

Growth and characterisation of sustainable transparent conducting oxides

A thesis submitted to Trinity College Dublin, the University of Dublin
for the degree of Doctor of Philosophy

Peter J. Callaghan
April, 2025



Trinity College Dublin
Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

Declaration

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and apart from the advice, assistance and joint effort acknowledged and mentioned in the text, it is entirely my own work.

I agree to deposit this thesis in the University's open access institutional repository or allow the library to do so on my behalf, subject to Irish Copyright Legislation and Trinity College Library conditions of use and acknowledgement

I consent to the examiner retaining a copy of the thesis beyond the examining period, should they so wish (EU GDPR May 2018)

Name Peter Callaghan

Date: 31/10/2024

Dedicated to Joan Sunderland and Dodie Callaghan.

Truly standing upon the shoulders of giants

Summary

In this thesis the growth and optoelectronic properties of the ternary n-type amorphous zinc tin oxide (a-ZTO) and p-type crystalline V_2O_3 are discussed in the context of providing suitable and sustainable candidates for transparent conducting oxide applications.

As an amorphous ternary oxide the defect chemistry that controls the optical and electronic properties of a-ZTO is complex. While studies have investigated how the Zn/Sn cation ratio affects the charge carrier concentration and mobility, however how these key properties vary in the low thickness regime is not fully understood. a-ZTO thin films were grown by non-reactive magnetron sputtering, then using a combination of UV-vis spectrophotometry and Hall effect measurements the optoelectronic properties of these films were probed as the thickness was varied. Below 10 nm, the electrical performance is seen to degrade due to reductions in both charge carrier concentration and mobility. In this same range, the optical band gap is observed to rise 0.33 eV. Using X-ray diffraction (XRD) and an *in-vacuo* sample transfer from magnetron growth chamber to X-ray photoelectron spectroscopy (XPS) the structural and chemical environments of the films were investigated and found to be consistent across the thickness range. Finally, this *in-vacuo* sample transfer method was employed again to transfer to Scanning Tunneling Microscopy/ Scanning Tunneling Spectroscopy (STM/STS) systems to probe the surface topology and the electronic band gap of the films. STS measurements observe a similar shift in the electronic band gap of the material, confirming the presence and scale of the shift.

Next, the local bonding structure in amorphous zinc tin oxide (a-ZTO) is probed to gain insight into charge carrier generation and electron mobility in the material. As an amorphous ternary oxide that acts as an intrinsic semiconductor, the defect chemistry in the material is quite complex but extremely pertinent to its performance. Using a combination of X-ray Absorption Spectroscopy (XAS) techniques at the Zn and Sn K-edges, I examine the effect varying the inter-cation ratio has on the local chemical and bonding environment of a-ZTO prepared via two growth methods; spray pyrolysis and magnetron sputtering. It is seen that a-ZTO grown by magnetron sputtering shows no changes in the chemical environment as the cation ratio is varied, meanwhile XANES analysis of spray pyrolysis grown samples shows alterations to spectra likely due to the effects caused by different precursors. Although a slight shift

in Sn-O bond length is visible between magnetron sputtered and spray grown samples no correlation could be discerned between bond length and variation in cation ratio. It is concluded that a-ZTO, while amorphous over longer ranges, is locally comprised of ZnO and SnO₂ "building blocks". An alteration in the cation ratio changes the hybridisation at the conduction band minimum resulting in the observed variation in the mobility, charge carrier concentration and band gap.

Finally, I performed a study into the growth and optimisation of V₂O₃ as a candidate p-type TCO. Initial work focused on the growth of high quality, epitaxial V₂O₃ films on (0001) Al₂O₃ substrates by reactive magnetron sputtering. High performance p-type behaviour was observed, with a Figure of Merit (FOM^G)= $455.3 \pm 45.5 \Omega^{-1}$ observed. Following this the effectiveness of Mg as a dopant in the V₂O₃ films was examined. XPS spectra confirmed the Mg presence in the films, and X-ray Diffraction (XRD) spectra showed the Mg²⁺ cations did not affect the crystallinity of the V₂O₃ lattice. However, Mg inclusion was found to have no clear impact on the optical or electrical properties of the V₂O₃ films. To investigate the Mg incorporation in the V₂O₃ films a high resolution scanning transmission electron microscopy (STEM) study was performed. This indicated the growth of both corundum and bixbyite phases in both doped and pure V₂O₃ films. Moreover the bixbyite phases was observed to grow directly on the corundum (0001) Al₂O₃ substrate. Through energy dispersive X-ray spectroscopy (EDX) mapping the Mg content was observed to be homogeneous amongst the V₂O₃ films indicating that clustering of MgO along grain boundaries did not occur. Finally, the growth of epitaxial Cu₂O thin films was investigated as suitable material to pair with V₂O₃ in order to form bilayers and nanolaminates with the goal of increasing the p-type conductivity of the composite material. Using XPS the chemical and oxidation state of the films was confirmed while XRD measurements exhibited that epitaxial Cu₂O [111] was grown on (0001) Al₂O₃ substrates. UV-vis spectroscopy measurements indicated an optical band gap of 2.2 eV, in agreement with the expected value from literature.

Acknowledgements

I am indebted to many who have helped and supported me throughout my PhD. Firstly I would like to thank Prof. Igor Shvets for giving me the opportunity to pursue a PhD, and for his guidance and mentorship over the last 4 years. I have learned an immense amount over this period and Igor's supervision has helped shape me into the researcher I am today.

I would also like to thank Dr. David Caffrey for his supervision, guidance and support. I would have been in considerably worse stead if it had not been for his advice and chats. A gentleman and a scholar.

Additionally I would like thank Dr. Kuanysh Zhussupbekov, and particularly Dr. Ainur Zhussupbekova for their generosity and support. The impact they have had on my work has been immeasurable and it is all thoroughly appreciated.

