence of metal infiltration into P2VP and PMMA brushes and simultaneous rejection by PS brushes. This preliminary study was performed on-site in a home-built ALD vacuum system.

The results in section 4.3 provides a comprehensive study of TMA interaction with P2VP, P4VP, and PS brushes. The experimental parameters were built around a newly commissioned Oxford Instruments FlexAl system. Process parameters – and how they affect metal infiltration, process speed and area selectivity were investigated.

4.1 Aluminium oxide formation via atomic layer deposition using a polymer brush mediated selective infiltration approach

4.1.1 Introduction

It has been discussed that ASD is an emerging method for the patterning of electronic devices as it can significantly reduce processing steps in the industry, with a potential methodology in the field linked to the infiltration of metal precursors (in gas phase) into patterned polymer materials. This chapter demonstrates this potential by examining P2VP-OH as the ‘receiving’ polymer and TMA and H₂O as the material precursors in a conventional ALD process. Fundamental understanding of the surface process was achieved using XPS and EDX mapping via TEM. The resulting analysis confirms aluminium inclusion within the polymer film. Spectroscopic and microscopic characterisation show metal infiltration throughout the polymer to the underlying silicon dioxide interface. Exposing the infiltrated film to an oxygen plasma results in the removal of the organic component and resultant fabrication of a sub 5 nm aluminium oxide layer.¹

4.1.2 Experimental Details

4.1.2.1 Materials and Characterisation

P2VP-OH (P7544-2VPOH) (PDI: 1.05) with a molecular weight of 6 kg mol⁻¹ was purchased from Polymer Source. The P2VP-OH was dissolved in THF to form a 0.2 wt% solution and prepared in the same manner as described in section 3.2.1 of the previous chapter. Aluminium infiltration into the P2VP-OH film via ALD was performed in a commercial reactor at Tampere University (Picosun Sunale ALD R200 Advanced reactor), using TMA and H₂O as precursors and N₂ as the carrier gas. The substrate was heated to a temperature of 200°C (well within the range of polymer thermal stability) and a recipe was implemented that would normally be expected to yield a 2 nm thick film of Al₂O₃ on

a blanket, OH terminated Si surface. One cycle consisted of a 0.1 s TMA pulse followed by a 3 s N₂ purge. This was then followed by a 0.1 s H₂O pulse followed by a 4 s N₂ purge. N₂ was continuously flowed through the TMA and H₂O lines at 150 sccm and 200 sccm respectively. A total of 20 cycles were performed.

XPS data was obtained using a ThermoFisher-VG instrument equipped with an Al K α ($h\nu = 1486.7$ eV) X-ray source and a 3-channeltron electron analyser (base pressure; 5×10^{-10} mbar). XPS data analysis was performed using AAnalyzer,² with spectra fitted using the simultaneous fit method and by using Voigt functions. All XPS spectra were shifted so that the Si 2p_{3/2} component was located at 99.4 eV^{3,4}. The oxygen plasma process was performed in a purpose-built chamber with a custom-made plasma source coupled with the XPS analysis chamber, to ensure the sample did not have to break vacuum after the polymer removal / metal oxidation step. The plasma process took place at a pressure of 1×10^{-2} - 2×10^{-2} mbar of oxygen at 30 W for 600 s.

Sample preparation for TEM (FEI OSIRIS TEM) and subsequent EDX cross section imaging was undertaken in a FEI Helios Nanolab 450 S. Samples were capped with Pt via a gas injection system.

4.1.3 Results

4.1.3.1 XPS

Photoemission analysis was performed on the P2VP-OH films pre- and post-ALD deposition, as well as after oxygen plasma processing to examine the effects of polymer removal and metal oxidation. The XPS intensity of the relevant core levels at each stage of the fabrication process (sample of P2VP as received, sample of P2VP after ALD, sample after oxygen plasma) are shown in Figure 4.1. XPS spectra of the N 1s and C 1s (Figure 4.2 (a) and (b), respectively) reveal the presence of the P2VP film before and after the ALD step, with the significant loss of intensity seen in Figure 4.1 (a) after the oxygen plasma step attributed to the polymer being removed. The peak maximum of the N 1s the spectrum for the P2VP pre ALD processing occurs at 399.6 eV binding energy, close to the position of pyridinic nitrogen. The overall structure of the peak remains relatively unchanged after the ALD deposition, confirming that the polymer is still present after the ALD step. After oxygen plasma processing, the pyridinic nitrogen signal is no longer visible, confirming that the polymer has been successfully removed. This behaviour is also observed in the C 1s spectra.

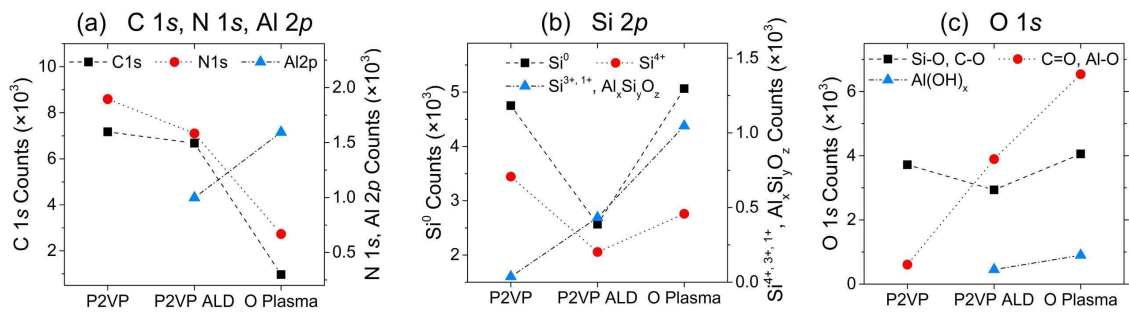


Figure 4.1: XPS counts of the (a) C 1s, N 1s & Al 2p, (b) Si 2p and (c) O 1s core levels for the polymer pre and post ALD, and post O plasma processing. The counts presented are non-normalized and obtained from area under the curve calculations.

The spectra of the Si 2*p* and Al 2*p* results are shown in Figure 4.3 (a). For the P2VP film prior to ALD deposition, no Al is present, and the Si 2*p* spectra is dominated by the Si bulk and Si⁴⁺ signal, with the 2*p*_{3/2} components located at 99.4 and 103.4 eV binding energy, respectively. Post ALD processing, the TMA appears to have reacted with the P2VP film, with the Al 2*p* maximum occurring at 75.1 eV binding energy. The Al 2*p* peak was not fitted due to the unresolvable splitting distance of 0.4 eV between the 2*p*_{1/2} and 2*p*_{3/2} components. P2VP can undergo chemical coordination with metal species, facilitated by the electron lone pair in the polymer's pyridinic N.⁵⁻⁷ It is believed that the Al exists in a complex mixed oxidation state at this stage which includes Al - pyridinyl nitrogen bonding.⁸ This type of metal – pyridine bonding has been observed for the P2VP-OH brush films that have been infiltrated with Cu through a liquid phase infiltration process as seen in chapter 3.⁹

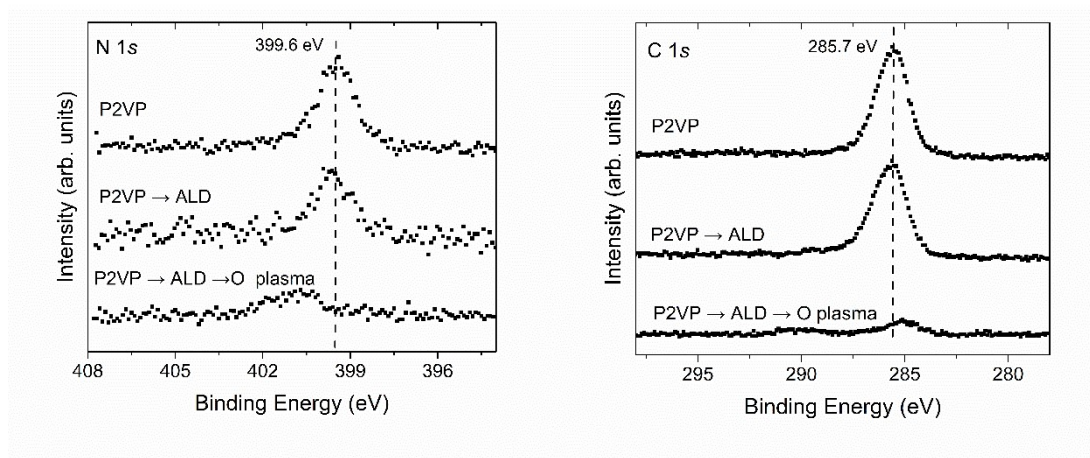


Figure 4.2: N 1*s* (a) and C 1*s* (b) for the poly(2-vinylpyridine) (P2VP) pre and post atomic layer deposition (ALD) processing, as well as after oxygen plasma processing.

Following the ALD process, Si¹⁺ and Si³⁺ components become apparent in the Si 2*p* fit, with the 2*p*_{3/2} components located at 100.4 and 101.9 eV binding energy, respectively. This is shown on the inset of Figure 4.3 (a). These peak positions are consistent with the binding energies of Si suboxide states as reported by Himpsel et al.¹⁰ Another peak, it's 2*p*_{3/2} component located at 103.0 eV binding energy, was required to obtain an accurate

curve fit to the raw data, and, combined with the presence of Si^{1+} and Si^{3+} oxides, represents evidence of the interaction of the Al precursor with the SiO_2 layer, resulting in the formation of Al-silicates ($\text{Al}_x\text{Si}_y\text{O}_z$) at the polymer- SiO_2 interface. This confirms that the Al has fully penetrated the polymer film and chemically interacted with the SiO_2 layer. The O 1s spectrum in Figure 4.3 (b) for the P2VP film is made up of two components – the predominant signal at 532.6 eV binding energy represents a combination of C-O bonds in the polymer chain and Si-O bonds (SiO_2 and Si sub oxides) in the layer below. The signal at 531.6 eV binding energy is associated with carbon oxygen bonds that have arisen due to atmospheric exposure.^{9,11,12} After ALD deposition, the peak profile of the O 1s significantly broadens. The Si-O (now also including $\text{Al}_x\text{Si}_y\text{O}_z$ bonds), C-O signal coexists with two other components located at 531.7 and 533.7 eV binding energy. The

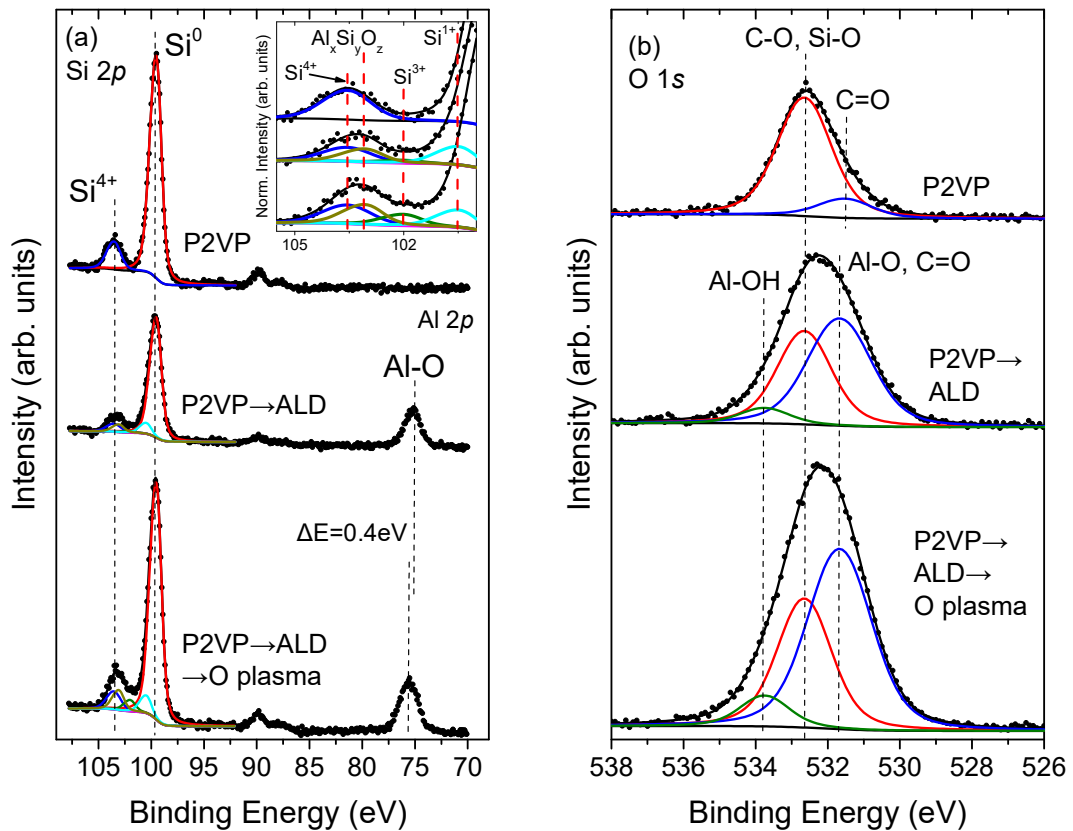


Figure 4.3: (a): XPS spectra of the Si 2p and Al 2p. Al is observed after ALD processing, and shifts to a higher binding energy after the O plasma treatment. The Si 2p spectra shows evidence of sub oxide formation after the ALD step, suggesting Al interaction with the SiO_2 layer. (b): O 1s XPS spectra. The peak sees significant broadening post ALD with the addition of Al-O bonds, with this signal dominating after the O plasma step.

former, fitted with a larger Gaussian component, represents a combination of C=O and oxidised Al bonds, while the latter represents hydroxyl Al groups,^{13,14} or sub oxides.

The oxygen plasma treatment results in a rise in counts for both the Si 2*p* and Al 2*p* signals (Figure 4.1 (a) & (b)), linked to the removal of the polymer film as evidenced by the significant reduction in the C 1*s* and N 1*s* signals after in situ processing. The Si¹⁺ and Si³⁺ sub oxides remain, along with the Al_xSi_yO_z component at 103.0 eV binding energy. The maximum of the Al 2*p* shifts 0.4 eV to 75.5 eV binding energy, which is consistent with the position of Al₂O₃ reported in other studies.^{14,15} However, the reported Al 2*p* binding energy of Al₂O₃ varies considerably in the literature^{13,16–18} and as such the exact stoichiometry of the film is uncertain. While the binding energy and stoichiometry is debated, it is apparent that the observed shift to higher binding energy suggests a transition from a lower to higher oxidation state,¹⁹ and the substantial reduction in C and N signals confirms that a pure Al-oxide layer (Al_xO_y) remains above the SiO₂ layer. For the O 1*s*, Al-O bonds now dominate the spectra, at the expense of the Si-O, C-O component due to polymer removal as seen in Figure 4.1 (c). A rise in hydroxyl Al groups is also observed. It is noted that the area of the Si-O/C-O component increases, consistent with the presence of a thin layer of Al oxide on the Si substrate, and this increase in intensity (from the SiO₂ and Si sub-oxides signals) is greater than the intensity loss that the component experiences due to the removal of C-O bonds.

4.1.3.2 TEM & EDX

TEM and EDX cross sections of the fabricated P2VP-OH films in the outlined process have previously revealed that the resultant polymer films are ~ 4 nm in thickness.²⁰ The images in Figure 4.4 show the resultant cross sections arising from the ALD and oxygen plasma process. The EDX mapping/TEM imaging of P2VP after the ALD process in Figure 4.4 (a-c) reveals that the Al exists in the polymer layer showing that the metal has infiltrated into the P2VP and has not been limited to growth on top of the film. The mapping images also show that the Al signal has reached the SiO₂/P2VP interface. This correlates with the appearance of sub oxides and Al silicates in the insert of Figure 4.3 (a) for the Si 2p fit consistent with Al interacting with the SiO₂ layer at the P2VP/SiO₂ interface.

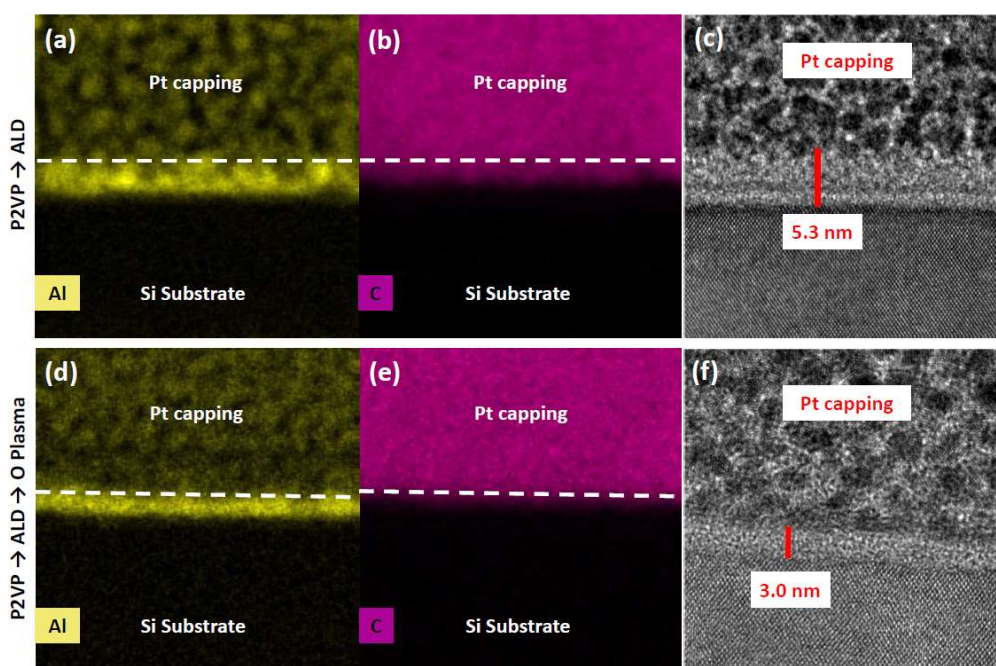


Figure 4.4: EDX Al and C mapping images ((a), (b) respectively) and TEM (c) of the P2VP-OH film after ALD deposition. Both Al and C signals are detected in the film above the Si. EDX mapping of Al (d) and C (e) and TEM after O plasma processing (f). A uniform Al film of 3nm is observed with no C signal detected. The white dashed line in the EDX images shows where the Pt cap ends, and the film begins.

The EDX and TEM images of the film following oxygen plasma processing in Figure 4.4 (d-f) reveal that a thin, uniform film of Al oxide now resides on the Si substrate, with no

carbon remaining in the film, correlating with the XPS results. Furthermore, the decrease in film thickness is consistent with the subsequent increase in intensity for the Si^0 and Si sub-oxide components as seen in the photoemission spectra.

4.1.4 Conclusion

By optimizing a conventional, relatively quick ALD process, thin layers of Al oxide have been successfully grown through the infiltration of a P2VP film, without the need for precursor hold times found in SIS-like approaches. Clear evidence of the brush layer being receptive to aluminium via a TMA and H_2O recipe has been reported for the first time. Further work is now required to optimize the reported process for maximum precursor infiltration into the polymer. XPS and EDX-TEM cross-sectioning reveals that Al resides within the polymer film all the way through to the SiO_2 interface, confirming that the brush layer is highly receptive to TMA infiltration. The reported results show a unique way of confirming whether a potential acceptor material can be entirely infused with a metal, through the detection of precursor interaction with the underlying substrate. A fast, simple oxygen plasma ashes the polymer and oxidises the Al, creating a uniform metal oxide layer. This concludes that thin brush layers can be quickly removed, without the loss of the ALD-infiltrated metal. The in-situ aspect of this process allows for the confirmation that polymer removal is complete. These results highlight the promising potential that P2VP and other brush films have in future ASD processes that seek to implement rapid ALD methods for device fabrication.

4.2 Preliminary area selective vapor phase infiltration studies into polymer brushes

4.2.1 Introduction

The success of P2VP in facilitating metal infiltration in section 4.1 led to the desire to perform a VPI – based experiment that demonstrates the area selective capabilities of the polymer brush approach. P2VP and PMMA brushes were exposed to a TMA VPI process with the objective of quantifying the level of aluminium incorporation into P2VP and comparing it to the well understood PMMA – TMA mechanism. Additionally, PS was compared to the two active polymers to assess whether the P2VP brush is capable of polymer ASD applications.

4.2.2 Experimental Details

4.2.2.1 Materials and Characterisation

P2VP, PS and PMMA polymer powders of 6 kg mol^{-1} were dissolved into 0.2 wt% solutions and prepared as outlined in section 2.8, spin-coated onto O_2 plasma treated Si. A VPI recipe was performed in a home-built ALD vacuum chamber (base pressure 1×10^{-1} mbar), coupled in-situ to a non-monochromatic Al $\text{K}\alpha$ X-ray source and a home-built plasma chamber (as in section 4.1.2.1). Prior to VPI processing, the polymers were heated to 100°C . After 20 minutes, a 10s N_2 purge was emitted to the chamber. Once the pressure had recovered, the chamber was placed in static vacuum (all pumping ceased, with valves closed to ensure stable pressure), and a 0.2 s TMA (purchased from Merck) dose was emitted into the chamber. The partial pressure of TMA was approximately 1 mbar. The chamber was held at this pressure for 5 minutes, before pumping resumed. This was immediately followed by a 10 s N_2 purge. Post VPI plasma processing took place at a pressure of 1×10^{-2} - 2×10^{-2} mbar of oxygen at 30 W for 720 s.

Sample preparation for TEM (FEI OSIRIS TEM) and subsequent EDX cross section imaging was undertaken in a FEI Helios Nanolab 450 S. Samples were capped with Pt via a gas injection system.

Atomic force microscopy was performed using a Bruker Dimension ICON AFM. Scans of $2\ \mu\text{m}^2$ were obtained using a tapping mode cantilever (Tap300Al-G, force constant = 40 N/m, resonant frequency = 300 kHz).