Continuing on, I would like to thank Prof. Karsten Fleischer for our academic discussions. They were sometimes challenging but always educational, and this work is all the better for them.

Next I would like to thank the Centre for Doctoral Training in the Advanced Characterisation of Materials (CDT ACM) for the help and support they provided throughout my PhD journey. There are too many people to name individually but being part of Cohort 7 has been an honour and the breadth of techniques I used in this work is a credit to the CDT's teaching. In particular, I would like to thank Prof. Valeria Nicolosi and Prof. Lewys Jones. Our pastoral care meetings were a godsend when I was feeling lost and they always dealt with our conversations with warmth and empathy.

I would like to thank Prof. Rafal Dunin-Borkowski and Dr. Janghyun Jo for hosting me during my placement at the Ernst Ruska-Centre for Microscopy in Forschungszentrum Julich. Although my time there was limited I learned so

much; both inside and outside of the lab.

I would like to thank the past and present members of the Applied Physics Research Group, especially Brian Walls. Their continued support has allowed me to develop and improve as a researcher, and their assistance and advice on various techniques has truly been invaluable.

I would like to extend a massive thank you to the lab technicians and workshop staff of the School of Physics, CRANN and the AML. In particular, Clive Downing who readily gave up his time to train me on the STEM and help me make sense of things when they inevitably became complicated than envisioned. Additionally, I would like to thank Prof. Robert J. Baker for his advice and guidance when it came to x-ray absorption spectroscopy analysis. As a newcomer to the technique having someone to verify and substantiate methods was invaluable.

I would like to thank all my friends and companions, in particular Cian, Tom, Adam and Jack. It is often said that a PhD is an individual journey, and while they could not be in the lab with me, through our (mis)adventures they invariably lightened my burden.

Finally, I would like to thank my family. My parents, Elizabeth and Eugene have never been anything but supportive of my academic journey without any judgment or expectation, and undoubtedly without their support I never would have reached this far. In addition, I would like to thank my sisters; Emma, Sarah and Roisín. The constant support and love they have provided me along this journey has been immense. I hope our coffee catch-ups continue long into the future.

List of Publications

Parts of this thesis have been previously published

1. Callaghan, P.J., Caffrey, D., Zhussupbekov, K., Berman, S., Zhussupbekova, A., Smith, C.M., Shvets, I.V.
” *Variation in Bandgap of Amorphous Zinc Tin Oxide: Investigating the thickness dependence via in-situ STS*”
ACS Omega 2024, **9**, 7262 - 7268
2. Callaghan, P.J., Fleischer. K., Caffrey, D., Zhussupbekov, K., Ansell, S., Gun'ko, Y., Shvets, I.V., Zhussupbekova, A.
” *Investigating the local bonding structure of amorphous zinc tin oxide to elucidate the effect of altering the inter-cation ratio*”
Journal of Physical Chemistry C 2024, **128**, 16733-16739

In preparation

1. ” *Functionalisation of 2H-MoS₂ with organoiodides*”
Krajewska, A.M., Callaghan, P.J., Shvets, I.V., McDonald. A.R.

List of abstracts presented

1. *Band gap variation in amorphous zinc tin oxide thin films*
Peter J. Callaghan*, David Caffrey, Kuanysh Zhussupbekov, Samuel Berman, Ainur Zhussupbekov, Igor V. Shvets.
EMRS fall meeting, Warsaw, Poland, September 2022
2. *Band gap variation in amorphous zinc tin oxide thin films*
Peter J. Callaghan*, David Caffrey, Kuanysh Zhussupbekov, Samuel Berman, Ainur Zhussupbekov, Igor V. Shvets.
TCO TOEO, Crete, Greece, October 2022
3. *Investigating the local bonding structure of amorphous zinc tin oxide by X-ray absorption spectroscopy*
Peter J. Callaghan*, Karsten Fleischer, David Caffrey, Kuanysh Zhussupbekov, Stuart Ansell, Yurii Gun'ko, Igor V. Shvets, Ainur Zhussupbekova.
TCO2024, Leipzig, Germany, September 2024
4. *Heterostructures for advancing properties of p-type TCOs: Growth and characterisation of V_2O_3/Cu_2O bilayer*
Theo Bolger*, Peter Callaghan, Brian Walls, Igor V. Shvets.
TCO2024, Leipzig, Germany, September 2024
5. *Crystallographic structure and electrical and optical properties of $V_2O_3-Cu_2O$ bilayers*
Brian Walls*, Peter Callaghan, Theo Bolger, Igor V. Shvets.
TCO2024, Leipzig, Germany, September 2024

Contents

1	Introduction	1
2	Literature review	5
2.1	Overview of transparent conducting oxides	5
2.1.1	Band Theory	5
2.1.2	Moss-Burstein shift	7
2.1.3	Band structure considerations	7
2.1.4	Reflection edge	8
2.1.5	Figure of merit	9
2.2	N-type TCOs	11
2.2.1	Historical overview	11
2.2.2	Binary oxide TCOs	11
2.2.3	Multicomponent TCOs	12
2.2.4	Issues with indium	13
2.2.5	In free alternatives	15
2.3	P-type TCOs	19
2.3.1	Motivation and historical overview	19
2.3.2	Doping binary oxides p-type	20
2.3.3	Cu 3d ¹⁰ based materials	21
2.3.4	Oxychalcogenides	23
2.4	Transparent Conducting Materials (TCMs)	24
2.4.1	Copper Iodide	25
2.4.2	Boron Phosphide	26
2.5	Correlated metals as TCOs	27

3	Methodology	33
3.1	Thin film synthesis	33
3.1.1	Sputtering	33
3.1.2	Magnetron sputtering	34
3.1.3	RF Magnetron sputtering	35
3.1.4	Reactive sputtering	37
3.1.5	Structure of the deposition chamber	39
3.1.6	Spray pyrolysis	40
3.2	Optical characterisation	42
3.3	Electrical characterisation	44
3.4	X-ray characterisation	47
3.4.1	X-ray diffraction	47
3.4.2	Grazing Incidence XRD	49
3.4.3	X-ray Reflectometry	49
3.4.4	X-ray Photoelectron Spectroscopy	50
3.5	Synchrotron X-ray characterisation	54
3.5.1	X-ray Absorption Spectroscopy	54
3.5.2	X-ray Absorption Near Edge Structure	55
3.5.3	Extended X-ray Absorption Fine Structure	57
3.5.4	XAS data analysis	58
3.6	Microscopic characterisation	60
3.6.1	Scanning Tunneling Microscopy	60
3.6.2	Scanning Tunnelling Spectroscopy	61
3.6.3	Scanning Electron Microscopy	62
3.6.4	Scanning Transmission Electron Microscopy	63
3.6.5	Energy-Dispersive X-ray Spectroscopy	64
3.6.6	Electron Energy Loss Spectroscopy	65
4	Band gap variation in amorphous zinc tin oxide thin films	67
4.1	Introduction	67
4.2	Deposition	68
4.3	Physical characterisation	70
4.4	Electrical measurements	75
4.5	Optical measurements	76
4.6	STS measurements	80

4.7	Conclusion	83
5	Investigating the local bonding structure of amorphous zinc tin oxide by X-ray absorption spectroscopy	85
5.1	Introduction	86
5.2	Deposition	87
5.3	Physical characterisation	88
5.4	XANES at Zn K-edge	93
5.5	XANES at Sn K-edge	95
5.6	EXAFS at Sn K-edge	98
5.7	Conclusion	102
6	Exploring V_2O_3 as a p-type TCO	103
6.1	Introduction	103
6.2	Deposition	106
6.3	Growth of V_2O_3 films	107
6.4	Mg doping of V_2O_3	111
6.5	Electron Microscopy of V_2O_3	115
6.6	Growth of Cu_2O	123
6.7	Conclusion	127
7	Conclusions and Future Work	131
8	Appendix	137
8.1	Section I - Thickness study on a-ZTO	137
8.2	Section II - XPS and XAS study on a-ZTO	142
8.3	Section III - Exploring V_2O_3 as a TCO	146

Glossary

Abbreviations

TCO	-	Transparent Conducting Oxide
OLED	-	Organic Light Emitting Diode
ITO	-	Indium Tin Oxide ($\text{Sn:In}_2\text{O}_3$)
AZO	-	Aluminium Zinc Oxide (Al:ZnO)
STM	-	Scanning Tunnelling Microscopy
STS	-	Scanning Tunnelling Spectroscopy
XANES	-	X-ray Absorption Near Edge Structure
EXAFS	-	Extended X-ray Absorption Fine Structure
ZTO	-	Zinc Tin Oxide
a-ZTO	-	Amorphous Zinc Tin Oxide
IGZO	-	Indium Gallium Zinc Oxide
RF	-	Radio Frequency
DC	-	Direct Current
DOS	-	Density of States
UV-vis	-	Ultraviolet-visible
VB	-	Valence Band
VBM	-	Valence Band Maximum
CB	-	Conduction Band
CBM	-	Conduction Band Minimum
XPS	-	X-ray Photoelectron spectroscopy
IQW	-	Infinite Quantum Well
FWHM	-	Full-Width Half Maximum
FoM	-	Figure of Merit
TFT	-	Thin Film Transistor
HTL	-	Hole Transport Layer
ETL	-	Electron Transport Layer
CMVB	-	Chemical Modulation of Valence Band
TCM	-	Transparent Conducting Material

MIT	-	Metal to Insulator Transition
XRD	-	X-ray Diffraction
XRR	-	X-ray Reflectivity
GIXRD	-	Grazing Incidence X-ray Diffraction
SEM	-	Scanning Electron Microscopy
STEM	-	Scanning Transmission Electron Microscopy
EDX	-	Energy Dispersive X-ray Spectroscopy
EELS	-	Electron Energy Loss Spectroscopy
FIB	-	Focused Ion Beam
HAADF	-	High Angle Annular Dark Field
RSM	-	Reciprocal Space Map
RSF	-	Relative Sensitivity Factor
IMFP	-	Inelastic Mean Free Path
CCM	-	Constant Current Mode
UPS	-	Ultraviolet Photoelectron Spectroscopy
IPES	-	Inverse Photoelectron Spectroscopy

Symbols

μ	-	Carrier Mobility
ρ	-	Resistivity
σ	-	Conductivity
n_e	-	Carrier concentration
e	-	Fundamental charge of an electron
R_{Sh}	-	Sheet resistance
E_g	-	Band gap
E_F	-	Fermi level
λ	-	Wavelength
t	-	Thickness
V_X	-	Vacancy at X site
T	-	Transparency
R	-	Reflectivity
A	-	Absorption
I	-	Current

V	-	Voltage
α	-	Absorption coefficient
ϵ_0	-	Dielectric constant of free space
ϵ_r	-	Relative permittivity
Z	-	Atomic number
d	-	Interatomic spacing
2θ	-	Sum of the angle of incidence and diffraction
θ_C	-	Critical angle for internal reflection
n	-	Refractive index
h	-	Planck's constant
$\hbar$	-	Reduced Planck constant
F_L	-	Lorentz force
B	-	Magnetic field
m^*	-	Effective mass of a charge carrier
ω_p	-	Plasma frequency
Z_k	-	Renormalisation factor
U	-	Coulomb repulsion term
W	-	Bandwidth of occupied d and O 2p states
Φ	-	Work function
γ	-	Tauc coefficient
$\mu(E)$	-	X-ray absorption coefficient
k	-	Wavenumber