4.2.3 Results

4.2.3.1 Post VPI

P2VP, PMMA and PS films were immediately analysed in-situ with XPS for clarification of whether Al interaction had occurred. Al is visible in the XPS spectra shown in Figure 4.5 (a), with a strong signal occurring in the P2VP and PMMA samples, but a weaker signal is also observed in the PS film. The experiment was repeated to obtain Figure 4.5 (b), which shows the intensity (area under the curve) ratio of the Al 2p to Si 2p. Enhanced Al intake is visible in the P2VP and PMMA brushes compared to the PS, which is strong initial evidence of the capability of the PS brush as a blocker. The inconsistency of the

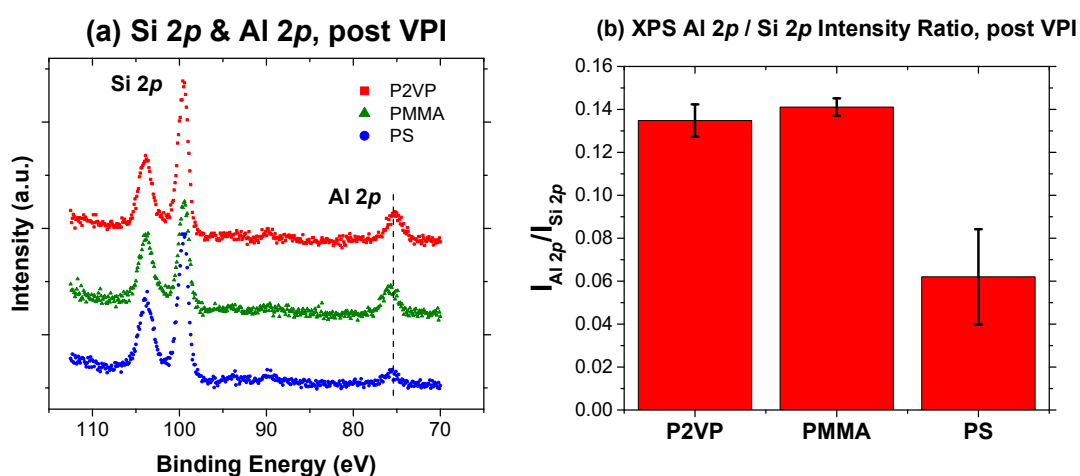


Figure 4.5: (a) XPS spectra of the binding energy region containing Si 2p and Al 2p core level signals for a P2VP, PMMA and PS brush post VPI processing. The process was repeated for the three polymers to obtain a (b) XPS intensity ratio of Al 2p / Si 2p.

metal concentration on the PS film is attributed to non-uniform distribution of the Al – possibly forming ‘islands’ across the surface, whereas a more homogeneous infiltration is witnessed for the P2VP and PMMA films (assumed from the greatly reduced error bar). It was discussed in chapter 3 that the proposed interaction mechanism between P2VP and metal stems from the nitrogen lone pair contained in the pyridine ring. The current study includes another active polymer, PMMA. The functionality of PMMA in ASD and BCP applications is well established, with the reaction mechanism between the polymer and TMA previously studied in detail – TMA bonds interact with the carbonyl group, forming an Al–O covalent bond as shown in Figure 4.6.²¹ Two reaction paths are then proposed, with (a) Biswas et al. proposing the transfer of a methyl group from the Al to the PMMA structure,²² whereas (b) Dandley et al. suggests release of ethane as a consequence to the reaction.²³ Based on the XPS of the C 1s alone, it is reasonable to conclude that route (a) is at least partially occurring, due to the significant reduction in the peak associated with the carbonyl group of the PMMA.

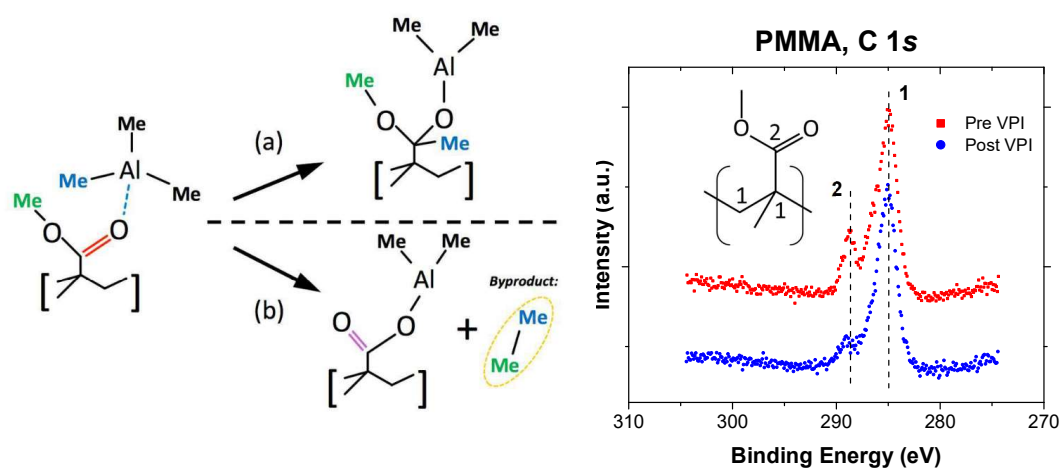


Figure 4.6: Proposed reaction mechanisms between PMMA and TMA,²¹ with the resulting XPS spectra of the C 1s for the PMMA film pre and post the VPI.

TEM and EDX cross sectional images of the polymers are shown in Figure 4.7. The TEM images reveal the presence of a film approximately 4 – 5 nm thick above the silicon substrate. The EDX imaging reveals the presence of a uniform layer of aluminium across the P2VP and PMMA samples, with no clear signal detected for the PS. The lack of Al visible across the PS sample suggests that the Al is present intermittently across the surface, rather than a uniform thin film as with the P2VP and PMMA. This correlates with the large variation of Al signal in the PS XPS spectra as opposed to the P2VP and PMMA.

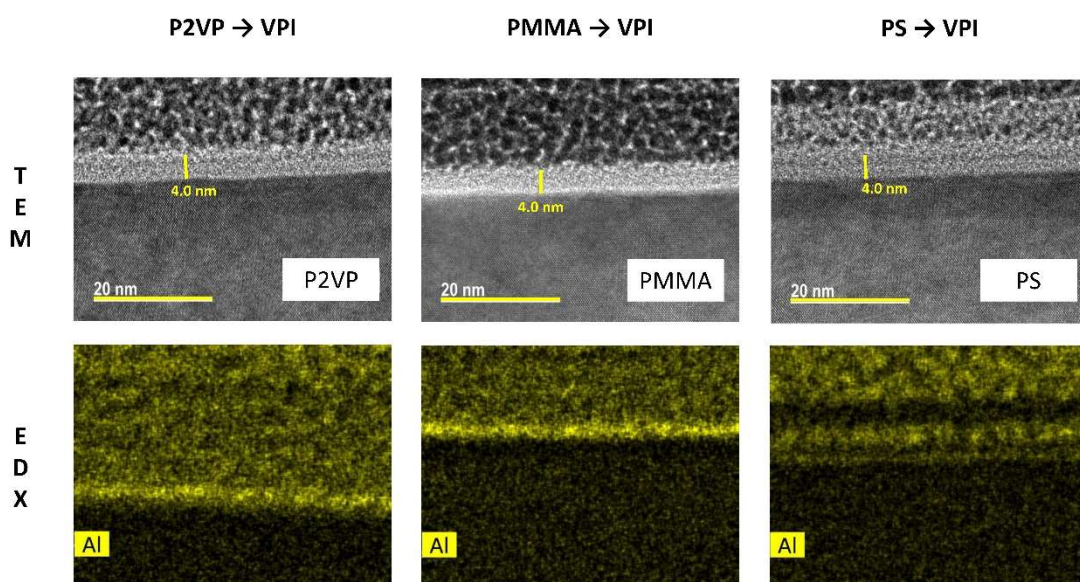


Figure 4.7: TEM and Al EDX cross sectional images of P2VP, PMMA and PS post a TMA VPI exposure.

4.2.3.2 Post O₂ plasma

Samples exposed to the VPI process were also exposed in-situ to an O₂ plasma process of similar design to section 4.1. XPS survey scans confirmed the removal of all but trace carbon and nitrogen signals, with only oxygen, aluminium and silicon core levels detected. As in section 4.1, the position of the Al 2p spectra occurs at approximately 75.5 eV – 76.0 eV and is attributed to Al₂O₃.^{14,15} The XPS spectra of the Si 2p and Al 2p core

levels and the resulting intensity ratio of Al 2p to Si 2p is shown in Figure 4.8 (a) and (b) respectively. Al is present across all three samples, indicating that plasma treatment does not remove the Al that was present non – uniformly on the PS sample.

The overall behaviour of the Al remains consistent as with the post VPI spectra; the P2VP and PMMA brushes contain similar amounts of Al, with a smaller signal observed in the PS brush. The ratio indicates an increase in Si – but this is expected due to polymer removal causing the Si 2p photoelectrons to be less attenuated.

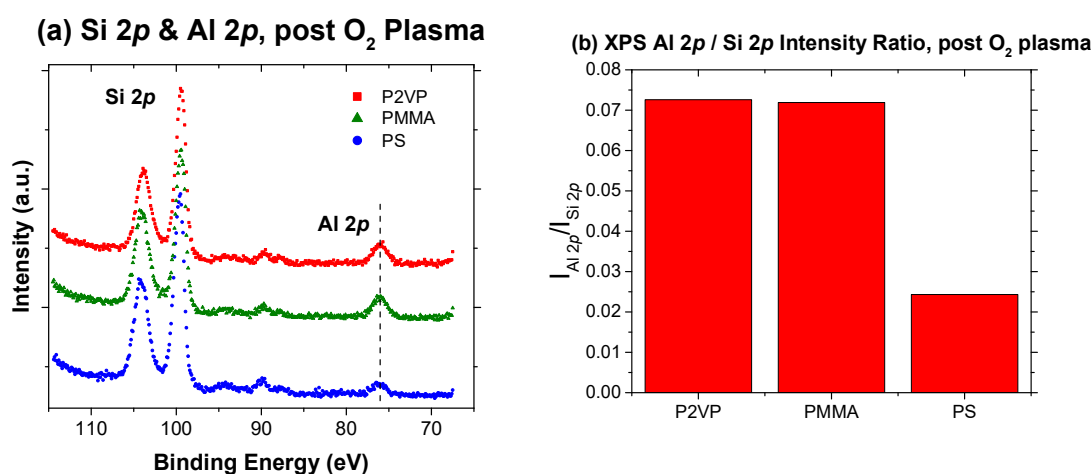


Figure 4.8: (a) XPS spectra of the binding energy region containing Si 2p and Al 2p core level signals for a P2VP, PMMA and PS brush post O₂ plasma processing. The XPS intensity ratio of Al 2p / Si 2p of the spectra is shown in (b).

TEM and EDX cross section images, as well as AFM height images, are shown in Figure 4.9. From the TEM images alone, it is difficult to distinguish unambiguously the alumina layer from the SiO₂ film, however, the EDX imaging again reveals a strong Al signal in the P2VP and PMMA. No indication of an alumina film is present for the PS sample, again suggesting that, despite Al residing on the surface of the PS sample, it is not a uniform film. AFM height images of a 2 μm^2 area however reveal no consistent surface defects across the PS sample compared to the P2VP and PMMA brushes. The lack of Al signal in the EDX imaging in Figure 4.7 and Figure 4.9, combined with the variation of

aluminium signal seen in Figure 4.5, still however strongly suggest the islanding of Al in small discrete regions for the PS film.

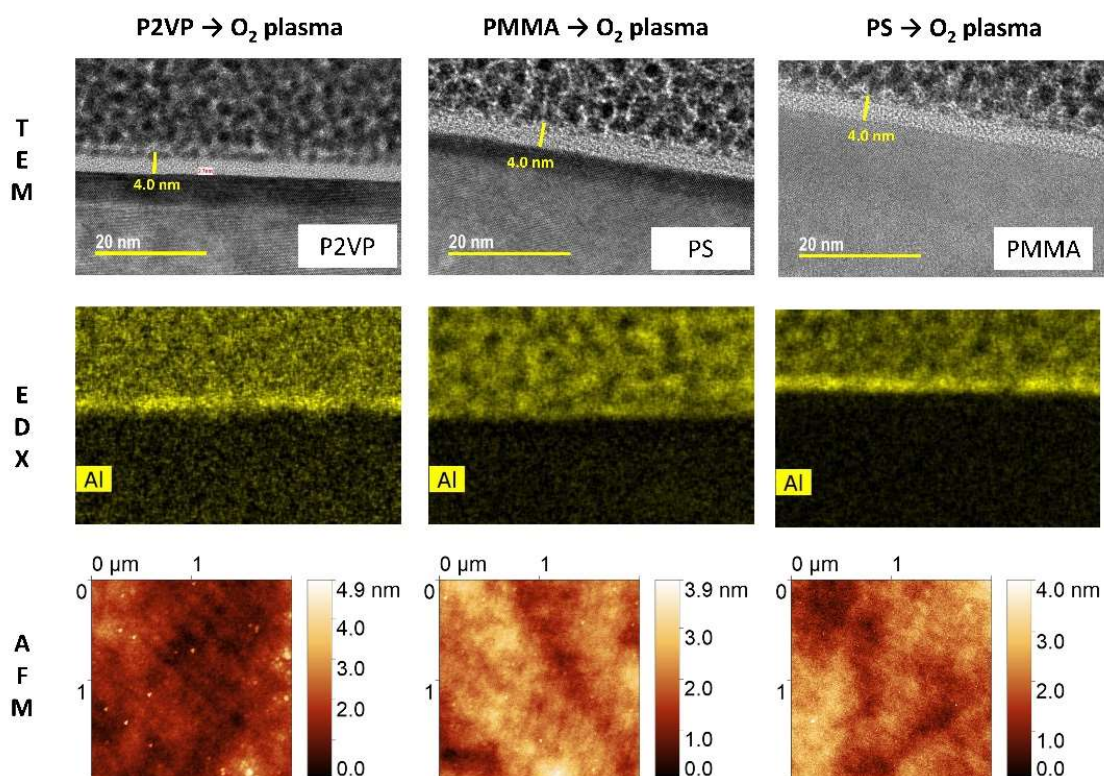


Figure 4.9: TEM, EDX and AFM height images of P2VP, PMMA and PS brushes post VPI and O_2 plasma processing. XPS analysis reveals all polymer has been removed at this point.

4.2.4 Conclusions

The VPI experiment allowed for fundamental aspects of the polymer brush infiltration to be established. P2VP and PMMA brushes were shown to accept considerable levels of aluminium into the film, facilitating a sufficient reaction for metal oxide formation without the need for a co-reactant in the process. Additionally, the P2VP brush was shown to be as receptive to TMA interaction as the well understood PMMA mechanism. Area selective capabilities were also shown – PS brushes of the same molecular weight contained significantly smaller amounts of Al on the film, with no evidence of a film forming for these films.

4.3 Analysing trimethylaluminum infiltration into polymer brushes using a scalable area selective vapor phase process

4.3.1 Introduction

Developing VPI processes for area selective polymer nanopatterning requires substantial advancement in understanding of the precursor infiltration, precursor-polymer interaction and process parameters. In this work, infiltration receptive P2VP and P4VP brushes were exposed to a TMA VPI process and compared to a non-receptive PS system. The interaction that takes place between TMA and P2VP/P4VP was analysed in detail and this section reports on notable advantages in the use of P4VP, arising from the difference in position of the pyridinic nitrogen. The VPI process was performed in a commercial atomic layer deposition reactor and the effect of the fundamental process parameters on the three polymer brushes were investigated to ensure optimal area selectivity. In-situ XPS measurements were supported by GA-FTIR and HAXPES. The report identifies several important factors when developing a VPI process to ensure area selectivity, while also demonstrating the use of novel pyridine containing polymers for VPI area selective purposes.²⁴

4.3.2 Experimental Details

4.3.2.1 Materials and Characterisation

Hydroxy terminated P2VP (P41306-2VP) (PDI: 1.04), P4VP (P9755-4VP-OH) (PDI:1.28) and PS (P9405-S) (PDI: 1.03) powders were purchased from Polymer Source (Canada) and used without further modification. The molecular weights of the P2VP, P4VP and PS were 6 kg mol⁻¹, 5, kg mol⁻¹ and 6 kg mol⁻¹ respectively. Samples were prepared as outlined in section 2.8 and summarized here.²⁵ Native oxide silicon substrates were placed in a THF bath and ultrasonicated for 20 minutes before being oxygen plasma

treated for -OH group termination. The polymer powders were dissolved into a solution (THF for P2VP and P4VP, toluene for PS) of 0.2 wt.%. by stirring at room temperature overnight. The solution was then spin coated onto the -OH terminated Si (room temperature, 3000 rpm) for 30 s. Samples were then annealed for 2 minutes at 230°C. To remove ungrafted polymer material after the anneal, samples were placed in solution as before and ultrasonicated in two sets of 20 minutes. Ellipsometry measurements (Woollam XLS-100) revealed that the P2VP and PS had thicknesses of approximately 5.0 nm, while the P4VP thickness was approximately 4 nm. The three polymers were exposed to all subsequent processing steps concurrently.

4.3.2.2 In-situ VPI, Plasma Processing and XPS

VPI processing and XPS analysis was performed in a custom designed Oxford Instruments Flexal ALD system (base pressure 5×10^{-7} mbar), which was coupled in-vacuum by a fast-transfer robotic handler to a Scienta Omicron XPS (monochromatic Al K α x-ray source, base pressure 5×10^{-9} mbar) with a 128 channel Argus CU detector. Transfer time between chambers is approximately 1 minute. This setup allowed for photoemission analysis to be performed on VPI processed samples without the need for the sample to break vacuum.

Several parameters were investigated to see the effect of infiltration into the PVP and PS brushes:

Dose time: The effect of whether longer dose time increases polymer – precursor interaction was investigated.

VPI cycles: In order to analyse whether there is a polymer saturation point – in which Al growth ceases – the number of cycles in the process was varied.

Hold time: The effect of whether longer hold time increases polymer – precursor interaction was investigated.

Substrate temperature: The effect that polymer temperature had on the VPI process was considered.

It is important to note that, unlike in conventional ALD, all experiments outlined in the results section did not include a co-reactant, with the notable exception of the final experiment, where the effect of adding the oxidant, H₂O, into the process was investigated. Prior to entering the ALD chamber, each sample was cleaved to approximately 2 cm² and then exposed to compressed N₂ to remove dust particles. The coupons were then placed on a 100 mm diameter steel carrier-wafer for ALD/XPS loading. Each batch of samples loaded for VPI processing were initially analysed by XPS to ensure film consistency.

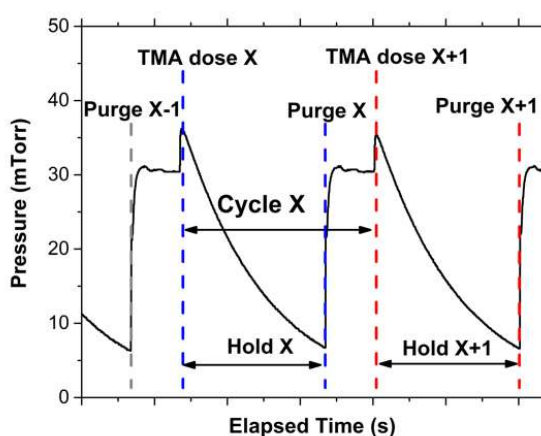


Figure 4.10: A typical pressure versus time graph for one of the many VPI processes implemented through the experiment. For this process, a single cycle consists of a TMA dose of 0.02 s duration, followed by a 60 s hold time. A 20 s purge completes the cycle.

The infiltration process used represents a combination of VPI techniques, edited to ensure that the process was compatible with the industry-scalable tool used for the experiment. Prior to each VPI process, samples were heated for 20 minutes at the desired substrate temperature, with the chamber under flow of 200 standard cubic centimetres per minute (SCCM) of Ar gas to ensure good thermal conductivity. The substrate temperature was kept within the desired range for TMA deposition as outlined by the manufacture for the

Flexal (120 °C – 400 °C) to prevent unwanted precursor decomposition/condensation. The substrate temperature was additionally kept below the polymer degradation temperature (P2VP $\approx$ 320 °C, P4VP $\approx$ 290 °C, PS $\approx$ 260 °C).²⁵ All depositions (with the exception of P4VP in part of experiment 4) took place above the bulk glass transition temperature (T_g) of the polymers (P2VP $\approx$ 100 °C, P4VP $\approx$ 150 °C, PS $\approx$ 100 °C).^{26,27} The chamber was kept pumped in such a way that the pressure was maintained at 200 mTorr ($\sim$ 0.27 mbar) for this stage. The cyclic VPI process then began. TMA was admitted to the chamber for a designated dose time. Ar (200 SCCM) was used as the precursor carrier gas. The chamber was then isolated from pumping. This involved the automatic closing of the valve used to regulate the pressure in the ALD chamber, which is located between the reactor chamber and pumps. It should be noted that when in the closed position, this valve does not provide a perfect vacuum seal between the chamber and pumps, and therefore a gradual decrease in chamber pressure during the hold step was observed. Once the predetermined hold time had passed, the chamber was exposed to vacuum pumping again and purged by Ar gas (200 SCCM) for 20 s. An example of a typical chamber pressure versus time relationship for the process is shown in Figure 4.10.

An O₂ plasma was used to remove the polymer and convert the infiltrated TMA into alumina. This was achieved by using an inductively coupled plasma source. Samples were heated to 200 °C with the chamber being constantly flushed with a 200 SCCM flow of Ar. After 10 minutes, the Ar flow ceased, and the samples were exposed to a 15-minute, 300 W O₂ plasma. The flow of O₂ was 100 SCCM, and the pressure during the plasma process was 40 mTorr.

Table 4.1: Gaussian and Lorentzian values used for fitted spectra in the AAnalyzer software.

Core Level Peak	Chemical Environment	$h\nu$ (eV)	Spin Orbit Splitting (eV)	Gaussian (eV)	Lorentzian (eV)
Si 2p	Si ⁰ /Si ⁴⁺	1486.7	0.6	0.50/1.26	0.11 ^{10,28}
C 1s	P4VP/P2VP/PS	1486.7	-	0.79/0.76/0.70	0.17 ^{29,30}
N 1s	P4VP/P2VP	1486.7	-	0.86	0.28 ³¹
O 1s	all	1486.7	-	1.32	0.25 ⁹
Al 2p	all	1486.7	0.4	-	-
Si 2p	Si ⁰ /Si ⁴⁺	3008	0.6	0.40/1.28	0.10 ^{10,28}
C 1s	P4VP/P2VP/PS	3008	-	-	-
N 1s	P4VP/P2VP	3008	-	-	-
O 1s	all	3008	-	1.18	0.25 ⁹
Al 2p	all	3008	0.4	-	-
Al 1s	all	3008	-	1.7	0.33 ⁸

Analysis of all XPS data was performed using the software, AAnalyzer.² Prior to fitting, all data was shifted so that the Si⁰ 2p_{3/2} signal occurred at 99.4 eV binding energy (BE) unless otherwise stated.³ All XPS core level fits implemented a Shirley-Sherwood type background. In addition, all fits used a combination of Gaussian and Lorentzian values (Voigt curve), displayed in Table 4.1. The Lorentzian value was, where possible, carefully referenced for each core level. All spectra counts were converted to counts per second (cts/s) to ensure consistency. Atomic sensitivity factors were obtained from Wagner et al.³² and used for estimations of surface stoichiometry.

4.3.2.3 *Ex-situ GA-FTIR, HAXPES and AFM*

GA-FTIR was performed using a Nicolet iS50 FTIR Spectrometer with a Harrick VariGATR attachment. Prior to sample analysis the germanium crystal was cleaned using butanone to remove any dust from its surface. A background of the atmosphere was then taken. Each sample was placed face down on the crystal and a force of approximately 600 N was applied to the sample to ensure sufficient sample-crystal contact. The sample was scanned at an unpolarised angle of incidence of 65° for a total of 128 scans at 8 cm⁻¹ resolution.

HAXPES measurements were performed at the National Institute of Standards and Technology beamline 7-ID-2, located at the National Synchrotron Light Source II, Brookhaven, New York (NSLS-II) to accurately assess the quality of the alumina films created post plasma processing. Samples were placed at 45° from the analyser normal and a photon energy of 3008 eV was used for all measurements, allowing for the acquisition of the Al 1s. Acquiring the Al 1s eliminates the need to analyse the Al 2p, which is difficult to study accurately due to the small spin orbit splitting value of approximately 0.4 eV, and the low sensitivity factors associated with it.^{32,33}

Atomic force microscopy was performed using a Bruker Dimension ICON AFM. Scans of 2 µm² were obtained using a tapping mode cantilever (Tap300Al-G, force constant = 40 N/m, resonant frequency = 300 kHz).

4.3.2.4 *Acknowledgements*

GA-FTIR analysis was performed by Ms. C. McFeely.

4.3.3 Results

4.3.3.1 Photoemission

Experiment 1: Precursor uptake versus dose time

The initial process parameter considered was the dose time, with the goal of determining whether an extended TMA dose results in an increase in aluminium incorporation into the acceptor polymers. This was a logical initial parameter to investigate, as excessive use of the expensive precursor material would then, if possible, be avoided subsequently.

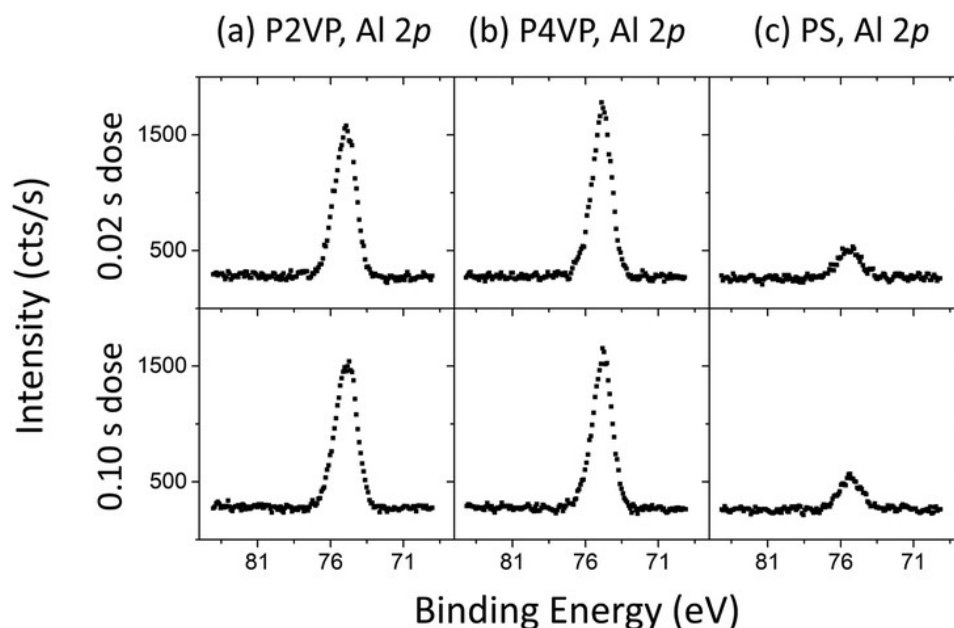


Figure 4.11: Al 2p for (a) P2VP, (b) P4VP and (c) PS post two VPI processes that implemented a different dose time (0.02 s and 0.1 s). The large increase in dose time reveals no significant change in aluminium incorporation into any of the polymers.

The basic parameters for the ALD process in experiment 1 are shown in Table 4.2. Two dose times were selected. The shorter time (0.02 s) was selected as it was recommended by the ALD system manufacturer as the optimal dose time for a thermal Al₂O₃ ALD recipe using TMA, with the second dose selected as 0.1 s. Estimations for the total partial pressure of TMA admitted to the reactor were obtained by noting the change in pressure of the chamber immediately before (carrier/purge gas present only) and during (carrier gas + TMA) the dose step. Approximately 5.3 mTorr and 39.0 mTorr of TMA was permitted into the chamber for the 0.02 s and 0.1 s dose times, respectively.

Table 4.2: Table of the chosen ALD parameters, split into the experiments 1-4 (1: Dose time, 2: VPI cycles, 3: Hold time, 4: Deposition temperature). Cells underlined were purposely left undecided until the results of the prior experiment were assessed (e.g. the dose time for experiment 2 was not decided until the results from experiment 1 were analysed). A final, 5th experiment was run to record the effect of adding a co reactant to the procedure. The area selectivity, calculated from equation (2a) and (2b), are also shown (See ‘Selectivity Considerations’ section). Poor selectivity is observed in experiment 5, and during low and high hold times in experiment 3. P4VP systematically exhibits higher selectivity values at low cycle numbers.

Experiment		1		2	3				4			5	
Dep. Temp (°C)		200	200	200	200	200	200	200	120	200	250	200	
Hold Step (s)		60	60	60	0	60	120	300	<u>60</u>	<u>60</u>	<u>60</u>	0	
Cycles		20	20	1 - 100	<u>2</u>	<u>2</u>	<u>2</u>	<u>2</u>	<u>80</u>	<u>80</u>	<u>80</u>	80	
Dose Time (s)		0.02	0.1	<u>0.02</u>	0.02	0.02	0.02	0.02	<u>0.02</u>	<u>0.02</u>	<u>0.0</u>	0.02	
											<u>2</u>		
P2VP	Selectivity,	0.61	0.61	0.47	-	0.07	0.28	0.37	0.06	0.50	0.59	0.4	0.04
S _{P2VP}				0.64								0	
P4VP	Selectivity,	0.63	0.61	0.61	-	0.44	0.51	0.59	0.05	0.51	0.52	0.4	-
S _{P4VP}				0.61								2	0.10

To assess the level of aluminium incorporation into, or on the polymer film, the aluminium 2p intensity (area under the curve) from XPS scans for each polymer was considered. The Al 2p spectra are presented in Figure 4.11. Despite increasing the dose time by an order of magnitude, little difference in aluminium intensity is observed between the two dose times for each polymer. It is therefore preferable to use the lower dose time to avoid wastage. The superior reactivity that the PVP brushes have with TMA compared to the PS brush is visible here, however it is important to note that both PVPs

contain similar amounts of aluminium despite the P2VP being approximately 1 nm thicker.

The XPS spectra of the C 1s before and after the two different VPI processes (of 0.02 s and 0.10 s TMA doses) are shown in Figure 4.12. The spectra for the polymers pre-ALD processing were fitted using the work by Beamson and Briggs as a reference.³⁴ The spectra have been charge-referenced so that the carbon backbone signal occurs at the same position as the reference. The bonding diagrams for the three polymers are shown, and the components in each fit associated with the different bonds in each diagram are labelled.

The as-loaded P2VP C 1s spectrum in Figure 4.12 (a) is comprised of a carbon backbone signal at 285.0 eV, and two components located at 285.5 eV and 286.0 eV, attributed to carbon in the pyridine ring. An additional peak at 286.6 eV is associated with C-O bonding.⁹ This signal arises from the interface between the polymer and the SiO₂ layers, as well as from polymer – ambient interaction resulting from adventitious carbon. The two post-ALD spectra alter from the original polymer in similar fashion, which is to be expected as both dose times yield approximately the same Al 2p signal intensity. Two high binding energy (BE) components at 287.3 eV (iii) and 287.9 eV (iv) are associated with carbon in a higher oxidation state, showing that the film is incorporating residual oxygen during the process. The most significant change in the spectra however is the development of two lower binding energy components, located at 284.2 eV (ii) and 283.6 eV (i). Metal carbide signals are typically observed at ~283 eV,^{35,36} and thus the peak at 283.6 eV can be attributed to Al-C bonds. This arises from TMA that has interacted with the polymer, but not fully decomposed. The peak at 284.2 eV is associated with CH₃ interacting with the pyridinic N and is discussed in more detail in the discussion of the N 1s peak Figure 4.13.

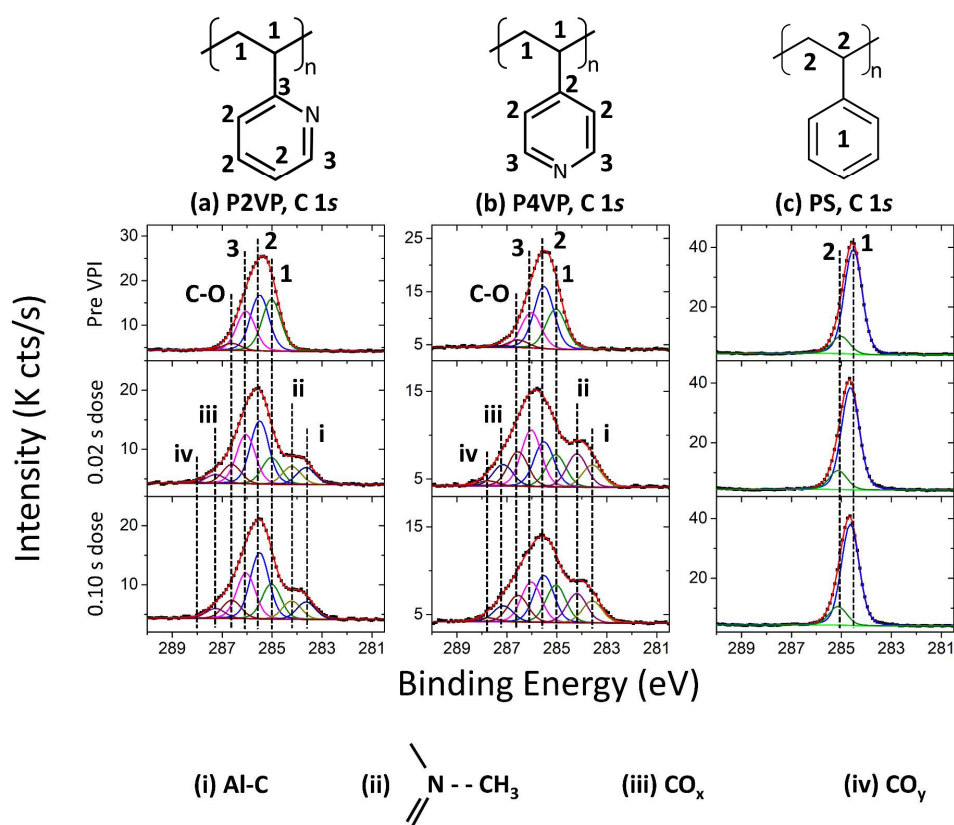


Figure 4.12: C 1s spectra of (a) P2VP, (b) P4VP and (c) PS pre VPI and post the two different dose time processes.

The P4VP in Figure 4.12 (b) shows that the carbon backbone signal is located at 285.0 eV BE. Two signals attributed to the pyridine ring are located at 285.5 eV and 286.0 eV. There is evidence of C-O bonding at 286.5 eV, as was also observed for P2VP. The composition of the spectrum following ALD is consistent with that from P2VP – two C-O related peaks grow, located at 287.1 eV (iii) and 287.7 eV (iv). The two low BE components are required to ensure a good fit to the data, at 284.2 eV (ii) and 283.6 eV (i). The former is attributed to CH₃ - N interaction and the latter to Al-C as in the P2VP spectra.

The PS in Figure 4.12 (c) has two main components, the carbon backbone signal at 285.0 eV, and the carbon signal arising from the phenyl ring, at 284.5 eV.³⁷ The spectrum

undergoes no significant change after ALD deposition, showing that the aluminium has not chemically bonded with the polymer.

The C 1s spectra reveal several important mechanisms when the polymer brushes are exposed to TMA. The PS sample was observed to contain a small amount of Al after VPI as shown in Figure 4.11, however, PS-TMA chemical interaction does not appear to take place, as the C 1s spectra pre- and post-VPI are identical. For the pyridines, the impact of oxidation may be the cause of the unexplained growth in component **3** of the fit in Figure 4.12 (a) and (b). Critically, in the case of both pyridine films, evidence of C-Al bonding show that the TMA precursor has not fully decomposed during this VPI process. As the molecule TMA consists of Al-CH₃ bonds, full precursor decomposition would have no Al-C bonding visible.

Figure 4.13 (a) & (b) show the P2VP and P4VP N 1s spectra, respectively, pre- and post- the 0.02 s and 0.10 s TMA doses. The N 1s peak associated with the P2VP film in Figure 4.13 (a) is comprised of a peak at 400.0 eV, which is associated with the nitrogen in the pyridine ring. Gaussian and Lorentzian values for the N 1s were left free for this fit, with the resulting Lorentzian of 0.28 eV agreeing with literature.³¹ The pyridine-associated peak also occurs at 400.0 eV for the P4VP spectra in Figure 4.13 (b). The C-N=C peak in both pyridines is reported to occur at 399.3 eV,³⁴ and a shift of -0.7 eV BE was applied to both spectra so that the C-N=C peak corresponds to this position. The total intensity of the pre-VPI P2VP N 1s is slightly greater in intensity than the P4VP, which is attributed to the higher film thickness observed in the P2VP from the ellipsometry measurements.

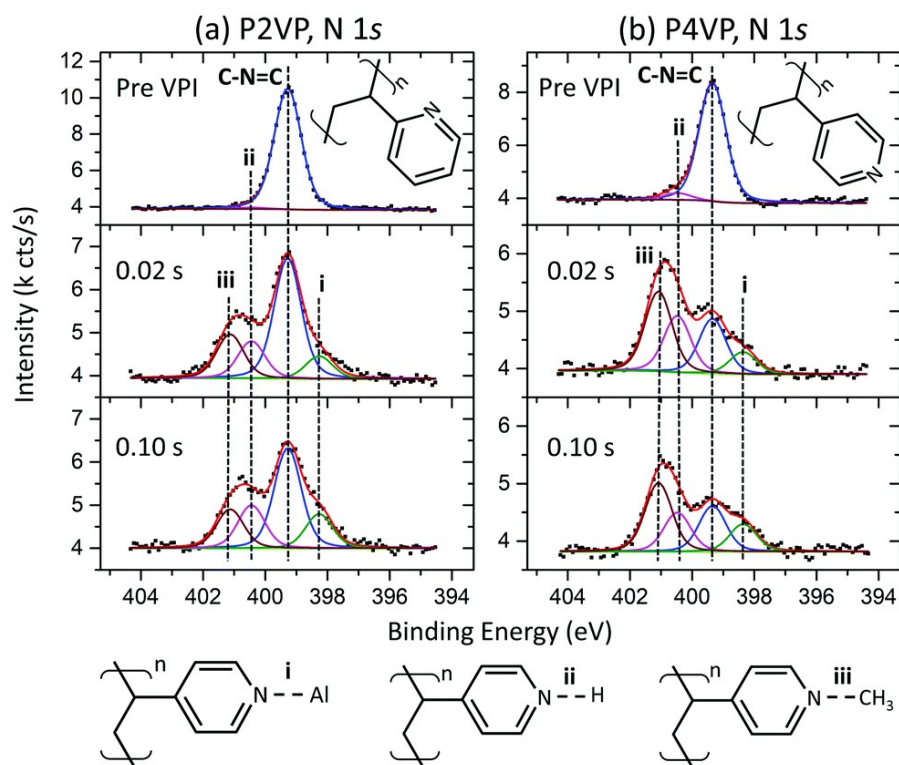


Figure 4.13: *N* 1s spectra of a P2VP (a) and P4VP (b) reference sample (pre VPI) and after 0.02 s and 0.10 s TMA dose time VPI process. The schematics below the spectra show proposed reactions occurring during the VPI process (for P4VP).

For both PVPs, the spectra for the post-VPI processes show that no significant differences occur between the two different precursor dose times. This strengthens the conclusions drawn from Figure 4.12, that increasing dose time does not affect the rate of Al uptake or polymer interaction with the TMA. Both PVPs contain a component at 398.3 eV (i), and two components at a higher BE than pyridine, occurring at 400.4 eV (ii) and approximately 401.1 eV (iii). Peak (i), occurring at a lower BE than the C-N=C signal, is attributed to Al-N bonding, reported by P.G. Mani-Gonzalez et al. and others.^{8,14,17,38} Peak (ii) is unique in that it occurs in the pre VPI pyridines as well. This peak has been assigned previously as pyrrolic nitrogen (C-NH-C). However, the significant growth of this component post VPI suggests that this component is directly related to the VPI process, as pyrrolic nitrogen growth is not expected here. The component may represent the protonation of pyridinic nitrogen (C-N⁺H=C), which has been reported to occur at a higher BE than C-N=C,³⁹ with the resulting high temperature exposure to TMA leading

to an increase in this component. Peak (iii) is not observed pre VPI, and the peak is attributed to the quaternisation of the pyridine through CH interaction ($C=N^+CH_x-C$), provided through precursor exposure. By considering this case, P4VP is observed to be more readily quaternized, with the N reacting at a much higher rate than the P2VP. This is consistent with steric hinderance of the lone pair in P2VP owing to the proximity that the N has to the carbon backbone, when compared to P4VP.

O 1s spectra for the polymers pre and post the 0.02 s TMA dose are shown in Figure 4.14. Pre VPI, all spectra are dominated by an SiO₂ associated peak at approximately 533.3 eV.^{40,41} A second peak at 532.1 eV, 532.0 eV and 531.7 eV in the P2VP, P4VP and PS spectra respectively is associated with C-O bonding as observed in the C 1s spectra in Figure 4.12, within the expected BE range.³⁴ It may also represent interaction of the polymer with the ambient. Post VPI, accurately fitting the data results in the necessity of an additional, third component, located at 532.6 eV, 532.8 eV and 531.9 eV for the P2VP, P4VP and PS respectively. This addition is associated with Al-O bonding, showing that the Al incorporated in the polymer is partially oxidising due to the residual oxygen in the process chamber. The BE position for the Al associated peaks for the pyridine is at a higher value than one would expect for Al³⁺,¹³ expected due to the oxygen deficient environment in which the process is taking place. The Al associated signal is insignificant in the PS sample (as expected, in line with Figure 4.12), with the lower BE position suggesting the Al on/within the PS is in a higher oxidation state compared to the pyridines. Unlike the SiO₂ component, the CO is not attenuated, expected from the growth of CO associated peaks post VPI as seen in the C 1s spectra (Figure 4.12).

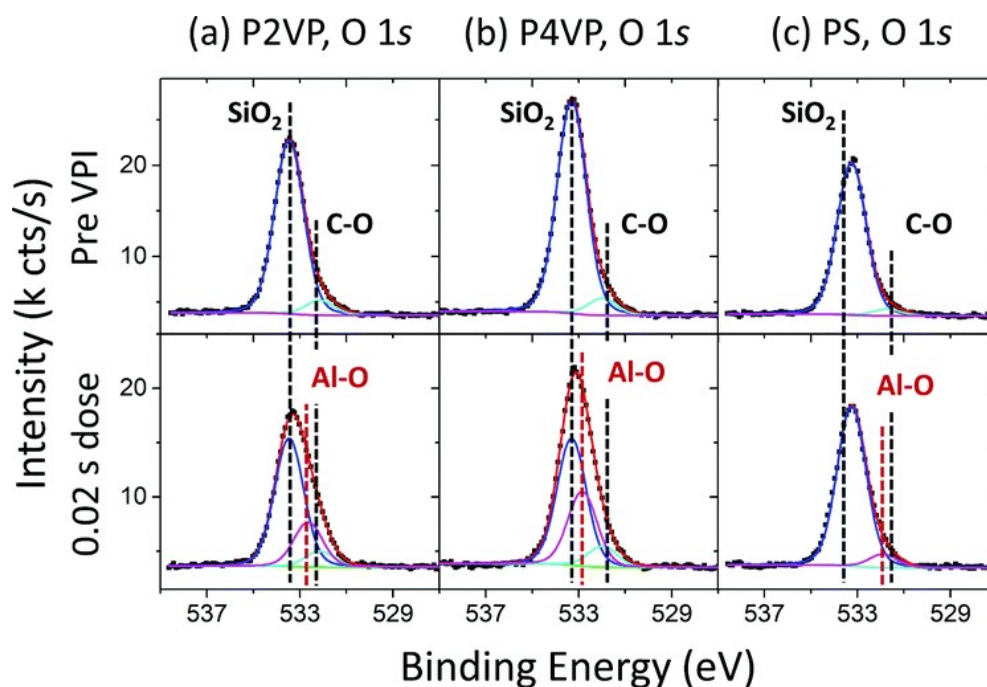


Figure 4.14: *O 1s* spectra for (a) P2VP, (b) P4VP and (c) PS pre VPI and post a 0.02 s dose time process.

To summarise experiment 1, the following conclusions are established: **(1)** Increasing the dose time does not by itself affect the degree of precursor inclusion in the polymer. **(2)** Al deposition is observed across all three polymers, however chemical interaction between PS and TMA does not occur. **(3)** TMA does not decompose completely when interacting with pyridines, with evidence of Al-C bonding. **(4)** The reaction mechanism proposed for P2VP and P4VP here includes the coordination between the pyridinic N and Al, along with protonation and quaternization of CH₃ groups with the pyridinic N. **(5)** P4VP is shown to be more receptive to TMA interaction, with the VPI generated reactions occurring in the C 1s and N 1s spectra appearing in greater amounts for P4VP compared to P2VP. **(6)** Oxidation occurs to the Al and C, even in vacuum, showing that the process is highly sensitive to residual O exposure.