List of Figures

2.1	Illustrative example of the band structure of a Transparent Conducting Oxide and the Moss Burstein shift	6
2.2	Illustration of the s-orbital nature of multicomponent n-type TCOs allowing high mobility even while amorphous	13
2.3	Heatmap of the effective mass of electrons at the CBM of binary oxides	15
2.4	Electrical dependence of a-ZTO on the Zn/Sn ratio within films.	18
2.5	Schematic diagram of the structure of n-i-p and p-i-n perovskite solar cells	20
2.6	Histogram of the effective masses of electrons and holes in binary and ternary oxides	21
2.7	Schematic of valence band modification due to electron correlation	28
2.8	Illustration of attempts to balance the plasma frequency with high conductivity in n-type TCOs	29
2.9	Schematic of a nanolaminate structure used to modulate a materials refractive index.	31
3.1	Illustration of the effect of a magnetron on sputtering plasma . .	35
3.2	Illustration of the self-biasing effect observed on sputtering targets in RF magnetron sputtering	36
3.3	Schematic of the deposition rate hysteresis loop observed in reactive sputtering	38
3.4	Structure of the RF magnetron sputtering system used for sample growths	40
3.5	Image of the spray pyrolysis chamber used for sample growths of zinc-tin oxide	41

3.6	Illustrative Tauc plot	44
3.7	Schematic diagram of the Lorentz force which occurs when a magnetic field is applied perpendicular to the flow of current	45
3.8	Schematic diagram of the van der Pauw configuration used to measure Hall mobility	46
3.9	Illustration of the X-ray diffraction process which forms the basis for XRD	48
3.10	Example of a XRR plot used to calculate film thickness	50
3.11	Illustration of the photoemission process	51
3.12	Illustration of XANES spectra at the Fe K-edge for various ligand groups	56
3.13	Illustration of the spline function μ_0 used to calculate the EXAFS signal	58
4.1	Illustration of the sample holder used for <i>in-vacuo</i> transfers to the STM and XPS instruments	69
4.2	Illustrative XRR fit for a 57 nm a-ZTO film	70
4.3	GIXRD plot on a-ZTO thin films	71
4.4	SEM imaging of high and low thickness a-ZTO films	72
4.5	XPS spectra of the Sn 3p _{3/2} , Zn 2p _{3/2} and VB regions of a-ZTO for high and low thickness films	74
4.6	Variance of the electrical properties of a-ZTO with thickness	76
4.7	Transmission and reflectance spectra for a-ZTO films	77
4.8	Illustration of the blueshift in the optical band gap of a-ZTO films	78
4.9	STM images examining the surface topology of a-ZTO films	81
4.10	Interpolated STS heat-maps used to calculate the electrical band gap and illustrative dI/dV curves to show the band gap calculation process	82
5.1	XPS spectra of the Zn 2p and Sn 3p regions used to quantify the inter-cation ratio in a-ZTO films	89
5.2	GIXRD spectra on a-ZTO thin films	91
5.3	Absorption and Tauc plots for various cation ratios in a-ZTO	91
5.4	XANES spectra at the Zn K-edge from magnetron grown a-ZTO	94
5.5	XANES spectra at the Zn K-edge from spray-pyrolysis grown a-ZTO	95

5.6	XANES spectra at the Sn K-edge from magnetron grown a-ZTO	96
5.7	XANES spectra at the Sn K-edge from spray-pyrolysis grown a-ZTO	97
5.8	$\chi(R)$ spectra calculated from EXAFS measurements at the Sn K-edge and corresponding FEFF8 fits for magnetron grown a-ZTO	99
5.9	$\chi(R)$ spectra calculated from EXAFS measurements at the Sn K-edge and corresponding FEFF8 fits for spray-pyrolysis grown a-ZTO	101
6.1	XRD spectra of vanadium oxides with varying O_2 pressure supplied during growths	108
6.2	XPS core level spectra of V 2p and O 1s region of V_2O_3 film. . .	109
6.3	SEM imaging of a V_2O_3 film	110
6.4	Core level XPS spectra from sample V_2O_3 -50W of the V 2p/O 1s region and V 3s and 3p region	112
6.5	XRD 2θ scan of Mg doped V_2O_3	113
6.6	The transmittance, absorption and Tauc plots of Mg doped V_2O_3 films	114
6.7	FIB SEM preparation of V_2O_3 STEM lamella	116
6.8	Atomic resolution STEM imaging obtained for pure V_2O_3 lamella	118
6.9	Low-loss EELS spectrum from pure V_2O_3	119
6.10	Atomic resolution STEM imaging obtained for Mg: V_2O_3 -50W . .	120
6.11	STEM imaging illustrating the effects of lamella degradation . .	121
6.12	XRD spectra of the crystalline phases of V_2O_3 with thickness . .	122
6.13	XRD 2θ , ϕ scan and reciprocal space map on Cu_2O films	124
6.14	XPS spectrum of the Cu 2p core level	126
6.15	Transmittance and Tauc plot of a Cu_2O film	127
8.1	XPS survey spectrum and O 1s core level spectrum for a 57nm, and 6 nm a-ZTO film.	138
8.2	Variance of the electrical properties of a-ZTO with thickness after exposure to ambient conditions for 48 months.	140
8.3	Histograms showing the range of band gap values during STS measurements of the band gap.	141
8.4	Survey spectra of the a-ZTO films studied by XAS.	143
8.5	XPS core level spectrum of the O 1s region for sample MAG1. .	144

8.6	$k^2\chi(k)$ spectra calculated from EXAFS measurements at Sn K-edge for the a-ZTO films studied by XAS.	145
8.7	XPS survey spectra of pure V_2O_3 before and after the film underwent an Ar sputter and anneal cycle.	147
8.8	XPS survey spectrum of an unspattered Mg: V_2O_3 film.	148
8.9	XPS survey spectrum and O 1s core level peak of an unspattered Cu_2O film.	150

List of Tables

2.1	Comparison of the performance of a-ZTO films prepared via different growth techniques.	17
3.1	Tauc plot coefficients	43
4.1	XPS fitting parameters of Zn 2p _{3/2} and Sn 3p _{3/2} peaks in a-ZTO for a high and low thickness film.	74
4.2	Electrical and optical properties of a-ZTO films as thickness is varied	79
5.1	XPS fitting parameters used to estimate the Zn/Sn ratio in the a-ZTO thin films studied by XAS	90
5.2	Electrical and optical properties of a-ZTO films as cation ratio is varied	92
5.3	Absorption edge positions for the Zn K-edge and the Sn K-edge for measured XANES spectra.	96
5.4	Fit parameters from FEFF8 ab initio modelling of Sn K-edge EXAFS data	100
6.1	XPS fitting parameters of the V 2p peak region before and after Ar sputtering.	109
6.2	Fitting parameters of the V 2p core level peaks from Mg:V ₂ O ₃ -50W.	111
6.3	Electrical properties and FoM of Mg doped V ₂ O ₃ films	114
6.4	XPS fitting parameters of the Cu 2p peak region	126
8.1	XPS fitting parameters of core level spectra for a 56 nm and 6 nm a-ZTO film.	139

8.2	Electrical properties of a-ZTO thin films as thickness is varied after 48 months of exposure to atmospheric conditions.	140
8.3	The mean, median, standard deviation and kurtosis of the band gap heat-maps measured by STS.	142
8.4	Stoichiometries of the a-ZTO films studied by XAS.	144
8.5	XPS fitting parameters of the O 1s peak in V_2O_3	149
8.6	XPS fitting parameters of the O 1s peak in Cu_2O	149

Chapter 1

Introduction

In the modern era, transparent conducting oxides are becoming increasingly integral to our day-to-day lives. These materials which combine seemingly mutually exclusive properties of concurrent high optical transparency in the visible range, and high electrical conductivity, are utilised in a wide variety of optoelectronic applications such as photovoltaics, thin film transistors, and flat panel displays. Although Si-based electronic technology has been well established for several decades, it is not suitable for transparent electronic applications due to its low optical band gap of 1.12 eV. For this reason the development of high performance, chemically stable and easily manufactured transparent conducting oxides (TCOs) is essential.

Few can argue that the rise of smartphones and digital devices has changed society. Even 30 years ago, it would have been difficult to foresee the immense effect they have had on the way we live our lives. With an increasing percentage of our time spent looking at screens, the digital world is growing in size and influence and has changed the way people across the world communicate. The global organic light emitting diode (OLED) market alone was estimated to be worth € 53.5 billion in 2024, and is expected to grow to € 404.9 billion over the next ten years [1]. Despite the demand for better electronics, bigger screens, and flexible devices, few consider how crucial optoelectronics, and indeed TCOs, are to the performance of the technologies upon which many of our lives depend. Furthermore, considering the impact these devices have had not only on the information and communication industry, but also in fields such as education, arts, and manufacturing, the sphere of influence of optoelectronics

Introduction

seems likely to grow. Similarly, due to climate emission agreements, such as the 2015 Paris Agreement and the European Union's 2030 emission reduction targets, photovoltaics have seen a surge in popularity in recent years with the hope they will help society move away from a dependence on fossil fuels. There is a number of obstacles that must be overcome to reach this goal, nevertheless the popularity of photovoltaics is expected to grow over the coming years as more countries switch towards renewable sources of energy. TCOs are frequently used in solid-state photovoltaics as hole or electron transport layers to collect charge. Therefore, increasing the electrical performance while lowering the cost of the TCO layer represents an obvious path for increasing the cost efficiency of these devices. Despite the growing demand and applications of TCOs, the predominant n-type, $\text{Sn:In}_2\text{O}_3$, is not suitable from a cost or sustainability point of view. Moreover, the performance of p-type TCOs to date is unsatisfactory and has limited the development transparent electronics such as transparent pn junctions, p-i-n solar cells and higher efficiency OLEDs. In this thesis, I investigate amorphous zinc-tin oxide as a low-cost, sustainable n-type TCO. a-ZTO is known to be comprised solely of common and abundant materials [2], and has previously been prepared through a variety of different growth techniques. In this work, I sought to explore, characterise and optimise the performance of a-ZTO thin films, through thickness and composition studies, with the goal of making a-ZTO a viable alternative to $\text{Sn:In}_2\text{O}_3$ for TCO applications. In the penultimate chapter, I examine the growth and performance of V_2O_3 as a high potential p-type TCO. This is achieved by preparing crystalline V_2O_3 thin films and then attempting to improve the material's electrical performance through the lens of extrinsic doping and subsequently by combining it with Cu_2O to prepare nanolaminate structures.

In Chapter 2, a review of the relevant TCO literature is presented. First, the physical principles upon which TCOs operate are discussed, and following this an oversight of the field is provided, explaining the strengths and shortcomings of the materials which historically have seen considerable use in industrial applications such as $\text{Sn:In}_2\text{O}_3$ (ITO) and Al:ZnO (AZO). Next, more recent developments in the field of n-type TCOs are outlined, with particular emphasis placed on amorphous multicomponent oxides as this subject shall be the focus of the results presented in Chapters 4 and 5. Following this, a critical assessment of the performance of p-type TCOs is presented. A considerable amount of literature has been published on p-type TCOs, yet their performance remains subpar. In this assessment, the factors that contribute to this poor performance

are discussed along with an overview of the approaches researchers have taken to overcome these inadequacies. Finally, transparent conducting materials (TCMs) and correlated metals are considered as alternative approaches towards realising high p-type conductivity in transparent materials.