Experiment 2: Precursor Uptake vs. Number of VPI Cycles

The difference in reaction rates between the three polymers was observed in a single VPI process, which was interrupted after specific cycle numbers for in-situ XPS analysis. The process parameters included a 60 s hold and a 200°C substrate temperature (Table 4.2). Building upon the results from experiment 1, a dose time of 0.02 s was chosen for this and all remaining experiments. Plots of XPS Al 2p intensity versus the number of VPI cycles are shown in Figure 4.15 (a). Both pyridines have a much greater uptake of Al compared to the PS brush. All three polymers appear to exhibit the same behaviour – high Al growth is seen for the first approximately 20 cycles. Growth becomes negligible in the 50 – 100 cycle region. At 100 cycles, P2VP contains a slightly higher concentration of Al than the P4VP, however this is hypothesized to be from the slight difference in thickness between the two polymers as revealed by the ellipsometry measurements mentioned in the experimental details.

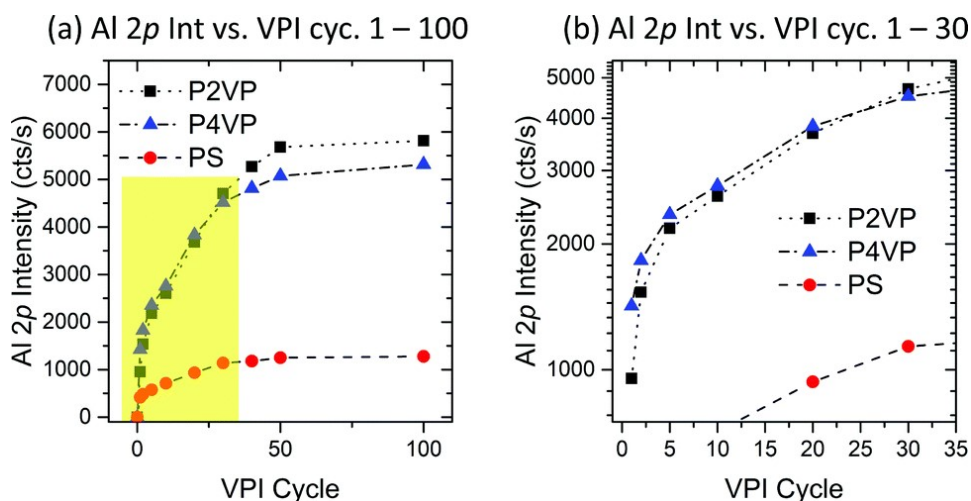


Figure 4.15: (a) Al 2p intensity on P2VP, P4VP and PS samples versus VPI cycle number. All samples experience a high Al intensity growth at low cycle numbers, with the growth rate saturating upon reaching 50 cycles. (b) An expanded view of the highlighted region in Figure 7a, showing the relationship between P2VP and P4VP Al 2p intensity for the region 1 – 30 cycles. P4VP has a higher intake of Al for the first 20 cycles.

Considering the behaviour of the two pyridines within the first 30 cycles in Figure 4.15 (b), it is observed that the P4VP has a higher uptake of Al until 20 – 30 cycles are reached. Although P4VP ultimately shows no capacity to hold more Al than P2VP, this feature

provides distinct evidence that P4VP is more reactive and facilitates quicker infiltration of Al, discussed earlier as most likely influenced by the position of the nitrogen contained in the pyridine ring.

N 1s spectra for the P2VP and P4VP at the different cycle stages of the experiment are displayed in Figure 4.16 (a) and (b) respectively. The spectra exhibit similar peak profile behaviour to that discussed in experiment 1 (Figure 4.13) – prior to VPI, with both spectra being dominated by pyridinic N ($C-N=C$). N-Al, $C=N^+H-C$ and $C=N^+CH_x-C$ features develop after the initial VPI cycle, increasing in intensity with the rise in the number of cycles. The intensity trend for these three peaks, each divided by the corresponding pyridinic N peak are shown in Figure 4.16 (c) and (d) for the respective P2VP and P4VP samples, so as to observe the relationship between the reacted and unreacted (pyridinic N) nitrogen components. The enhanced reactivity the P4VP has with the TMA is clearly evident from the intensity profiles. All three VPI-related components are observed to have greater intensity with respect to the pyridinic N of the P4VP, when compared to P2VP. This complements the hypothesis that the slightly greater amount of Al for the P2VP at higher cycles observed in Figure 4.16 is due only to the small variation in thickness between the two PVPs. The intensity of these peaks also increases rapidly in the initial cycles for P4VP, unlike the P2VP. Additionally, the reactions in the P4VP appear to be dominated by the $C=N^+CH_x-C$ component, unlike the P2VP, which sees the metal coordination bond as the most dominant, suggesting that the P4VP is more susceptible to quaternisation.

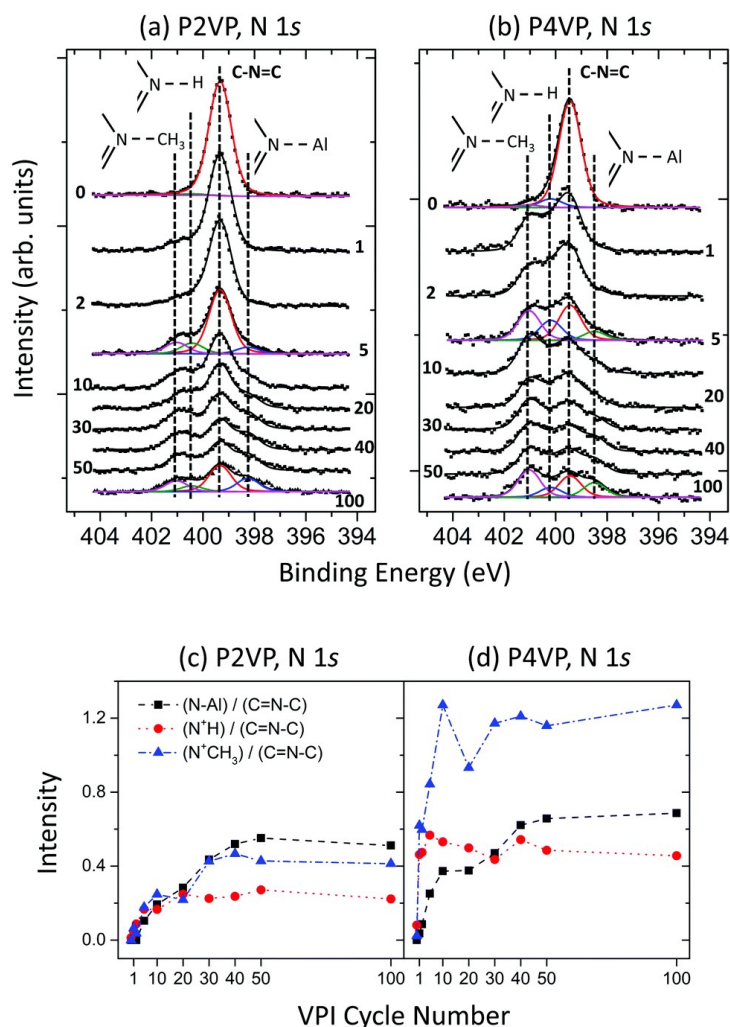


Figure 4.16: XPS N 1s spectra recorded at different stages of a 100 cycle VPI process for (a) P2VP and (b) P4VP. Area intensity versus ALD cycle time plots for P2VP (c) and P4VP (d).

The results arising from experiment 2 reveal that active and inactive polymers will facilitate growth rapidly (relative to each polymer) in the initial number of cycles. This rate of growth will decrease with increasing cycles, with each polymer appearing to slowly reach a saturation point. For the PVPs, this process is driven by the precursor interaction with the pyridinic nitrogen, a reaction that occurs at a quicker pace in P4VP over the P2VP brush. Being more receptive to TMA interaction results in the P4VP incorporating more aluminium at lower cycle numbers.

Experiment 3: Precursor Uptake vs. Hold time

Determining an optimal hold time for a VPI process is necessary to increase efficiency in precursor uptake and ensure that the process remains area selective. To investigate how P2VP, P4VP and PS brush layers react with increasing hold time, XPS scans took place after 4 different durations as displayed in Table 4.2; 0s (where precursor purging took place immediately after the precursor dose step – similar to conventional ALD), 60 s, 120 s and 300 s. A 2-cycle process with a dose time of 0.02 s was used. The process temperature was kept at 200°C.

The C 1s peak associated with the PS film is shown in Figure 4.17 (a). The spectra exhibit typical PS behaviour for all hold times except for 300 s, where asymmetry associated with a high BE component is observed. The three additional components arising from this asymmetry are associated with C-O like bonding. The low BE component at approximately 283.7 eV, observed at 60 s and higher, is attributed to Al-C bonding as observed previously. The sudden alteration in the C 1s profile is attributed to the PS losing selectivity and no longer blocking the TMA at such a long hold time, with Al now making up a larger portion of the chemical composition calculations also displayed in Figure 4.17 (a).

The Al 2p intensity (normalized to the Si⁰ 2p signal) versus hold time for the three polymers is plotted in Figure 4.17 (b). The difference in Al intensity between the pyridines and PS brush increases with increasing hold time, with low hold durations providing minimum difference between the PVPs and PS, highlighting the importance of VPI approaches in achieving maximum Al interaction. At a 300 s hold however, the Al intensity on the PS sample greatly increases. The increase in Al concentration is correlated with the asymmetry development in the C 1s peak seen in Figure 4.17a, with the C-O bonding attributed to a by-product forming as a result of TMA depositing upon

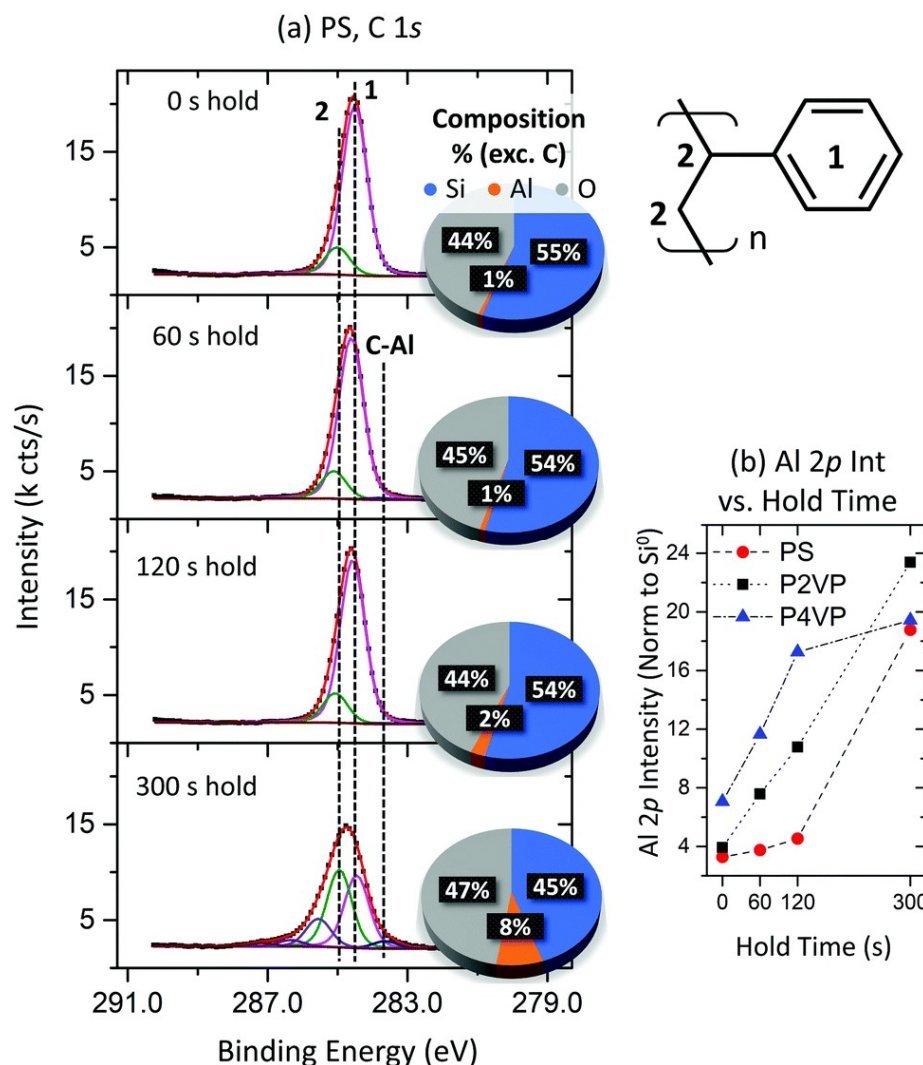


Figure 4.17: (a) XPS C 1s spectra of the PS for the 4 different hold times investigated; 0 s, 60 s, 120 s and 300 s. The carbon is unaffected except by the longest processing time, where asymmetry at high BE develops. The pie chart shows the chemical composition (excluding C) calculated from the survey scans for each hold time. (b) Al 2p intensity (normalized to the Si⁰ signal) for PS, P2VP and P4VP at the different VPI temperatures. Good area selectivity is observed until somewhere in the region between 120 – 300 s.

the PS surface and interacting with the residual oxygen contained in the chamber. The significant change in the ratio of intensity between the carbon backbone and phenyl ring signals may also suggest the degradation of the phenyl ring as a result of prolonged TMA exposure. For this process, an optimal hold time is found to lie somewhere between 60 s and below 300 s. Increasing the hold time initially results in the blocker polymers accumulating more Al, albeit at a slower rate than the reactive polymers. However, at some stage in this VPI process (between 120 and 300 s), the PS ceases to block growth

and allows for Al deposition, taking in as much Al as the pyridines. Including a purge step before this occurs is of significance here, as the previous experiments involve longer total exposure time but at far smaller single precursor hold steps. To summarize experiment 3, thin-film polymer brush VPI processes require carefully chosen hold times to assure contrasting behaviour between reactive and non-reactive polymers. This hold time will depend on how readily the chosen precursor decomposes on the non-growth surface without requiring any significant sample – metal interaction.

Experiment 4: Effect of deposition temperature

With optimal VPI parameters identified, (0.02 s dose time, 60 s hold time and 80 VPI cycles) the effect of deposition temperature, and whether this variation has implications for the final metal oxide film, was investigated with HAXPES measurements, which allowed for the acquisition of the Al 1s core level. Table 4.2 shows the three different deposition temperatures investigated: 120, 200 and 250 °C. The Al 1s spectra for P2VP, P4VP and PS samples, post oxygen plasma processing, are shown in Figure 4.18. The intensity has been normalized to each peak's corresponding Si⁰ spectra for comparison purposes. The symmetric peaks show that most of the Al can be attributed to a single chemical state. The main peak attributed to the spectra is Al³⁺, occurring at 1562.4 ± 0.09 eV, 1562.8 ± 0.12 eV and 1562.2 ± 0.16 eV for the P2VP, P4VP and PS respectively. The standard deviation accounts for the variation in the Al³⁺ BE position for each polymer between the 3 temperatures. Small peaks at approximately 1561.0 eV and 1564.3 eV are attributed Al sub oxide¹⁹ and surface based, Al-O like bonding, respectively.⁴²

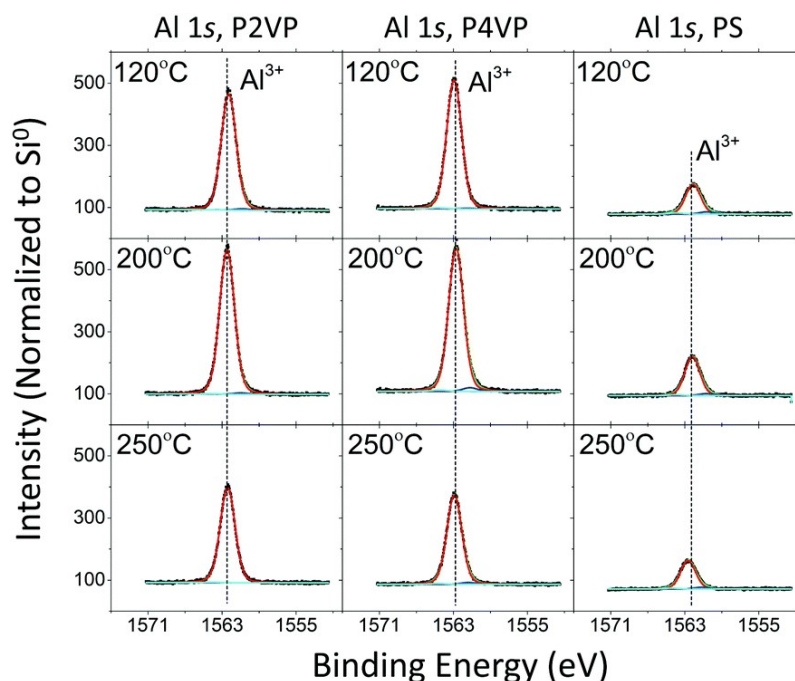


Figure 4.18: HAXPES spectra of the Al 1s ($h\nu = 3 \text{ keV}$) for P2VP, P4VP, and PS at three different ALD processing temperatures.

Negligible difference in Al concentration is observed between the two pyridine structures. Although the Al intake is slower initially with the P2VP brush, similar amounts of Al reside in both PVPs when sufficient cycles are completed. While there is significantly less Al residing on the PS sample, efforts must be made to reduce the amount of Al on the surface of the PS to improve area selectivity. AFM imaging of the 3 polymers from the 200°C process (post plasma) is shown in Figure 4.19. The three surfaces reveal the presence of smooth films (RMS roughness estimated $< 1 \text{ nm}$), with no defects visible or suggestion of islanding on the PS processed sample, suggesting a thin film of alumina exists upon all three samples.

Changing the process temperature has a universal effect on the brush films. The resulting trend of aluminium intensity versus process temperature is the same regardless of the polymer under analysis. The maximum Al 1s area for all three polymers was observed

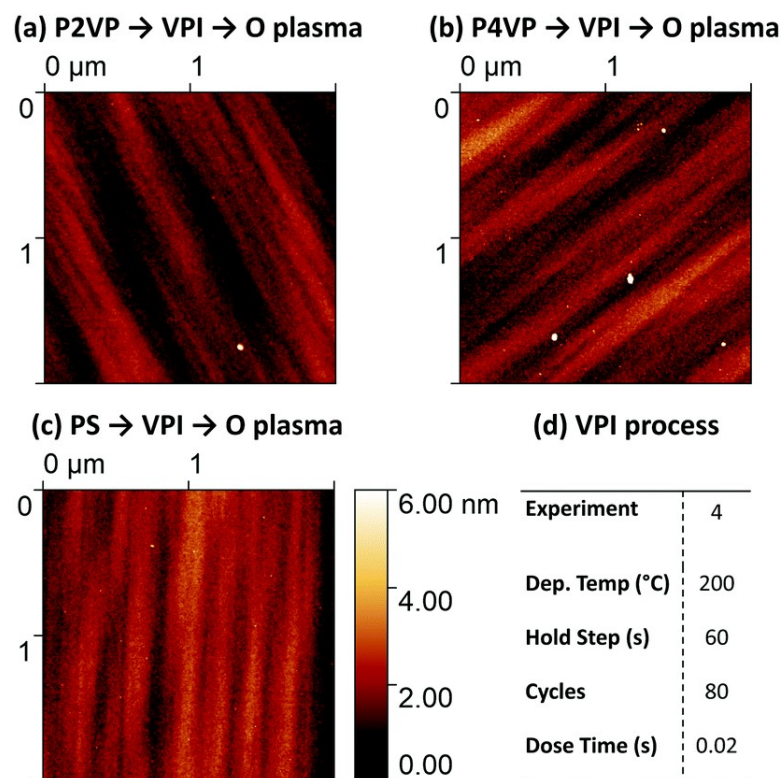


Figure 4.19: AFM height images of (a) P2VP, (b) P4VP and (c) PS. The images have been acquired after the polymers were exposed to a 200°C, 80 cycle process shown in (d) and subsequent O plasma treatment.

from the 200°C process, while the 250°C process yielded the least. The reduction at 250°C indicates that precursor interaction is directly affected by temperature regardless of the surface that is exposed to it. This decrease in aluminium at higher temperatures is consistent with previous studies concerning PMMA-TMA interaction, where precursor sorption into the polymer film lowers with temperature.⁴³ The behaviour of the Al signal post 120 °C processing for the P4VP does not show any major changes, despite this process taking place below the polymer's glass transition temperature.

All spectra of the O 1s for the different depositions contain a dominant peak at 532.9 ± 0.15 eV BE, which is attributed to oxygen in SiO₂. As in section 4.1, the second largest peak located at 531.9 ± 0.15 eV BE is associated with Al³⁺. As discussed in the Al 1s spectra, minor peaks at 530.7 ± 0.15 eV and 533.9 ± 0.15 eV represent surface-based Al-O bonding and aluminium sub oxides respectively. The intensity profile of the O 1s spectra complements that of the Al 1s spectra. There is significantly less Al³⁺ in the PS

sample following oxygen plasma treatment compared to the pyridines, however the asymmetry of the O peak for all three samples is present, again highlighting that aluminium oxide formation is not completely limited to the pyridine films.

4.3.3.2 Selectivity Considerations

Gladfelter⁴⁴ defined selectivity (S) based on nucleation on active and inactive surfaces;

$$S = \frac{\theta_1 - \theta_2}{\theta_1 + \theta_2} \quad (4.1)$$

Where θ_1 , θ_2 represent the fraction of surface 1 and 2 respectively that are covered by nuclei, with ‘perfect selectivity’ resulting in $S = 1$. This equation has been adapted to highlight the selectivity of the P2VP and P4VP brushes purely from an XPS standpoint;

$$S_{P2VP} = \frac{I_{P2VP} - I_{PS}}{I_{P2VP} + I_{PS}} \quad S_{P4VP} = \frac{I_{P4VP} - I_{PS}}{I_{P4VP} + I_{PS}} \quad (4.2)$$

Where I_{P2VP} , I_{P4VP} , and I_{PS} represents the intensity (in cts/sec) of the Al 2p (or Al 1s where possible) for P2VP, P4VP and PS. The selectivity for each experiment is tabulated in Table 4.2.