In Chapter 3, the techniques and methods used to grow and characterise the thin films discussed in this work are outlined. Particular attention is paid to magnetron sputtering as this was the main deposition method used in this thesis, and a key aspect of my research. As a student of the CDT ACM program, another key aspect of my PhD was the training I received in a wide variety of characterisation techniques. A brief discussion of the experimental techniques relevant to this work is presented thereafter. These range from basic electrical and optical characterisation which are used to evaluate the performance of the various TCOs to more involved techniques such as scanning tunnelling microscopy (STS), x-ray absorption spectroscopy (XAS), and high resolution electron microscopy.

Chapter 4 examines the role that thickness plays upon the performance of a-ZTO. Films were grown via non-reactive radio frequency (RF) magnetron sputtering and show impressive electrical performance with a peak conductivity of 394 S/cm observed for a 12 nm thick film. Examination of the optical band gap indicates a blueshift occurs in the films as the thickness is reduced. Following this the chemical environment of the films is probed using an *in-vacuo* x-ray photoelectron spectroscopy study, while scanning electron microscopy is utilised to examine the films' morphology. Finally STM and STS are performed to further investigate the band gap shift, the results demonstrate a shift in the electronic band gap of the material in agreement with the UV-vis data presented. Mechanisms that may be responsible for this band gap blueshift are then evaluated.

In Chapter 5, the results of a XAS study on a-ZTO as the inter-cation ratio is altered are presented. As the inter-cation ratio is known to affect both charge carrier density and carrier mobility, XAS is employed to investigate this effect and examine the local chemical and bonding environment in a-ZTO as the film composition is varied. The results demonstrate that the chemical environment in a-ZTO does not vary greatly as the cation ratio is changed and while $\chi(R)$ spectra indicate a slight shift in the Sn-O bond length, no longer range bonding order could be observed in these a-ZTO films. With this knowledge, I update the hypothesis to explain the observed variation in conductivity with inter-cation ratio, and propose a theory of the local bonding environment in a-ZTO thin

films.

Chapter 6 provides a study into the growth and characterisation of V_2O_3 as a p-type TCO material. V_2O_3 is a correlated metal and thus exhibits extremely high conductivities making it an attractive option for p-type TCO applications. However, although the material possesses metal-like charge carrier densities the hole mobility of the film remains low which limits the overall conductivity of the material. In this work I examine two approaches to increasing the conductivity of the V_2O_3 films, firstly by substitutional doping with Mg, and then by considering a nanolaminate approach. Using a combination of electrical, optical and x-ray characterisation the performance of pure and Mg: V_2O_3 thin films are evaluated. Furthermore, an electron microscopy study is performed to examine the Mg dopant incorporation into the V_2O_3 thin films, which also provides valuable insight into the crystalline growth of the V_2O_3 films. Finally, the growth of Cu_2O by films is investigated and optimised in preparation of creating V_2O_3/Cu_2O bilayers and nanolaminates. Using a combination of XPS and optical characterisation it is confirmed that Cu_2O is grown. Then through a combination of reciprocal space mapping, and 2θ and ϕ XRD scans, epitaxial [111] orientated Cu_2O films are observed to grow on (0001) Al_2O_3 substrates. Although no nanolaminate or multilayer samples are produced in this work, the results presented are encouraging and form a strong basis for future V_2O_3/Cu_2O nanolaminate studies.

Chapter 2

Literature review

2.1 Overview of transparent conducting oxides

2.1.1 Band Theory

In molecular orbital theory, electron energy levels in atoms are quantised by well defined atomic orbitals. When two atoms combine to form a molecule their atomic orbitals hybridise to form molecular orbitals. In this molecular orbital theory, the highest energy molecular orbital occupied by electrons is referred to as the HOMO, while the lowest unoccupied molecular orbital is referred to as the LUMO. If a large number, N , of atoms come together to form a solid, each discrete energy level is split into N levels. Energy levels that are extremely close in energy to one another may hybridise and as the number of atoms in a solid is extremely large ($N \approx 10^{22}$), the energy levels can be considered as a continuum, or as an energy band. The equivalent of the HOMO is the valence band maximum (VBM), while the energy band formed from LUMOs is referred to as the conduction band minimum (CBM). The difference in energy between these two energy bands is referred to as the band gap (E_g) and is described in Eq. 2.1, where

$$E_g = E_{CBM} - E_{VBM} \quad (2.1)$$

A metal is defined as having an overlap between the valence band (VB) and the conduction band (CB) while an insulator is defined as having a large energy gap between the two bands. This leads to high conductivity in metals as it is easy to generate itinerant charge carriers, while in an insulator the large

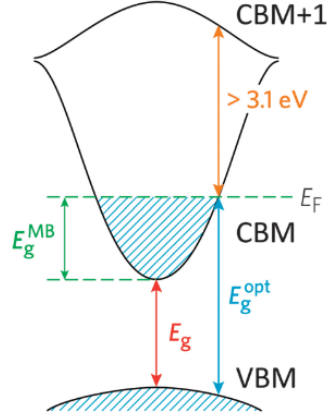


Figure 2.1: Electrons must have sufficient energy to be excited from the valence band in order to act as free charge carriers. In a degenerately doped semiconductor, additional electrons must be excited to higher energies to act as charge carriers, known as the Moss Burstein shift. Adapted from Dixon et al. [3].

bandgap limits charge carrier concentration leading to low conductivities. A semiconductor is a material that has a small bandgap such that charge carriers may be generated and promoted to the CB of the material if sufficient energy, generally in the form of heat or light, is provided. Thus, the conductivity of semiconductors is temperature dependent. It is expected therefore that as the bandgap of the material decreases the conductivity will increase as it becomes less difficult to excite charge carriers from the VB to the CB. Conversely, as the bandgap decreases the transparency of the material will decrease as more incoming photons are absorbed in charge carrier excitation processes. If the bandgap of the material exceeds 3.1 eV, the maximum energy of the visible light spectrum, then the material will be transparent to visible light. Thus when one considers transparency and conductivity with traditional band theory, they are generally seen as mutually exclusive properties. TCOs operate by simultaneously possessing a large bandgap ($>3.1 \text{ eV}$), while also having a donor defect level that lies close to the CBM. This discussion shall be dealt with in more detail in Section 2.2.2, however these defect levels should be shallow ($< 0.025 \text{ eV}$) relative to the CBM so that at room temperatures a significant charge carrier concentration may be generated.