Correlating with the XPS results, changing the dose time does not affect the selectivity of either brush (experiment 1). VPI processes with a low cycle number show that the P2VP brush is less selective than P4VP (experiment 2). Varying the hold time in experiment 3 has a significant effect on the selectivity for both brushes, with the optimal hold time for this process suggested to be above 60 s but below 300 s. Experiment 3 reveals that the polymer brushes are influenced more by length of exposure rather than the increase in exposure amount as analysed in experiment 1. VPI deposition temperature has a minimal effect on selectivity, however high process temperatures appear to reduce the ASD compatibility for both pyridines.

It is important to mention that an additional experiment (5) to measure the impact of adding a co-reactant (H_2O) to the process to analyse a more conventional ALD-like procedure was performed. A 200°C , 80 cycle process was edited so that after a precursor dose (0.02 s), hold (0s) and purge, H_2O was admitted to the chamber with a 0.1 s dose, followed by an Ar purge. While this increased the amount of Al incorporation in both pyridine brushes, the effect was seen to reduce the area selectivity of the process significantly, with the Al core level signal intensities on the PS sample being of similar intensity to both PVPs (S_{P2VP} , $S_{\text{P4VP}} \approx 0$).

4.3.3.3 GA-FTIR

GA-FTIR analysis was performed on the PS, P2VP and P4VP pre- and post- a VPI process of 0.02 s dose time, 50 cycles and a 60 s hold time at 200°C . The spectra are displayed in Figure 4.20. P2VP and P4VP exhibit near-identical behaviour and are shown in Figure 4.20 a and b respectively. Both PVPs contain a aliphatic C-H stretching peak at 2920 cm^{-1} , associated with the PVP backbone⁴⁵. C=C stretching vibrations (attributed to the pyridine ring) are observed at 1726 cm^{-1} and pyridine associated stretching modes at 1600 cm^{-1} .^{46–49} Peaks at 1416 cm^{-1} and 1232 cm^{-1} are associated with C-H deformation vibrations. The 1232 cm^{-1} peak may also be linked to C-O stretching.⁵⁰

It is observed in Figure 4.20c that the region $1500 - 1800\text{ cm}^{-1}$ undergoes changes after the VPI processing for both PVPs. Pre VPI, the region contained a single, clearly distinguishable peak at 1600 cm^{-1} , attributed to pyridine. After VPI exposure, a new broad peak at a higher wavenumber can be observed. This change has been attributed to the quaternization and protonation of pyridine,^{46,48,49} which correlates with the observations made from the photoemission analysis that that PVP is undergoing quaternisation and protonation when exposed to the TMA VPI process.

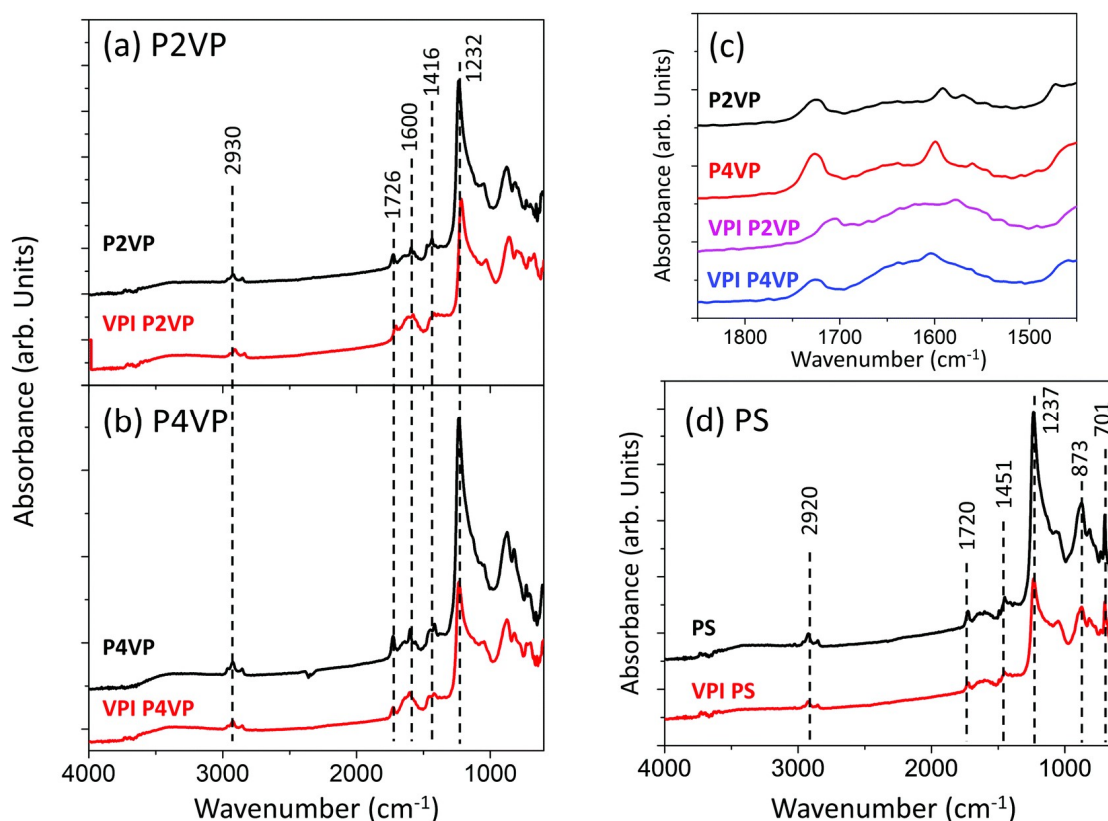


Figure 4.20: GA-FTIR spectra of (a) P2VP and (b) P4VP pre and post VPI processing. The region 1450 – 1850 cm^{-1} in (a) and (b) shows considerable change pre and post VPI, and an inset of this region is shown in (c), highlighting the broadening occurring in the spectra. PS pre and post VPI is shown in (c), with no change observed between the two spectra.

The PS spectra in Figure 4.20 (d) does not change after VPI processing, with the exception of a slight loss in intensity, associated with the development of Al building atop of the PS brush. The C-H stretching peak at 2920 cm^{-1} is associated with the aromatic carbon in the PS backbone⁴⁵ C=C stretching vibrations are associated with the peak at 1720 cm^{-1} .⁵¹ C-H deformation vibrations are observed at 1451 cm^{-1} , while C-O stretching vibrations are located at 1237 cm^{-1} . C-H bending is attributed to peaks at 873 cm^{-1} and 701 cm^{-1} .⁵¹

4.3.4 Conclusion

Vapour phase polymer infiltration has been demonstrated using a commercial ALD system, with in-situ XPS analysis presenting several important contributions to the field. Firstly, increasing the precursor dose time does not yield more uptake of TMA by the

active polymers P2VP and P4VP. All polymers displayed the most interaction with the precursor during the initial (below 30) cycles of a VPI process, with the rate of Al incorporation decreasing with an increasing number of cycles. P4VP was shown to incorporate Al at a quicker rate than P2VP during the initial VPI cycles, with the N 1s spectra analysis agreeing with literature that metal bonding and the rate of interaction with TMA is determined by the pyridinic N and its position within the ring. A window for optimal precursor hold time was identified, with extremely short hold times insufficient to encourage pyridine – TMA interaction. However, it was found that increasing hold times too much will result in undesired TMA deposition onto PS, showing that the polymer brushes used for blocking growth purposes exhibit similar behaviour to that for SAMs where selectivity can be lost during metal exposure processes. HAXPES measurements revealed that better area selectivity was observed at lower temperatures. PS appeared to facilitate the deposition of thin, oxygen rich alumina films, highlighting the need for increased efforts in ensuring better area selectivity.

The results have shown that controllable and area selective alumina films can be acquired through synchronised PS and PVP TMA exposure. Where possible, P4VP should be chosen above P2VP when designing TMA VPI processes, particularly when speed and/or low metal incorporation procedures are desired. Exposure time should be prioritised over exposure amount (within reason) when designing a polymer process for area selectivity. Varying substrate temperature has less impact on the area selectivity of the procedure, however additional work must be focused on achieving VPI processes at lower temperatures. It should be noted that studying the pyridine – precursor reaction mechanism as a function of depth is desirable to further increase the scalability of the technique. Finally, this work has shown that it is not necessary for the introduction of a co-reactant to the precursor, with the introduction of H₂O leading to complications in the

achievement of polymer brush area selective infiltration. This means the process remains area selective even when PVP is used alongside an uncoated substrate, as no co-reactant is used for the process (with no deposition therefore taking place on the non-coated surface).

4.4 Concluding Remarks on Polymer Brush VPI

The success of TMA selectivity infiltrating PVP polymer brushes using the knowledge developed in section 4.2 and 4.3 spurred an investigation into several other precursors to assess their suitability for VPI processes. A list of precursors tested is shown in Table 4.3. The Ti precursor titanium isopropoxide (TTIP) also showed infiltration capabilities into PMMA and more recently PVP brushes.⁵² However, all other precursors tested in this work were largely unsuccessful.

The VPI process summarised in the review by C. Leng and M. Losego, explains that the first challenge in the technique requires the sorption/dissolution of the precursor into the polymer.²¹ This can be expressed by Henry's Law:

$$C = S \cdot p \quad (4.3)$$

Where C is the concentration of the penetrant molecule in a polymer, and p is the partial pressure of the precursor. S is the solubility coefficient, expressed by the van't Hoff equation:⁵³

$$S = S_0 \exp\left(-\frac{\Delta H_S}{kT}\right) \quad (4.4)$$

Where S_0 is a constant, k is the Boltzmann constant, T is the temperature, and ΔH_S is the partial molar enthalpy of dissolution. The sorption can therefore be maximised by increasing the partial pressure of the precursor, increasing the temperature of the system, or tailoring the process so that the precursor/polymer pair has the smallest ΔH_S . This however is an over simplification which does not take into account effects such as the polymer free volume or the glass transition temperature of the polymer in question.⁵⁴

The low partial pressure of the precursor may be a significant drawback in VPI, with larger amounts of gas required than typical ALD processes for precursors with less favourable sorption characteristics. An example of this is the hafnium chloride precursor

(HfCl). HfCl salt in the liquid phase was effectively infiltrated into P4VP brushes,⁵⁵ however a VPI recipe demonstrated that HfCl gas had no ability for infiltration into brush films at partial pressures similar to what was used for TMA in section 4.3. For precursors with less favourable sorption characteristics, it may be favourable to develop specialist VPI chambers as opposed to the optimisation of ALD systems.

However, while it may be favourable to increase the partial pressure of the vapor into the chamber, this may impact the area selectivity of the process, with physisorption and physical entrapment occurring in unactive polymers such as PS. It was witnessed that extended exposures of TMA caused a breakdown in the ASD compatibilities of the VPI process developed in section 4.3.

The sorption of the precursor is subsequently followed by diffusion/transport of the molecule into the polymer. Both these stages are linked to the infiltrating molecule's (penetrant) size. It has been previously demonstrated that the rate of diffusion into a polymer film is directly impacted by the infiltrating molecule's (penetrant) size – the larger the penetrant, the lower the diffusion rate.⁵⁶ This effect has been seen in polymer VPI – the sorption and diffusion rate of TiCl₄ (molecule diameter = 5.78 Å) was calculated to be higher than TTIP (molecule diameter = 8.54 Å) into PMMA.⁵⁷ Certain ALD precursors – such as those represented in Table 4.3, are larger and heavier than TMA, presenting a more difficult challenge in infiltration.

The final stage of the VPI process is the entrapment of the precursor. This requires an interaction between polymer and precursor – such as the TMA interaction with the carbonyl group in PMMA and the pyridinic nitrogen in P2VP/P4VP seen in this chapter. Hf, W and Co precursors showed no signs of chemical interaction with any polymer brush tested. This may be a cause of sorption or diffusion failure of the precursor, or may represent incompatibility between the penetrant and the polymer. An example seen in

section 4.3 is the increased reactivity seen between TMA and P4VP over P2VP. While infiltration and entrapment was ultimately successful in both, the steric hinderances caused by the close proximity of the nitrogen to the carbon backbone in P2VP caused a slower uptake of Al. It is envisioned that difficulty in entrapment may be felt further in larger molecules.⁵⁸

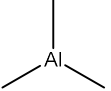
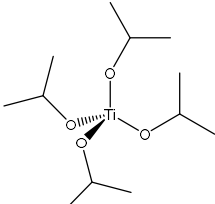
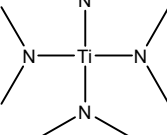
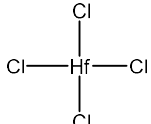
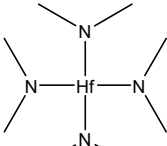
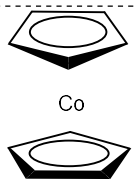
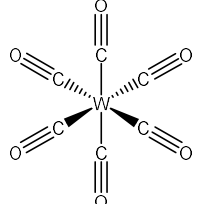
A solution to increasing the chances of precursor entrapment into the polymer is known as *seeding*. This involves infiltrating the polymer with a molecule more prone to entrapment before the VPI process effectively begins. The now manipulated polymer will ideally be more suited for interaction and entrapment of the chosen VPI precursor. This seeding process can implement solvents, H₂O and even TMA – the tungsten precursor WF₆ was successfully deposited onto polymer films post a TMA + H₂O exposure.^{54,59} As both PVPs studied in this work showed advance receptivity to TMA, this seeding method may be a route to achieving precursor entrapment. However, as is the case for HfCl – it is known from liquid phase infiltration that PVP successfully interacts with the precursor, meaning the difficulties may exist in the sorption and diffusion aspects of the VPI process, rather than incompatibility to bond.

If it is assumed that the VPI precursor is suitable for polymer brush infiltration, the obvious next question is which of the two infiltration mechanisms studied in this thesis is most suited as an infiltration method. As determined in chapters 3 & 4, both techniques can be successful in fabricating metals and metal oxides. While this depends on many factors, the basic elements of the answer will depend on the following points;

- Is there a process requirement for low temperature (< 100 °C) infiltration? One of the limitations regarding polymer VPI is that, if a lower temperature is required, condensation reactions of the precursor may occur, limiting the area selectivity of the process (precursor condensation on ‘blocking’ areas of the structure).

- Is there a need for variation in the metal oxide concentration *during* the infiltration process? As demonstrated from the results in this chapter, VPI recipes can be edited to obtain specific amounts of metal incorporation (up until polymer saturation). The liquid phase approach does not allow for this and is reliant on a change in the polymer's properties (such as molecular weight) prior to the infiltration process. This however may affect other properties, such as the density of the resultant metal oxide, which is reported to be affected by the molecular weight of the polymer.
- Is cost a critical issue? VPI is reliant on expensive chemical precursors. In comparison, the liquid phase relies on the use of metal salts which are cheaper and easier to store.

Table 4.3: Precursors tested in this work for VPI integration.

Metal	Name	Structure	Molar Mass (g/mol)	Comments
Al	TMA Trimethylaluminum		144.2	• Successful VPI into PVP and PMMA brushes • ASD compatible
Ti	TTIP Titanium isopropoxide		288.3	• Successful VPI into PVP and PMMA brushes observed
Ti	TDMAT tetrakis(dimethylamino) titanium		224.2	• No infiltration or polymer interaction observed
Hf	HfCl4 Hafnium Chloride		320.3	• No infiltration and polymer interaction observed • Infiltration achieved in liquid salt form
Hf	TDMAH Tetrakis(dimethylamino) hafnium(IV)		354.8	• No infiltration or polymer interaction observed
Co	CoCp2 Cobaltocene		189.1	• No infiltration or polymer interaction observed
W	Tungsten Hexacarbonyl		351.9	• No infiltration or polymer interaction observed

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5 Electrical Characterisation of Polymer Mediated Metal Oxide Films

5.1 Introduction

Chapters 3 and 4 characterised in detail the liquid and vapor phase infiltration processes into a range of polymer brushes, with the ability of pyridine containing polymers to interact with metals in liquid and gas form specifically demonstrated. Chapter 4 also established the area selective capabilities of P2VP and P4VP in a TMA VPI process. Subsequent work in the liquid phase mechanisms revealed similar area selective capabilities for a range of metal ions.^{1,2} While the results show successful and area selective metal ion intake, yielding high quality metal oxide films with minimal carbon and other impurity species, the ability of these metal oxides to perform in their intended role, such as the gate oxide material in MOSFET technology, is the subject of this chapter. This chapter focuses on the electrical characterisation of two high-k dielectrics that are of significant interest to Intel; aluminium and hafnium oxide, processed via a VPI and liquid phase process, respectively. The infiltration techniques are similar to those described in previous chapters. The unique fabrication process is then compared to conventional, ALD grown oxides of the same material using a variety of surface and electrical characterisation methods. The electrical measurements include the determination of breakdown field and dielectric constant – both vital properties for high-k materials – through IV and CV sweeping respectively. The objective is to assess whether the electrical properties of metal oxides synthesised via the polymer brush infiltration methods are comparable in quality (in terms of functionality) to oxides synthesised by industry standard techniques, either reported in literature or synthesised using our in-house ALD apparatus.

5.2 Vapor Phase Aluminium Oxide

5.2.1 Introduction

Alumina films fabricated via the area-selective polymer infiltration process described in chapter 4 are compared to a conventional PEALD process. The chemical makeup of the films is assessed via GA-FTIR and HAXPES. The aims of the study include the assessment of the electrical properties of metal oxides films instigated via VPI into poly-2-vinylpyridine polymer brushes. The success and challenges in area-selective dielectric formation via polymer VPI, the compatibility of pyridine in such a role, and the ability of the unique and rapid grafting-to polymer brush method in forming coherent metal oxides is evaluated, with a PEALD alumina film used as an industry standard reference.

5.2.2 Experimental Details

5.2.2.1 Materials and Characterisation

P2VP powder (6 kg/mol, PDI: 1.04) was dissolved in THF to form a 0.2 wt% solution and prepared onto piranha-treated native p-type silicon as described in section 2.8. Piranha treatment was selected here to ensure a minimal SiO₂ interlayer, as will be discussed in the results section of 5.2.3. The VPI process was based upon the results amounting from chapter 4, where the polymer samples are exposed to an ASD compatible TMA dose – hold – purge repeating cycle. The brushes were exposed to this repeating cycle until TMA saturation occurred (section 4.3.3.1 Experiment 2). To investigate the role of substrate temperatures, P2VP brushes underwent this process at 100°C, 200°C and 250°C. The polymer removal/metal oxidation was achieved by using an inductively coupled plasma source, with the sample maintained at the same temperature as was chosen for the VPI process. In-situ photoemission analysis was performed on a Scienta

Omicron XPS (monochromatic Al K α X-ray source,) with a 128 channel Argus CU detector.

To compare the films' electrical properties to more conventional metal oxide fabrication methods, alumina films were also synthesised via PEALD on IPA cleaned (ultrasonication, 15 minutes) silicon of the same type as used for the Polymer substrate. This process took place at 200°C, involving a 20 ms TMA dose, and a 2 s, 300 W O₂ plasma step. The pressure was maintained at 80 and 15 mTorr for the two doses respectively. PEALD synthesis of Al₂O₃ has been previously reported to yield favourable electrical properties, containing a high dielectric constant with less observed defects when compared to thermal ALD.^{3,4}

All VPI, ALD and Plasma processing took place in an Oxfords Instrument FlexAl – Scienta Omicron multitool system as in chapter 4. Following all processing steps, both VPI and ALD samples were heated to 400°C and exposed to a 20 minute 50 sccm flow of Ar to lower the fixed oxide charge.^{5,6} This was immediately followed by a H₂ exposure (same parameters) to reduce the D_{it}.⁷

To form MOSCAP structures, copper contacts were deposited using an Edwards E306A thermal evaporator. The sample was covered with a silicon mask (fabricated at Tyndall National Institute) with laser cut square openings of 100 × 100 μm in size. Optical microscopy revealed that this process produced contacts of approximately 8500 μm^2 .

Ellipsometer measurements were performed, using a Woolam XLS-100. The metal oxide films were measured post processing at the National Institute of Standards and Technology beamline 7-ID-2, located at the National Synchrotron Light Source II, Brookhaven, New York (NSLS-II) for HAXPES analysis. A photon energy of 2.4 keV was used, with spectra obtained at 5° from normal emission unless otherwise stated. All XPS/HAXPES spectra analysis was performed using the software AAnalyzer.⁸ All fitted

spectra used a Shirley Sherwood type background and a Voigt type curve profile, with spectra shifted so that the Si $2p_{3/2}$ (bulk) peak for each dataset was located at 99.4 eV.⁹ Current – voltage (IV) ramping measurements were obtained using a Keithley 4200-SCS. Capacitance – voltage (CV) sweeps were performed using an Agilent 4284A precision LCR meter. All electrical testing was performed at room temperature.

5.2.3 Results

5.2.3.1 Surface Characterisation

Prior to sample removal from vacuum, the Si/SiO₂/Alumina interface was monitored by XPS via acquisition of the Si $2p$. The intensity of the silicon oxide is plotted against its corresponding binding energy position in Figure 5.1. The Si $2p$ was fitted with two components – one that represents the silicon bulk (Si⁰) and the other representing Si⁴⁺. The data was shifted so that the Si⁰ peak occurs at 99.4 eV. For simplicity, silicon sub oxides were not included in the fit. The intensities of the Si⁰ and Si⁴⁺ in the Si $2p$ XPS spectra were also used in accordance with literature for an approximation of the SiO₂ interlayer thickness.¹⁰

The PEALD process results in a slight increase of Si⁴⁺, with the peak shifting to a lower binding energy. The growth in oxide may be attributed to the plasma dosing which results in the slight growth of the oxide, while the lower binding energy can be recognized as a consequence to aluminium silicates forming a thin interfacial layer between the Si and Al oxides.^{11,12} The final thickness of this Si⁴⁺ interlayer was calculated as 0.6 nm.

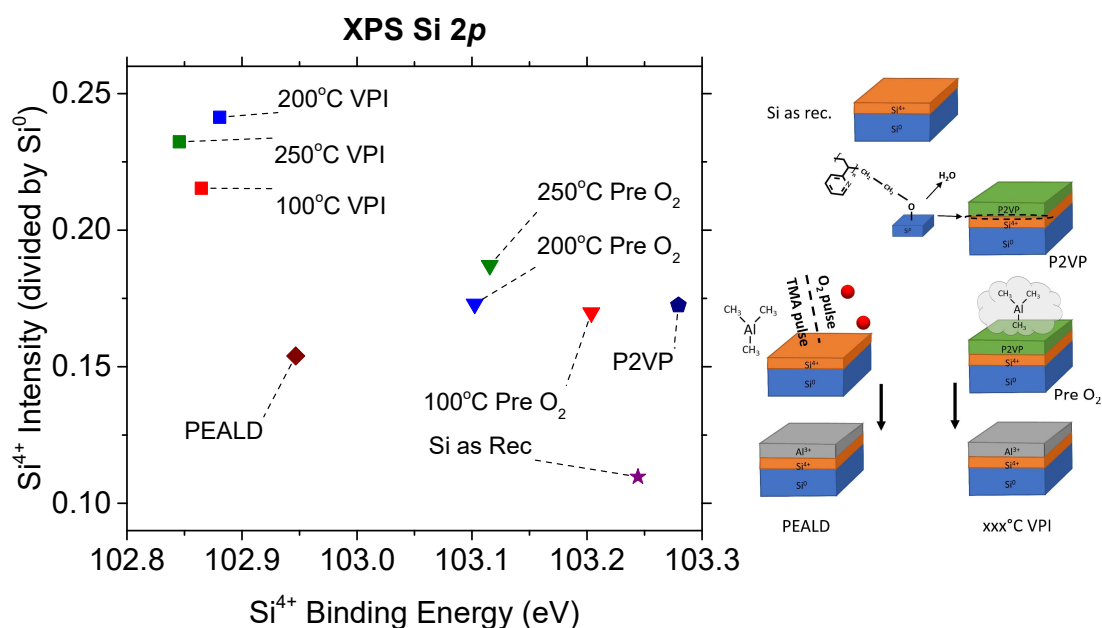


Figure 5.1: XPS intensity (using the Si 2p core level) of the Si^{4+} intensity versus it's corresponding binding energy position.

The silicon undergoes more processing steps during the VPI process, with an initial growth of Si^{4+} observed in the P2VP film prior to VPI processing, attributed to the piranha acid treatment. A shift to lower binding energy is then observed during the VPI process prior to the plasma treatment (pre O_2) which suggests Si-O-Al bonding as in the PEALD film. Unlike in the PEALD process, no growth of the oxide was observed here however as no oxygen was present in this stage. However, significant growth and shifting to lower binding energy is observed for the polymer ashing/metal oxidation step, with the VPI process containing significantly more of an Si oxide interlayer with potentially more Al silicates when compared to the PEALD approach (as observed in chapter 4). As is the case with the rest of our analysis, the different VPI temperatures behave consistently with respect to each other – all thicknesses of this interlayer were approximately 0.7 nm.

To accurately assess the thickness of the films and confirm the uniformity of both processes, high resolution TEM was performed on alumina films after all processing at the VPI temperature extremes (100°C and 250°C) and compared to a 35 cycle PEALD film. The resulting images shown in Figure 5.2 show the presence of a uniform film of approximately ~6 nm in thickness for all processes. This layer encompasses both the SiO₂ interlayer, and the alumina created from the VPI/PEALD methods. EDX imaging in Figure 5.3 confirms this layer is mostly Al, but also contains the SiO₂ interlayer and potential Al silicates. A more intense Al signal present in the PEALD film is seen, with the interface between the Si and Al more sharply defined, suggesting a denser film of alumina with less interaction with the underlying substrate.

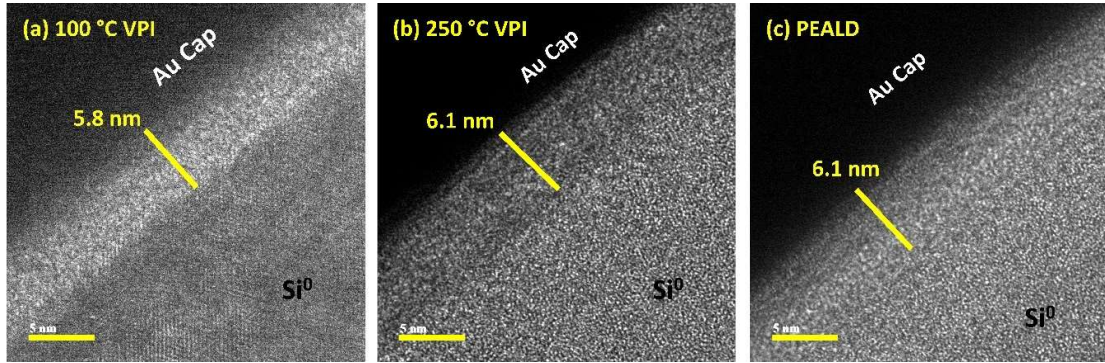


Figure 5.2: TEM images of alumina films processed from a (a) 100°C VPI, (b) 250°C VPI and (c) 35 cycle PEALD recipe.

The TEM measurements can be used as a starting point for the subsequent extraction of the optical properties of the films via ellipsometry. These measurements used a Cauchy model for the calculation of the A, B and C parameters for the obtainment of the refractive index (n);¹³

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (5.1)$$

The calculated value of n at a wavelength of 650 nm for the PEALD film was determined as 1.48 ± 0.01 , while the 100°C and 250°C VPI films had similar values of 1.28 ± 0.01 and 1.29 ± 0.01 respectively. These values, alongside the approximations for the SiO₂ interlayer and the alumina thickness as obtained from the XPS and TEM analysis respectively, are displayed in Table 5.1.

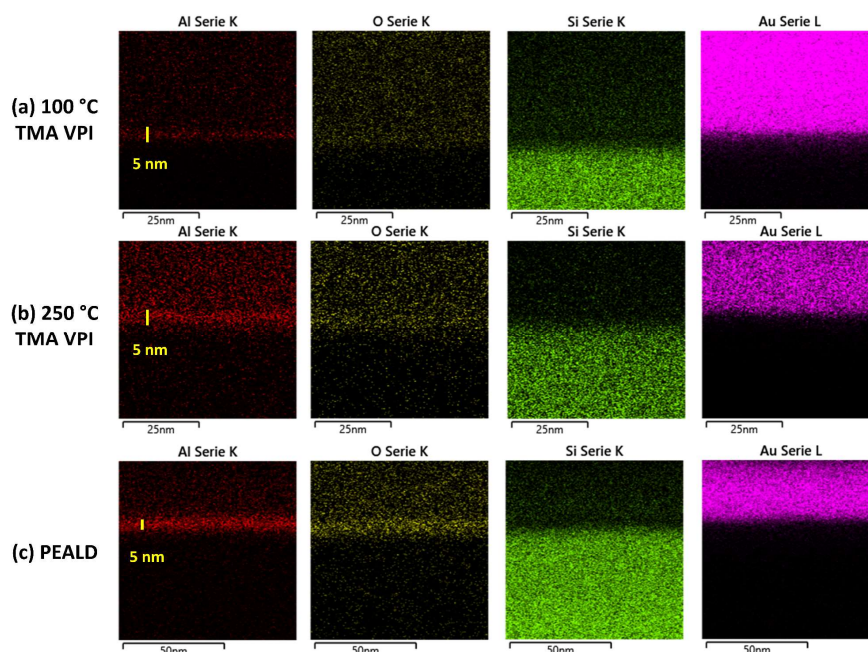


Figure 5.3: EDX images of alumina films processed from a (a) 100°C VPI, (b) 250°C VPI and (c) 35 cycle PEALD recipe, showing Al (red), O (yellow), Si (green) and Au (pink).

The change in refractive index suggests that the alumina films made via the polymer VPI method are less dense than conventional ALD films. This has been previously witnessed by Cianci et al. during the VPI of TMA into PMMA films.¹⁴ This work also showed that the density of the metal oxide was dependent on purge time (range: 45 – 500 s), with extended argon purges resulting in high porosity type metal oxides.¹⁴ Dandley et al. previously demonstrated that polymer molecular weight increases along with the porosity of the final metal oxide.¹⁵ The density of their alumina, which was also achieved through the TMA infiltration of PMMA, was noted to be increased through post annealing at 500°C, which may offer a route for non-temperature sensitive processes. While the effect of molecular weight is not expanded upon here, a second VPI process at 100°C was

performed with a shorter 10 s purge to investigate the effect of purge time, with preliminary results indicating a slight decrease in thickness (highlighting improved density). However, the Al 2p/Si 2p ratio was also reduced and thus a more extended investigation is required to address whether shorter purges can impact the density at this molecular weight range.

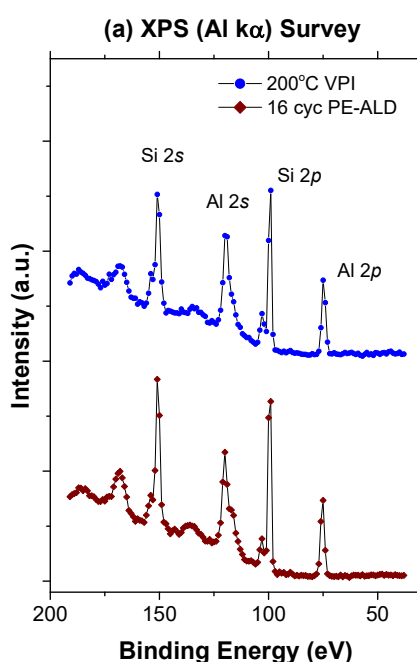


Figure 5.4: (a) XPS survey spectrum segment covering the Al 2p – Si 2s region. The PEALD process required only 16 ALD cycles for the film's Al 2p/Si 2p ratio to closely match that of the VPI alumina films.

The conclusions drawn from the ellipsometry, EDX and TEM results correlate with what was observed via XPS. The in-situ capabilities of the FlexAl – XPS system allows for the acquisition of ALD films of a specific thickness without the need to remove the sample from vacuum. By scanning a silicon substrate after a small number of PEALD cycles, it was found that a 16 cycle recipe produced alumina films with an Al 2p/Si 2p ratio that was almost identical to the films produced via a 100°C, 200°C and 250°C VPI process, as observed in Figure 5.4. As discussed in chapter 2, XPS is a quantitative technique, with the results from Figure 5.4 suggesting that similar amounts of aluminium are present in the 16 cycle ALD and VPI films. However, as the TEM showed, a further 19 cycles of

TMA PEALD are required for the film to be of roughly equal thickness to the VPI films.

This provides further confirmation that the VPI films are less dense with a higher degree of porosity.

Table 5.1: Thickness calculations of the SiO₂ interlayer and alumina film for a range of VPI and PEALD samples. The refractive index at $\lambda = 650$ nm is also shown. The thickness of the SiO₂ was obtained via XPS. The alumina film thickness was measured by TEM after accounting for t_{SiO_2} . This allowed for the determination of all thicknesses via TEM, except for the 200°C VPI sample, which was obtained via ellipsometry using the optical constants determined from the 100°C and 250°C samples.

Sample	t_{SiO_2} (nm)	t_{alumina} (nm)	$n_{\text{alumina}} (\lambda = 650 \text{ nm})$
100°C VPI	0.7	5.1	1.28
200°C VPI	0.7	5.5	1.29
250°C VPI	0.7	5.4	1.29
PEALD	0.6	5.5	1.48

GA-FTIR absorbance spectra of the alumina films in Figure 5.5 (a) exhibit almost identical behaviour, with each sample containing significant amounts of OH in the film. The notable shoulder at approximately 3400 cm^{-1} is well known to represent OH stretching.¹⁶ The peak at 1648 cm^{-1} is attributed to corresponding H₂O bending,^{17,18} while the peak at 1460 cm^{-1} is potentially associated to Al-O-H stretching.^{17,19} Adventitious carbon growth due to sample exposure to atmosphere are linked to the absorption bands at 879 cm^{-1} and 2919 cm^{-1} , which are associated with C-H bending and stretching respectively.²⁰ The peak at 1231 cm^{-1} is linked with C-O stretching.²¹

HAXPES core level spectra in Figure 5.5 (b-d) compares the PEALD film to the 250°C and 100°C VPI processed films. The Si 2*p* was fitted in accordance to the literature, with the binding energy positions and peak widths fixed (with the exception of the Si⁴⁺ position).^{22,23} All spectra have been charge referenced so that the Si 2*p*_{3/2} bulk peak (Si⁰), shown in Figure 5.5 (b), for each dataset occurs at 99.4 eV binding energy.⁹ Despite all processes using the same Si substrate, subtle differences in the Si 2*p* spectra are observed when comparing the VPI made alumina (at all temperatures) to the PEALD film. The binding energy of the component associated with the Si⁴⁺ occurs at approximately 103

eV. The intensity of this Si^{4+} peak is higher for the VPI films, with more intense Si^{3+} and Si^{1+} states witnessed also. These results cross compare well to the in-situ $\text{Si } 2p$ spectra taken immediately after processing (Figure 5.1). The plasma treatment during the polymer removal/metal oxidation process is attributed to the main cause of Si^{4+} growth, while increased Si dioxide – alumina interaction explains the increased sub oxide presence for the VPI films.^{11,12} These effects demonstrate that the VPI process has more

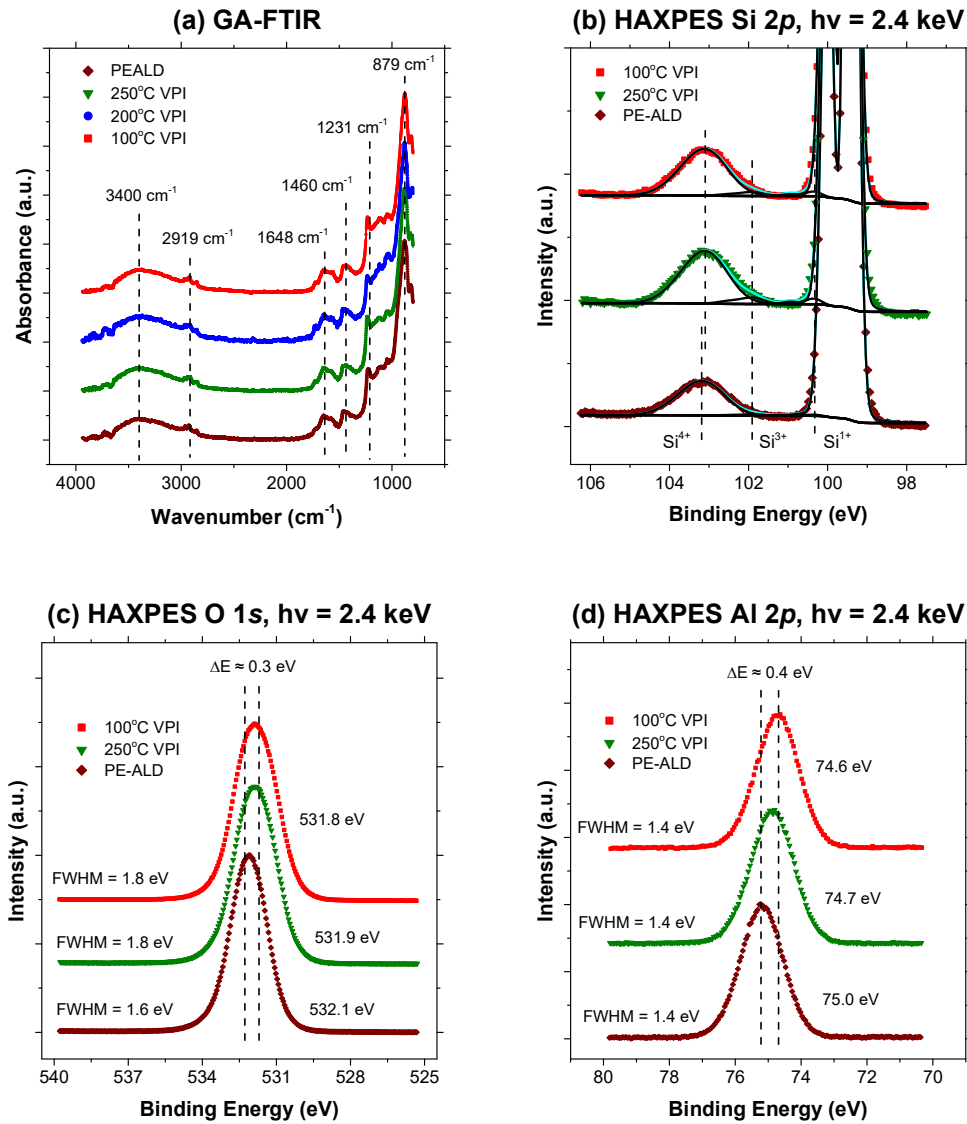


Figure 5.5: (a) GA-FTIR spectra of the PEALD and three VPI made alumina films with approximations of the main absorption peak positions. HAXPES spectra of the $\text{Si } 2p$ (b), comparing the PEALD film to the VPI alumina films at the temperature extremes. HAXPES spectra of the $\text{O } 1s$ (c) and $\text{Al } 2p$ (d) is also shown, with the binding energy positions of the spectra maxima are labelled.

impact on the SiO₂/Alumina interface than the PEALD film, which has relevance to the following CV analysis.

As seen from our previous work, no chemical difference in the alumina can be extracted between the different VPI temperatures via photoemission.²⁴ The O 1s spectra in Figure 5.5 (c) consists of a combination of Si-O (from the SiO₂ interlayer) and Al-O bonds. As was discussed in chapter 4, SiO₂ bonds are expected to occur at ~533 eV, slightly higher than reported positions of Al₂O₃ (~530–532 eV).²⁵ The higher binding energy position of the peak maxima for the PEALD sample (532.1 eV) compared to the VPI samples (~531.9 eV) is attributed to changes in the alumina film and the SiO₂ interface resulting from the different growth process. This has a secondary effect of decreasing the full width half maximum (FWHM) of the spectra as the Si-O and Al-O components overlap more. As in the O 1s spectra, a slight shift to higher binding energy is observed in the Al 2p spectra in Figure 5.5 (d) for the PEALD film, whereas no difference is observed between the two VPI samples. For the Al 2p, the peak maxima for the PEALD and VPI films occur at ~74.7 eV and 75 eV respectively. This trend in behaviour was also observed in the Al 1s spectra.

The range of binding energy positions for the Al₂O₃ in Al 2p spectra is broad, with reported positions (74.1 ± 1.0) overlapping with the hydroxides Al(OH)₃ (74.8 ± 1.0) and AlO(OH) (75.2 ± 1.2) according to the NIST database.^{26,27} Due to the presence of OH in the FTIR spectra however, it is reasonable to conclude the presence of significant hydroxyl groups in all films. Additionally, OH groups in the alumina film are reported to cause a shift to higher binding energy both in aluminium and oxygen core level spectra.^{11,12,28,29} It can therefore be concluded that the PE-ALD film contains a higher amount of hydroxyl groups, arising from the growth process within the ALD chamber. Previous work in PEALD of alumina using TMA has reported increased concentrations

of oxygen and hydrogen in the film, particularly at temperatures below 200°C.^{30,31} This effect is not attributed to differences in adsorbed water on the surface post atmosphere exposure, because the shift was observed before samples left vacuum. While carbon impurities have also been associated with higher binding energy components in metal oxides,³² this is not expected here as carbon accounts for only 6 ± 4 % of the chemical percentage of the films prior to atmospheric exposure.

5.2.3.2 Electrical Properties

In order to assess the quality of the films and their suitability for integration into microelectronic devices, current – voltage (IV) plots were obtained to compare the E_B of the VPI and PEALD methods. Weibull distributions of E_B is shown in Figure 5.6. Only datasets with a clear breakdown where the leakage current reached 0.1 mA before 10 V contributed to the distribution. The Weibull slope (β) and the 63% breakdown field value (E_α) are displayed in the plot legend. The breakdown field for the 200°C and 250°C films fall between 6.2 – 7.5 MV/cm, while the 100°C film was measured as significantly higher

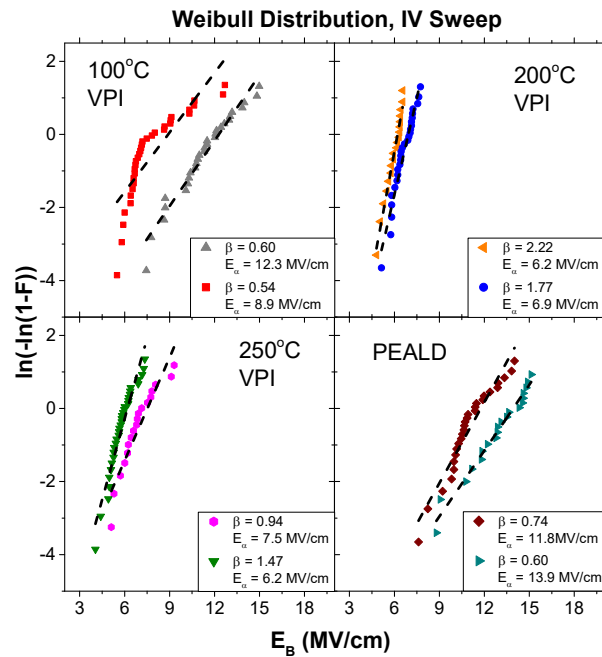


Figure 5.6: Weibull distribution of the breakdown field comparing different temperature VPI processes to PEALD films. Two samples for each process were analysed.

at 8.9 – 12.3 MV/cm. Despite the higher breakdown field, the 100°C sample has a β value of ~ 0.57 , lower than the 250°C (~ 1.21) and 200°C (~ 2.0). The PEALD film has a measured E_a value between 11.8 – 13.9 MV/cm and a β value of ~ 0.67 .

It has been reported that the breakdown field of ALD grown Al_2O_3 is typically in the range of 5 – 10 MV/cm.^{33,34} While a high breakdown field is a desired result, indicating highly insulating Al_2O_3 has been obtained via the ALD method, caution must be applied as the capacitors are effectively a bi-layer oxide stack. The presence of an interlayer of SiO_2 is expected to have an impact on the breakdown field even at thicknesses below 1 nm,³⁵ with increasing breakdown fields as the SiO_2 interlayer increases. Our results show the breakdown field of the 250°C and 200°C fall within the expected range, whereas the 100°C exceeds this, but possesses the lowest β value, indicating this process temperature is the most inconsistent electrically. The 200°C device had the highest β value, surpassing that of the tested PEALD film (but lower in E_a).