2.1.2 Moss-Burstein shift

As semiconductors, TCOs are inherently reliant on defects within the crystal lattice to generate charge carriers. Intrinsic TCOs rely on defects such as oxygen vacancies, hydrogen interstitials or metallic cation interstitials to contribute to the charge carrier concentrations [4, 5]. Frequently however, these intrinsic TCOs are doped with extrinsic elements to raise the charge carrier concentration and thus increase the conductivity of the material. In both cases as the charge carrier concentration increases, electronic states at the CBM become filled, and thus the Fermi energy moves into the CB. As electrons promoted by photoemission processes must be excited above the Fermi energy this leads to an effective widening of the optical bandgap. This effect was first described by Moss and Burstein independently in 1954 and is known as the Moss-Burstein shift [6, 7] and is demonstrated in Figure 2.1. This effect is often quite advantageous for TCOs as, due to the widening of the optical bandgap, it can increase the optical transparency of a material. The Moss-Burstein shift can be described mathematically as

$$E_g^{Opt} = E_g^{MB} + E_g \quad (2.2)$$

Where E_g^{Opt} is the optical bandgap of the material, and E_g^{MB} is the Moss Burstein shift energy.

2.1.3 Band structure considerations

Band structure is an important factor when it comes to designing and choosing a TCO material. There are several factors to consider for the band structure. N-type TCOs should possess a strong electron affinity. Electron affinity is the amount of energy released when an electron is added to a neutral atom, and thus acts as a guide as to the ease of doping to the system. Secondly, TCOs should have a large energy gap (> 3.1 eV) between the Fermi energy (E_F) and the next nearest energy band in the CB, known as CBM+1. This high degree of separation helps prevent free carrier absorption, where electrons acting as charge carriers are promoted to higher energy bands by optical absorption. Finally, and possibly the most important factor when considering the band structure of TCOs, is the dispersion of the valence and conduction bands. Conductivity in TCOs, described in Eq. 2.3, is proportional to the charge carrier concentration and mobility. The mobility, defined as the drift velocity of the carriers per unit electric field depicts the ease with which charge carriers can move through the

Overview of TCOs

crystal lattice. The conductivity is given as

$$\sigma = e(n_e\mu_e + n_h\mu_h) \quad (2.3)$$

where σ is the conductivity of the material, n is the charge carrier concentration, e is charge of an electron, and subscripts e and h refer to electrons and holes respectively. In the case of heavily doped semiconductors the contribution of the minority carrier towards conductivity is found to be insignificant and thus can be ignored.

The mobility is in turn inversely proportional to the effective mass (m^*) of an electron moving through the lattice. The effective mass describes the effective lowering of the rest mass of an electron (m_e) due to the periodic potential that exists within a crystal lattice. Using Band Theory the effective mass of charge carriers can be related to the structure of the VB and CB at the VBM and CBM. Assuming a periodic potential exists the energy in the conduction band can be expressed as

$$E(k) = E_0 + \frac{\hbar^2 k^2}{2m^*} \quad (2.4)$$

where $E(k)$ is the energy with wavevector k , E_0 is the energy at the point where $k = 0$, and $\hbar$ is the reduced Planck constant. Taking the second derivative of Eq. 2.4 with respect to the wavevector k , one can see that the effective mass is directly proportional to the curvature of the conduction band, a property known as dispersion.

$$\frac{d^2 E}{dk^2} = \frac{\hbar^2}{m^*} \quad (2.5)$$

A higher band dispersion therefore leads to a lower effective mass and thus higher charge carrier mobility in the material. In a practical sense this means that molecular orbitals with dominant s-orbital character at the CBM show the lowest electron effective mass. This is repeatedly shown in literature where materials with s-orbital such as In_2O_3 , ZnO , SnO_2 show consistently lower effective masses than materials with a d-orbital derived CBM such as TiO_2 [8].

2.1.4 Reflection edge

A further consideration that must be taken into consideration when designing a TCO is the reflection edge. One can observe from Eq. 2.3 that there are nominally two routes to increase the conductivity of a TCO material; either by increasing the charge carrier mobility or by increasing the concentration of

charge carriers present. It is found that increasing the free carrier concentration beyond $3 \times 10^{21} \text{ cm}^{-3}$ may introduce issues such as the solubility limits of dopants and a drop in mobility due to increased electron scattering at dopant sites, however a more serious issue for TCO materials is the shift of the reflection edge into the visible light region. Classical Drude theory gives that the plasma energy of a material is proportional to the charge carrier concentration of a material, this is shown in Eq. 2.6.

$$\hbar\omega_p = \hbar\left(\frac{e}{\sqrt{\epsilon_0\epsilon_r}}\right)\left(\sqrt{\frac{n}{m^*}}\right) \quad (2.6)$$

Where $\hbar$ is the reduced Planck constant, ω_p is the plasma frequency, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, and n is the charge carrier concentration. At energies below the plasma energy the material will begin to reflect a significant portion of the incident light. As the dielectric function, and thus relative permittivity of many TCOs lie within a similar range of values it is generally observed that as the charge carrier concentration exceeds $1 \times 10^{22} \text{ cm}^{-3}$, the plasma energy will begin to shift beyond 1.75 eV, and into the visible light spectrum. Any further increase in the charge carrier concentration will cause the transparency of the material to rapidly deteriorate. Thus it is the common approach in TCO research to optimise the charge carrier mobility to avoid the reflection effects seen when the charge carrier concentration is increased too high.