CV profiles taken at 1 MHz and 120 kHz are shown in Figure 5.7 (a) and (b) respectively, where each sample was scanned from inversion to accumulation (trace) and back (retrace). The CV profile for the 100°C VPI film was impacted by a significant amount of hysteresis. This hysteresis is linked to trapped charge in the film, which is causing this film to have a lower accumulation capacitance (C_{acc}). This result may also explain the high E_B and inconsistent behaviour observed of the 100°C VPI film for the IV analysis. A notable feature from Figure 5.7 is that the level of CV hysteresis for the 200 °C and 250 °C VPI samples is lower than the PEALD sample, indicating a lower density of defects in the 200 °C and 250 °C VPI samples which have capture and emission time constants longer than the time associated with the CV sweep.

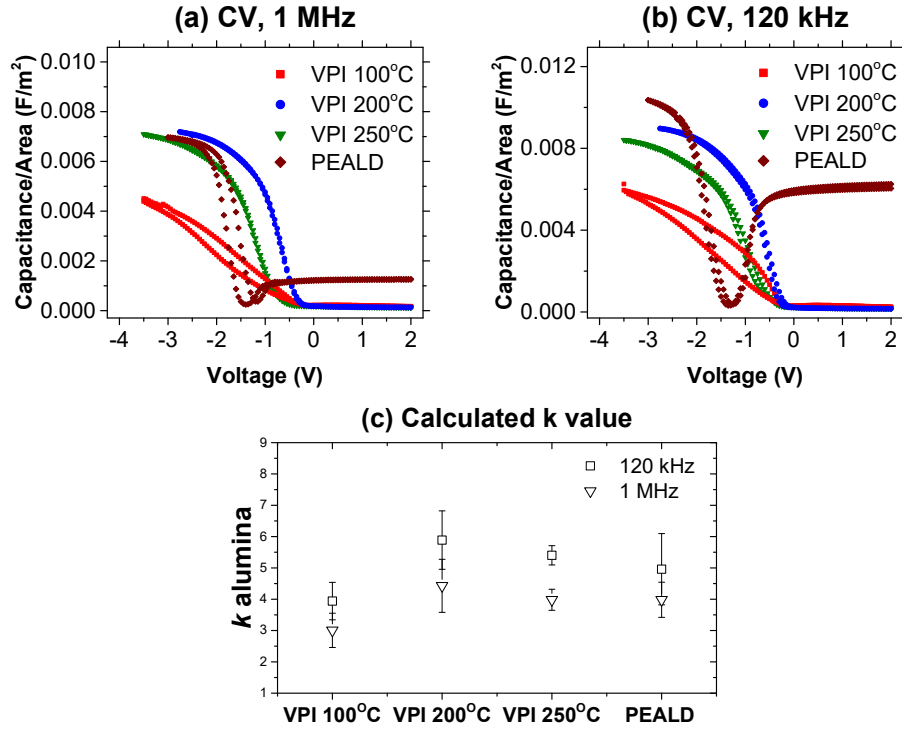


Figure 5.7: Sample CV profiles of the VPI and PEALD films recorded at (a) 1 MHz and (b) 120 kHz. The calculated k value for each frequency set is shown in (c). This was obtained by assuming the k value of the SiO_2 interlayer to be 3.9.

The k value for each alumina film is also shown in Figure 5.7 (c). This was determined using the following equation:

$$k_{\text{alumina}} = \frac{t_{\text{alumina}} C_{\text{alumina}}}{\epsilon_0 A} \quad (5.2)$$

Where C_{alumina} represents the capacitance attributed to the alumina layer of the MOSCAP device. This was calculated from:

$$\frac{1}{C_{\text{alumina}}} = \left(\frac{1}{C_{\text{acc}}} - \frac{1}{C_{\text{SiO}_2}} \right) \quad (5.3)$$

Where C_{SiO_2} was calculated theoretically, using the thickness as resolved in Figure 5.4, and with the assumption that the k value for the SiO_2 layer for both films was 3.9.³⁶ C_{acc} is the accumulation capacitance determined from the CV sweep.

A slight increase in C_{acc} and thus k value was seen for all films when comparing the 120 kHz sweep to 1 MHz in Figure 5.7 (c). While it was desired to perform further sweeps at lower frequencies, the VPI films were strongly affected by leakage as observed in Figure 5.8. The calculated k value for the PEALD film at 120 kHz was determined 5.0 ± 1.1 , which was surpassed by the VPI 250°C (5.4 ± 0.3) and VPI 200°C (5.9 ± 0.9) films. The VPI 100°C was lower at 3.9 ± 0.6 , but disregarded due to the large amount of trapped charge. This trend in behaviour was mirrored for the 1 MHz sweeps. While smaller contacts are desired for a potentially more accurate assessment of the true κ value, the ability of the VPI approach to compete with the PEALD film is observed.

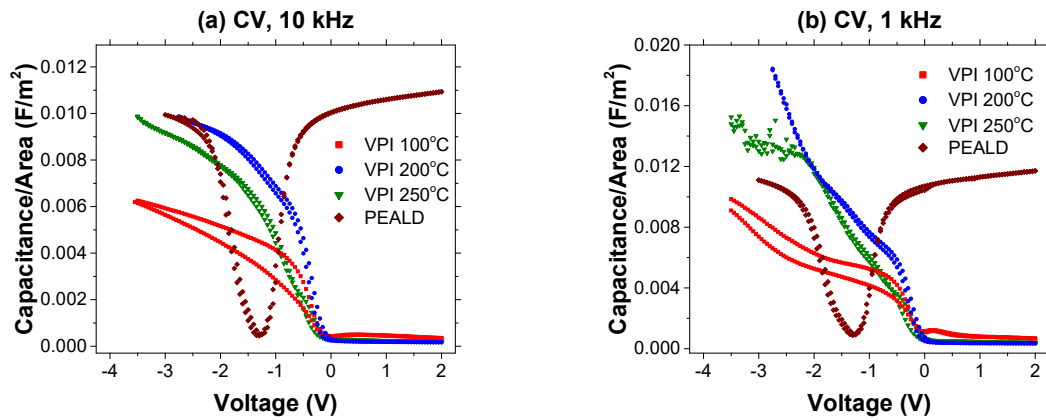


Figure 5.8: (a) 10 kHz and (b) 1 kHz CV profiles for alumina films. A clear accumulation region, particularly for the VPI processed films, is not observable at lower frequencies.

All VPI films contained an extended transition from inversion to accumulation, when compared to the PEALD film. This suggests a higher concentration of D_{it} are present via the VPI approach.^{5,37,38} This correlates with the observations seen in the Si 2p analysis in Figure 5.1 and Figure 5.5 (b) – the impact that the VPI process has at the Si/SiO₂/alumina interface, at any temperature, causes a degradation in the performance of the VPI films as capacitors.

It is also noted that a significant inversion capacitance is observed on the PEALD film, despite the high frequency range used. This is not expected for typical minority carrier

lifetimes in silicon,³⁹ and has been previously attributed to ‘peripheral inversion’ where charge exists in the oxide (both at the surface and within the layer) in the region outside the area under the gate electrode.⁴⁰ This effect has previously been witnessed on Al₂O₃ on Si processed via ALD, at annealing temperatures of 500°C.⁴¹ Combined with the negative flatband shift seen only in the PEALD film, there appears to be an abundance of positive charge in the ALD-made sample. This is despite the use of O₂ plasma for both processes, and the increased hydroxyl presence observed via HAXPES in the PEALD film.

5.2.4 Conclusions

In summary, this work provides insight into the current standing of metal oxides processed via P2VP VPI at and above its T_g compared to films synthesised using industry standard methods. A combination of in-situ XPS, TEM, EDX and ellipsometry confirmed the presence of uniform alumina films via the VPI approach, which was less dense than conventional PEALD films. GA-FTIR analysis revealed no significant variations between the VPI processes, despite a temperature range of 100 – 250°C investigated. All films contained hydrogen and excess oxygen in the film, with HAXPES analysis showing that the PEALD processes at the same temperature region as VPI processes produce alumina with slightly more OH groups. However, it was also observed that the Si/SiO₂/alumina interface is impacted during the VPI process.

Our results also show that although surface characterisation methods reveal good correlation between the VPI films in the chosen temperature range, the potential effects of temperature on the electrical performance can be significant in light of the desired application of the film. Lower temperature VPI processes appear to yield higher E_B values than higher temperature processes, however undesirable effects such as a large E_B

distribution, low C_{acc} and a high concentration of trapped charge become apparent. The temperature region of 200 – 250°C yielded films with an acceptable breakdown and capacitance values. While an increase of the E_B of these films is required to match the PEALD reference, the small distribution of values demonstrates that the VPI technique can obtain highly consistent devices. This may be envisioned through the densification of the metal oxides designed from the VPI approach, alongside a less intrusive polymer ashing process. While the C_{acc} and k values for the higher temperature VPI processes were within the same range as observed for the PEALD film, all VPI CV sweeps were stretched out and indicative of a large amount of interface traps present in the film.

To take further advantage of the VPI approach, it is envisioned that discrete alterations to the infiltration process must be made to improve the interface and densify the VPI made films. Nonetheless, the results presented here are very promising, as this highly area selective technique can produce alumina films that have electrical properties that closely resemble PEALD films in a similar temperature regime.

5.3 Liquid Phase Hafnium Oxide

The development of the liquid phase approach by our collaborators at AMBER leads to the characterisation of hafnium oxide films developed from the liquid phase, polymer-infiltration approach of similar design to the process as described in chapter 3. Hafnium and zirconium oxide were studied through AFM, XPS and TEM/EDX analysis and were shown to conformally cover the top/bottom/sidewalls of trenches across a patterned silicon nitride substrate.⁴² The use of P4VP instead of P2VP as a successful infiltration medium across a complex topographical surface confirmed the successful infiltration of the hafnium and zirconium salts (hafnium chloride and zirconium oxynitrate hydrate, respectively), with no issues concerning uniform coverage as observed for the copper salt solution in chapter 3. The process was also area selective, with no metal oxide developed on surfaces where PS or no polymer was present.

This section assesses the electrical properties of hafnium oxide, a high-k dielectric, designed from this liquid phase approach. As in section 5.2, the objective of this study is to validate this method as a successful route to synthesise films of high capacitance with an acceptable breakdown field. Complementary HAXPES is used to compare the properties of the film to a PEALD film.

5.3.1 Experimental Details

5.3.1.1 Materials

P4VP powder (5 kg/mol, PDI: 1.28) was dissolved in THF to form a 0.2 wt% solution and prepared onto O₂ plasma treated native silicon as described in section 2.8. Metal infiltration into the P4VP film was achieved through the liquid phase technique as described in chapter 3, and involved the spin-coating (room temperature, 3000 rpm, 30 s) of a HfCl₄ salt containing solution (0.5 wt % in ethanol) onto the polymer brush. The

polymer removal/metal oxidation was achieved by using an inductively coupled plasma source located on an Oxford Instruments FlexAl ALD system. The samples were heated to 200 °C and subsequently exposed to a 20 minute, 300 W O₂ plasma. The flow of O₂ was maintained at 100 sccm and the pressure during the plasma operation was set to 40 mTorr.

The PEALD films were grown on native silicon oxide in the FlexAl ALD system. Prior to deposition, samples were ultrasonicated in IPA and blown dry with compressed N₂, before being placed into the PEALD chamber and heated to 250 °C for 20 minutes at 200 mTorr under a constant 80 sccm Ar flow. The PEALD deposition consisted of a 1.6 s HfCl dose, assisted by a 200 sccm Ar flow through the bubbler. The chamber pressure was set at 80 mTorr. The subsequent precursor purge was then followed by a 6 s O₂ 300 W plasma, of which 60 sccm of O₂ was permitted to flow into the chamber. The growth per cycle (GPC) of this process was estimated at 0.7 Å/cyc.

5.3.1.2 Characterisation

In-situ XPS and post processing HAXPES measurements were obtained in the same manner as described in section 5.2.2. All XPS/HAXPES spectra analysis was performed using the software AAnalyzer.⁸ All fitted spectra used a Shirley Sherwood type background and a Voigt type curve profile, with spectra shifted so that the Si 2p_{3/2} (bulk) peak for each dataset was located at 99.4 eV.⁹

Hafnium oxide thickness was determined via a Woollam XLS-100 ellipsometer. The *P4VP HfO_x* films was measured as 6.6 ± 0.54 nm. The growth per cycle (GPC) of the *PEALD HfO_x* process was estimated at 0.7 Å/cyc. The silicon oxide interlayer (between the hafnium oxide and silicon bulk) thickness was obtained by considering the intensities of the Si⁰ and Si^{1+/2+/3+/4+} in the Si 2p XPS spectra.¹⁰ This was measured as 1.9 ± 0.04 nm

and 1.1 ± 0.06 nm for the *P4VP HfO_x* and *PEALD HfO_x* samples respectively. The slightly thicker silicon oxide interlayer for the *P4VP HfO_x* samples arose from the plasma step for silicon -OH termination for polymer grafting.

For electrical characterisation, metal contacts were fabricated onto the hafnium oxide samples using a combination of direct write maskless lithography and metallisation by evaporation. The metal oxides were spin coated (3000 rpm, 60 s) with 200 μ L of S1813 photoresist, followed by a 2 minute 180 °C bake, before being exposed to an intelligent micro patterning (IMP) tool. The IMP ensures the output from a UV lamp is directed towards a pixelated mirror array, in which individual pixel mirrors can be switched to reflect the incoming beam on to the sample to be exposed. This allowed for a CAD pattern (in this case a large array of 50 and 20mm square contacts) to be projected onto the photoresist coated sample. This obviates the requirement for a mask which is required in conventional UV aligners, and allows the user to continually change and optimise the pattern.

After exposure, the sample was developed for 45 seconds in MF319 developer so that the exposed photoresist is removed, and the contact array is now replicated in the remaining photoresist. The sample is then metallised in a Temescal FC2000 evaporator. In this application, the sample is mounted on a planetary, and a deposition of 5 nm Ti followed by 50nm Au is carried out. The final step, known as “lift-off”, involves immersing the sample in acetone using very gentle manual agitation, followed by IPA rinse and OFN dry. This dissolved the remaining photoresist, now coated with the metal, thereby removing or lifting off the metal outside the contact array. In those areas where there is no photoresist (ie the patterned contact array), the metal remains on the substrate, forming the contacts which allow electrical probing of the underlying film. Finally, all samples

were annealed in a H_2 ambient at 400 °C for 30 minutes prior to electrical testing to reduce the impact of charging effects during measurements.

The Ti/Au contacts greatly improves the quality of the MOSCAP structures compared to the Cu contacts used in section 5.2. This is evident in the optical microscope images in Figure 5.9, which shows (a) the Cu contacts designed by the silicon masking approach as outlined in section 5.2 and (b) the Ti/Au contacts processed in this section. The use of a photoresist based patterning procedure for the Ti/Au process allows for smaller contacts to be deposited, while also ensuring a high degree of accuracy was maintained. This is in comparison to the Cu contact process which was hindered by the limits of drill hole size in the Si mask, with effects such as shadowing (preferential deposition of the metal on one side of the contact) occurring from the Cu evaporation technique.

The Ti/Au contacts deposited onto the VPI and PEALD hafnium oxide films were subject to a tape test to measure the surface adhesion – the post optical microscope images are

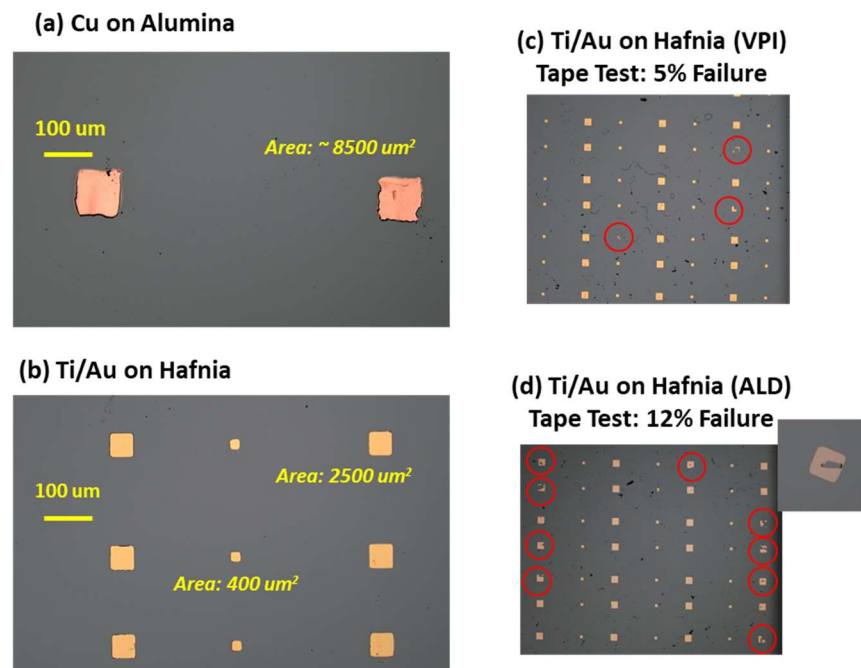


Figure 5.9: Optical microscope images of the (a) Cu contacts designed by the silicon masking approach as outlined in section 5.2 and (b) Ti/Au contacts processed in this section. The Ti/Au contacts were deposited onto hafnium oxide films made via P4VP VPI and conventional PEALD. The results of a tape test for the VPI and PEALD contacts are shown in (c) and (d) respectively. The PEALD contacts exhibited poorer adhesion, with complete delamination of the contact observed after the probe was placed onto it (d) – inset.

shown in Figure 5.9 (c) and (d) respectively. Delamination – where the contact was visible damaged after the test occurred in 5% of all contacts tested for the VPI film, while a 12 % failure rate was observed for the PEALD film (400+ sites tested for each). The poorer adhesion of the PEALD contacts was also seen when placing a probe onto the contact – the inset of Figure 5.9 (d) shows complete delamination after probe contact. Current – voltage (IV) ramping measurements were obtained using a Keithley 4200-SCS. Capacitance – voltage (CV) sweeps were performed using an Agilent 4284A precision LCR meter. All measurements were performed at room temperature.

5.3.1.3 Acknowledgements

The Ti/Au contacts were prepared by P. Gleeson at the Centre for Research on Adaptive Nanostructures and Nanodevices.

5.3.2 Results

5.3.2.1 Photoemission

In-situ XPS of both *P4VP HfO_x* films and *PEALD HfO_x* films of a comparable thickness immediately after the O₂ plasma processing and ALD deposition, respectively, was performed to obtain stoichiometry estimations of the hafnium oxide film. This was obtained by considering the area under the curve of the entire Hf 4f core level and the Hf-O component in the O 1s fit, followed by applying atomic sensitivity correction factors.⁴³ The stoichiometry for the polymer method was calculated as HfO_{2.1±0.02}, whereas the PEALD process yielded HfO_{2.0±0.02}. The polymer approach thus obtains near-stoichiometric hafnium oxide, yielding only a slightly more oxygen rich film when compared to the PEALD method.

Peak fitting was performed on high resolution HAXPES, with multiple sites scanned for each sample to obtain standard deviation in peak fitting parameters. The Si 2p spectra (Figure 5.10) for both oxides is dominated by peaks associated with the silicon bulk (Si^0) at 99.4 eV binding energy and silicon dioxide (Si^{4+}). The Si^{4+} peak is located at 103.6 and 103.3 eV for the *P4VP HfO_x* films and *PEALD HfO_x* films respectively.

The position of the Si^{4+} in the *PEALD HfO_x* film is consistent with binding energy positions from literature. It is worth noting that this hafnium oxide was deposited on identical silicon coupons to those used in the TMA vapor phase study in section 5.2. Figure 5.1 and Figure 5.5 showed how, after the PEALD deposition of alumina, a shift to lower binding energy for the Si^{4+} was observed. Interestingly, no shift in the Si^{4+} is observed for the PEALD deposition of hafnium oxide, which suggests less alterations to the SiO_2 – hafnium oxide interface occurs. More Si^{4+} is witnessed on the hafnium oxide

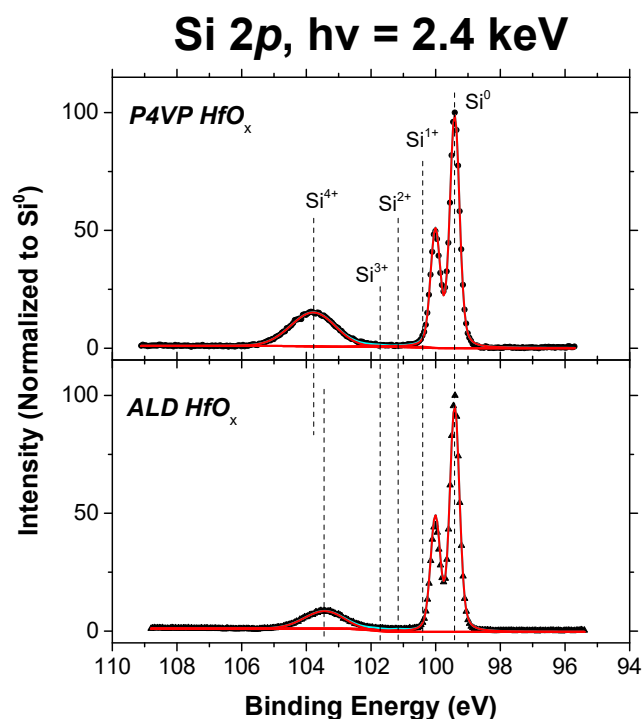


Figure 5.10: Si 2p normal emission spectra of a *P4VP HfO_x* and *ALD HfO_x* sample. The spectra have been charged referenced so that the silicon bulk position of the Si 2p_{3/2} component (labelled Si^0) occurs at 99.4 eV.

samples, but this is attributed to the extended plasma dosing step (a 6s 300W O₂ plasma was used as opposed to the 2s 300W for TMA PEALD process).

As was seen from the data in Figure 5.1 from section 5.2, it is possible to attribute some of the Si⁴⁺ growth in the *P4VP HfO_x* sample to the O₂ plasma process post hafnium infiltration. The extended O₂ treatment as opposed to the short pulses in conventional PEALD results in increased alteration of the SiO₂ interlayer at its interface with the metal oxide. The main contribution however must be attributed to the -OH termination plasma treatment of the silicon pre polymer grafting.⁴⁴ This also explains the observed shift to higher binding energy, which was not witnessed in the alumina films from the previous section as a piranha treatment was used.

The Hf 4f spectra for the two oxides are shown in Figure 5.11 (a). The spectra was fitted with doublet peaks, with the spin orbit splitting between the 4f_{5/2} and 4f_{7/2} set at 1.65 eV (a fixed area ratio of 3:4 was used).^{45–47} The position of the main 4f_{7/2} component was located at 17.7 ± 0.04 eV and 17.5 ± 0.07 eV for the *PEALD HfO_x* and *P4VP HfO_x* film respectively. These positions are in good agreement with a range of values (~17.6 eV) from studies concerning the growth of HfO₂ via PEALD at temperatures ≤ 350 °C.^{46–49} As witnessed in the alumina films, the main peak of the hafnium occurs at a slightly higher binding energy position for the PEALD film. This can be attributed to more hydroxyl groups present in the films as what was concluded with the alumina PEALD/VPI comparison in the previous section. Alternatively, a shift to higher binding energy in peaks associated with Hf⁴⁺ have previously been attributed to the addition of oxygen to vacancies and unstable bonds.^{50,51} However these conclusions are generally made when discussing HfO₂ grown at higher temperatures – where there is crystal structure present in the deposit – and it is noted that these Hf 4f spectra occur at a lower binding energy value (~16.7 eV) than those presented here.^{25,51–54} As discussed previously,

both PEALD and liquid phase hafnium oxide films in this study are exposed to process temperatures of 200°C during hafnium oxidation, and it is accepted that low temperature hafnium oxide processes using HfCl generate amorphous films.⁵⁵ As there is no crystal structure, it would be impossible to define peaks that have ‘lattice defects’. Similarly, the hypothesis that the high binding energies are attributed to more OH groups in these films is supported by other data, as significant OH was detected by GA-FTIR spectroscopy in both films, which can be linked to the oxygen rich environments of both processes.

Both the *PEALD HfO_x* and *P4VP HfO_x* films have a secondary peak, located at 18.1 ± 0.10 eV and 18.2 ± 0.03 eV respectively. While barely detectable in the PEALD film, it is of a much stronger intensity for the *P4VP HfO_x* film. Interestingly, by performing an off-angle HAXPES analysis, it is noted that this component decreases in intensity –

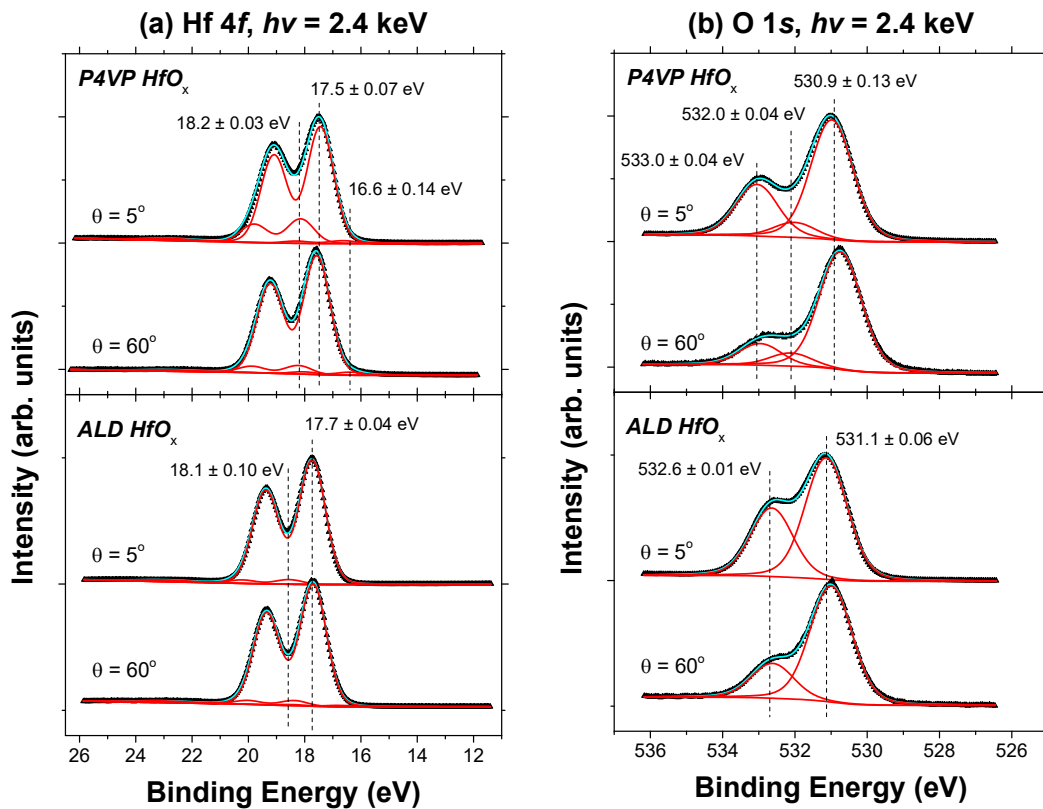


Figure 5.11: Hf 4f (a) and O 1s (b) spectra of a P4VP HfO_x and ALD HfO_x sample. Multiple sites were scanned so as to obtain standard deviations in the binding energy positions. Off angle (surface sensitive) scans at $\theta = 60^\circ$ were also performed.

suggesting that this chemical environment is present deeper in the oxide film. The binding energy position of this peak is within the same binding energy region as components attributed to hafnium silicates,^{46,56} which agrees with the angular dependence of this peak. It can be concluded that, like in the alumina films generated from the VPI approach, significant interaction between the metal and SiO₂ interface occurs as a result of the polymer removal O₂ plasma step. A minor component located at 16.6 ± 0.14 eV is also included in the fit for the *P4VP HfO_x* film, attributed to a lower oxidation state of hafnium oxide.

Figure 5.11 (b) shows the O 1s spectra for the two oxide films. Si-O bonding was attributed to the peak at 532.6 ± 0.01 eV and 533.0 ± 0.04 eV for the *PEALD HfO_x* and *P4VP HfO_x* film respectively. Both positions fit in the binding energy range associated with SiO₂,^{57–59} with the higher energy for the *P4VP HfO_x* associated with the plasma treatment that the substrate was exposed to pre polymer grafting.^{44,60} The largest peak, located at ~531 eV for both films, was associated with O²⁻ anions in HfO₂. As in the Hf 4f spectra, slightly more variation in the position of the peak was observed for the *P4VP HfO_x* sample. A final peak at ~532 eV is required for adequate fitting of the *P4VP HfO_x* spectra. The presence of a secondary, higher BE component in metal oxide O 1s spectra is common in XPS literature,⁵⁰ previously attributed to hydroxyl groups,^{29,52,61} carbon impurities³² and defects in the metal oxide,^{62,63} or, as in this case, silicates (Hf-silicate).^{64,65}

The photoemission analysis reveals several important chemical properties of the *P4VP HfO_x* film. Firstly, the film has a favourable oxygen to hafnium ratio, being slightly more oxygen rich when compared to conventional ALD films. The presence of hydroxyl groups appears to be substantial in both types of amorphous films, with the higher binding energy positions in the PEALD films suggesting that, like the VPI alumina study, the liquid phase

infiltration mechanism incorporates less OH. An increased interaction between the SiO₂ and hafnium oxide interface is clearly visible, which must be addressed in future studies in order to improve the resulting CV profile behaviour.

5.3.2.2 Electrical Properties

IV sweeps from 0 – 10 V were performed on a large array of sites (200+) across 4 P4VP HfO₂ samples to obtain electric field breakdown. A filter was applied at 2 V, with sites having a leakage current significantly different from the median (0.27 nA) discarded. Additionally, all samples with no clear breakdown were discarded. With these measures in place, approximately 60 % of measurements contributed to the resulting analysis.

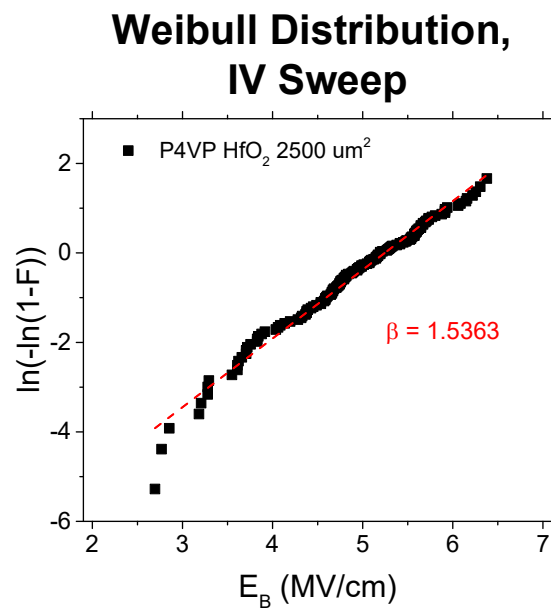


Figure 5.12: Weibull distribution of room temperature breakdown field for the P4VP HfO_x and ALD HfO_x, obtained through IV sweeps.

The resulting distribution plotted in Figure 5.12 reveals an E_a value of 5.2 MV/cm. This value falls in the expected E_B range for HfO₂ films ~4-8 MV/cm,^{66–69} however caution must be applied due to the presence of the silicon oxide interlayer. The β value was determined as 1.54, which is close to the β range for the best performing alumina film designed via P2VP VPI in section 5.2. The results are indicative of the liquid phase

approach being capable of producing oxide films that are within the same reliability range as the vapor phase regime. This is a highly promising outcome due to the greater availability of successful infiltration molecules via the liquid approach.

To obtain capacitance and dielectric values of the films, multi frequency CV profiles were obtained. The use of smaller metal contact structures significantly improved the reproducibility and performance of the devices tested. Unlike the Cu contacts as used for the VPI study in the previous section – which had somewhat relatable results in the frequency range of 120 kHz – 1 MHz – it was observed that CV sweeps in the range of 10 kHz – 1 MHz exhibited similar behaviour for the Ti/Au contacts as seen in Figure 5.13

(a). Figure 5.13 (b) displays 1 MHz CV profiles of 2500 μm^2 and 400 μm^2 MOSCAP

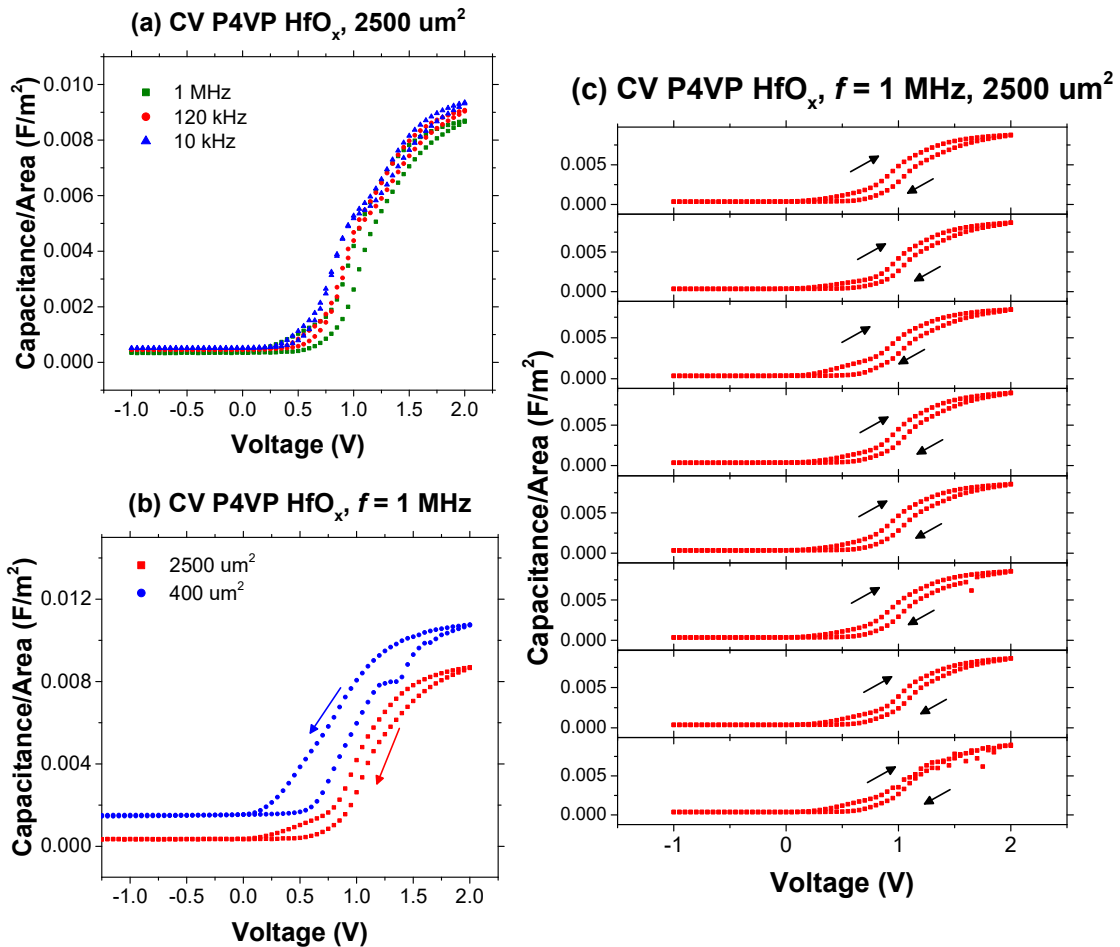


Figure 5.13: CV plots of (a) one site across a 10 kHz – 1 MHz frequency range, (b) two sites of different areas at 1 MHz and (c) different sites of the same area at the same frequency.

structures for the *P4VP HfO₂* samples. Accumulation, depletion, and inversion regions are clearly visible. Significant hysteresis is visible across both sweeps, indicating the presence of charges occurring in the MOSCAP structure. As was witnessed for the alumina films created from polymer VPI, the transition from inversion to depletion is gradual, suggesting the presence of interface states.³⁷ This arises from the interaction observed between the hafnium oxide and the SiO₂ spectra as witnessed in the HAXPES analysis. Additionally, the CV profiles were reproducible across other sites, as is observed in Figure 5.13 (c), presenting strong evidence that the liquid phase approach can create conformal metal oxide films.

By considering the SiO₂ interlayer (and assuming that the k value is 3.9), the k value of the hafnium oxide film can be determined from the measured C_{acc} value using equations (5.2) and (5.3). As the CV plots were highly reproducible, an estimation into the concentration of trapped charge was also determined from the voltage hysteresis in the depletion zone of the plot as in equation (2.34) (chapter 2). These results from 400 μm^2 and 2500 μm^2 are shown in Table 5.2. Amorphous hafnium oxide is reported to have a k value between 16 and 25.^{70–72} The measured k_{HfO_x} value for the 400 μm^2 devices are in good agreement with this, however the calculated N_{OT} values are considerable.⁷¹

Table 5.2: CV measurements extracted from 1 MHz CV curves.

	Area (μm^2)	C_{acc} (pF)	k_{HfO_x}	N_{OT} (cm^{-2})
P4VP HfO_x	400	4.2 ± 0.1	18.6 ± 1.5	$1.15 \pm 0.70 \times 10^{16}$
	2500	21.7 ± 0.5	12.4 ± 1.0	$0.72 \pm 0.08 \times 10^{16}$

5.3.3 Conclusion

The electrical properties of hafnium oxide films designed by the liquid phase polymer infiltration approach are determined through a mix of IV and CV measurements. The films have comparable breakdown and k values to literature values, with a respectable level of reliability that matches the VPI approach for the alumina films as seen in the

previous section. This, combined with the repeatable CV behaviour, addresses the concerns regarding film conformality mentioned in chapter 3.

One of the key limiting factors to the performance of the devices in the CV behaviour arises from the high concentration of trapped charge and interfacial states. This can be correlated to the interaction at the interface between the hafnium and silicon oxides, which is significant as observed in the HAXPES analysis. Like in the VPI study from section 5.2, a leading cause for this is the polymer removal and metal oxidation stage. A greater emphasis must be placed on this step to continually ensure all polymer is removed but resulting metal silicates are kept to a minimum.

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6 Future Work and Conclusions

6.1 Conclusions

The main conclusions arising from chapters 3 – 5 provide a solid foundation for further studies of metal infiltration into pyridine based polymer brushes, which can also be applied to BCP research. The main findings include:

Validation of the rapid, grafting-to method for polymer brush fabrication. All chapters demonstrated that the grafting-to polymer brush fabrication method was a route to producing highly coherent and functional polymer brushes such as P2VP and PS. Area activation and deactivation polymer brushes performed in their required role for several metal deposition processes. This confirmation is significant, as the grafting-to method is noticeably faster than traditional SAM area deactivation methods in ASD studies.

Confirmation of pyridine containing polymers as an active polymer for metal infiltration.

The ability of pyridine containing polymers to facilitate metal infiltration via a liquid phase approach, and subsequently allow for metal and metal oxide fabrication after polymer infiltration, was a critical finding in chapter 3, which proved this through the HAXPES study of Cu infiltration into a P2VP brush film. VPI into the pyridine films was subsequently proven in chapter 4. The basis of P2VP/P4VP as active polymers in ASD and BCP lithography – that metal infiltration was facilitated through metal-precursor interaction with the pyridinic nitrogen (because of the nitrogen lone pair) – was also shown experimentally in chapter 4, agreeing with literature sources. PVP polymers are therefore highly capable in being used as infiltration media over PMMA due to their ability to form smaller domain sizes when combined with PS in BCP architecture

Experimental proof of P4VP being more susceptible to metal infiltration over P2VP.

Another critical conclusion from chapter 4 was the experimental evidence of the superiority of P4VP over P2VP in terms of accepting a metal precursor for infiltration.

The metal intake rate of P4VP was shown to be significantly higher, which agrees with the literature that the positioning of the nitrogen in the pyridine ring effects metal incorporation.

The development of a highly area selective, TMA based process that implemented PVP as the accepting polymer. Chapter 4 also focused on the compatibility of PS brushes, which can be used as area deactivation sites in ASD/BCP lithography. Processes where high and low intakes of Al on PVP and PS sites respectively were realised. Unique to the process in this chapter, a VPI approach was developed that required no co-reactant, further showing the reactive capability of PVP polymers, and showing the addition of a blocker polymer is not necessary to make the process area selective – the active PVP sites can be combined with bare substrates (where the addition of a co-reactant such as water is necessary for metal deposition on the bare substrate). This was also proven via liquid phase infiltration by collaborators at AMBER.

Demonstration of the potential of VPI/Liquid phase routes to create gate oxides in MOSFET technology. Chapter 5 showed the success – and challenges – of metal oxide films created by both infiltration routes for the fabrication of gate oxide films. While concerns regarding the density and interface quality need to be addressed, the ability of both methods to yield IV and CV results that were of comparable quality to conventional ALD films shows that the PVP brush infiltration method can function in their intended demanding environment.

6.2 Future Work

Based on the results, and the associated discussions and conclusions from chapters 3 – 5, several key areas of further study are required. These include increasing the pool of successful metals for polymer infiltration via VPI. Polymer VPI is a highly area selective route in ASD and BCP architecture, with the limiting drawback associated with the lack of interaction seen between precursor – polymer in the standard pressure regime for ALD processes. A potential solution is the addition of seed layers – such as TMA – to the polymer prior to VPI processing. The construction of more specialist chambers that allow for a greater partial pressure of precursor to be exposed to the polymer can also potentially solve the issue of infiltrating and entrapping larger precursors commonly used for high- k dielectric formation in ALD.

Alteration of the polymer brush thickness is another important future research direction. The work presented in this thesis is concerned with polymer films of thicknesses generally no greater than ~ 5 nm. While in the required thickness regime for the semiconductor industry, applications for a thicker metal/metal oxide may be required. A thicker polymer film may also provide more information regarding the success of metal infiltration, the homogeneity of the film and allow for measurements such as the density (see below) to be extracted. It has been observed that a higher molecular weight polymer yields a thicker polymer brush. However, it was noted at the AMBER institute that the higher molecular weight of PVP (above 6K) results in the formation of crystal ‘islanding’ instead of monolayer coverage. This phenomenon can be attributed to weak intermolecular interactions or pi-pi stacking between the pyridine molecule inside the solution. As such, the desire to fabricate thicker polymer brushes of a high- χ value in PS BCP systems is a process feature of the grafting-to method that needs to be addressed, either through manipulation of the current PVP process or using other polymer materials.

It was suggested in chapter 5 that the density of VPI fabricated metal oxides was lower than conventional ALD films. This could be a critical factor in the electrical reliability of the metal oxides – with less dense films suggesting a high porosity. This measurement however was only suggested through a combination of TEM and ellipsometry measurements – and a more robust method of density extraction can be obtained through X-ray reflectometry (XRR). Further understanding, and improvement, of the densities of polymer VPI/liquid phase fabricated metal oxides is thus required. A detailed analysis of the densities of the resulting metal oxide films will allow for more comparative work between liquid and VPI based methods, but crucially relies upon the obtainment of thicker metal oxide films (>10 nm).

A somewhat overlooked aspect to polymer ASD/BCP architecture is the effect of the polymer removal and metal oxidation process. This was also highlighted in chapter 5, where the interface between the alumina/hafnia and the Si substrate was of poorer quality (a higher interface state density) than conventional ALD. The chapter concluded with the requirement to improve the metal oxide – substrate interface post polymer removal. This is attributed to the formation of aluminium or hafnium silicate generation, resulting from the O₂ plasma process that removes the polymer. The O₂ plasma process used in chapters 4 and 5 was highly desirable over the UV/Ozone used in chapter 3 due to the rapid and highly effective results (in terms of carbon and nitrogen removal). Little in the way of silicates was observed in Chapter 3 after the UV/Ozone process however, potentially suggesting such an ashing process may be more suited for ASD and BCP processes. For successful integration into processes such as gate oxide fabrication, the improvement of this interface is vital.

Finally, the investigation into other novel, high- χ polymers is desired. A major consequence of this work is the validation of PVP polymers for ASD and BCP integration.

Both P2VP and P4VP were shown to incorporate a range of metals in VPI and liquid phase processes, which, combined with the high- χ values that can be potentially taken advantage of in BCP structures with PS, gives PVP a unique advantage over PMMA. The infiltration mechanisms – and analysis techniques and procedures – can however be applied to a range of polymers such as PEO and PDLA (both of which are potentially infiltration receptive and have a higher χ parameter in BCP systems with PS compared to PMMA).