2.1.5 Figure of merit

TCO research has been an active field of research for several decades. As a result there is a multitude of TCO materials that have been synthesised and characterised using different growth methods and employing various dopants. It is thus useful when comparing TCO materials to have a metric with which to grade their performance. As the performance of a TCO material is dependent not only on its optical transparency but also its electrical conductivity any performance metric should taken into account both of these factors. A metric that is often used in literature for comparative purposes is a figure of merit (FoM). One of the first FoMs was introduced by Fraser and Cook in 1972 for sputtered Sn-doped In_2O_3 (ITO) [9], it follows the formula

$$F = \frac{T}{R_{Sh}} \quad (2.7)$$

N-type TCOs

where F is the FoM value, T is the average transmittance in the visible light region and R_{Sh} is the sheet resistance of the thin film. The main issue with the use of this FoM is the emphasis it places on the resistivity of the material. While T can vary from 0 % to 100 %, R_{Sh} can vary over several orders of magnitude, thus R_{Sh} becomes far more valuable in terms of optimisation for a higher FoM. This led to Haacke developing another figure of merit, shown in Eq. 2.8, which places a greater emphasis on transmittance using a normalisation factor q [10].

$$F = \frac{T^q}{R_{Sh}} \quad (2.8)$$

q is typically set to 10 which leads to a maximum F value for 90% transmittance which is perfectly adequate for a TCO. The Haacke FoM was used for several decades [11], however it too faces challenges in its application. As both T and R_{Sh} depend upon the thickness of a sample, using the Haacke FoM is not a fair and accurate measure to compare the performance of materials as F is found to be sample dependent rather than material dependent.

Gordon et al. developed a thickness dependent FoM based off equations 2.7 and 2.8 and using the thickness independent conductivity (σ) and absorption coefficient (α) [12].

$$F = \frac{\sigma}{\alpha} = \frac{1}{R_{Sh} \cdot \ln(T + R)} \quad (2.9)$$

The Gordon FoM, written as FoM^G and expressed in units Ω^{-1} , represents a fairer comparison between TCO materials. Typical values for this FoM include F:ZnO ($7 \Omega^{-1}$), Al:ZnO ($5 \Omega^{-1}$) and Sn:In₂O₃ ($4 \Omega^{-1}$) [12]. However, the Gordon Figure of Merit also has its shortcomings, as it is only concerned with the summation of $T + R$, any decrease in reflectivity creating a higher transmittance will have no net impact on the FoM despite an objectively improved performance. In addition, as many laboratories only have access to instruments to measure transmission data, this FoM is less commonly used and becomes difficult to use to compare published results. As the transmittance and R_{Sh} of many n-type TCOs are within similar ranges of values, there is not much variance in their calculated FoMs. In addition, due to the difficulties that many of the common FoMs face they have not been extensively used in this work. It should be noted that due to the greater variance in both T and R_{Sh} for p-type TCOs they see more frequent use and indeed are used to evaluate the performance of V₂O₃ in Chapter 6.

2.2 N-type TCOs

2.2.1 Historical overview

The first TCOs discovered by Karl Bädeker in the early 20th were simple binary oxides such as CdO, PbO and Cu₂O [13–15]. Although at the time of discovery a full description of their behaviour was not understood, it was shown that through varying the O partial pressure Cu₂O was exposed to, one could control its conductivity over 6 orders of magnitude [15]. Since that point, the research into TCOs has expanded rapidly, such that there is currently over 140,000 papers published on ZnO since the turn of the 21st century. TCOs are now used in a wide field of applications and can be prepared via a variety of growth methods such as atomic layer deposition (ALD), pulsed laser deposition (PLD), molecular beam epitaxy (MBE), sputtering, and spray pyrolysis allowing a high degree of control on size and morphology [3, 4, 16].

2.2.2 Binary oxide TCOs

The first TCOs that saw use in applications were simple binary oxides such as ZnO and SnO₂, which were used in the 1940s and 1950s to prevent the build up of frost and condensation on the windscreen of airplanes [17]. These binary oxides were used for several decades owing to the fact that they are both easy to produce and extremely low cost. However due to the low concentration of intrinsic defects, their overall conductivities remain poor which in turn limits their electrical applications. To address this issue, binary oxide TCOs are often doped with extrinsic elements to introduce donor and acceptor states into the crystal lattice. The theory was borrowed from the doping of conventional semiconductors where an element of differing chemical valency is introduced causing the generation of electrons or holes for charge transport. For the greatest efficiency the introduced donor defect level should be shallow, within 0.025 eV of the CBM, or resonant (above the CBM) so as to allow appreciable charge carrier concentrations at room temperatures. Deep donor defect levels (> 0.025 eV from the CBM) should be avoided as they are unlikely to contribute to significant charge carrier concentrations and may lead to intraband absorption, decreasing the transmittance of the material. Doping of binary oxides has found large success with Al-doped ZnO (AZO) and Sn-doped In₂O₃ (ITO) among the most popular [18–22]. The impressive performance of ITO in particular has led to it becoming the industry standard for TCOs since its development by Rup-

precht [23], and it has found countless applications as transparent electrodes in flat panel and liquid crystal displays [18, 24], photovoltaics [20], and thin film transistors [25, 26]. Although these binary oxides have proven to be extremely successful their performance is heavily reliant on having high crystallinity due to the scattering of charge carriers that occurs at grain boundaries in polycrystalline samples [3]. This requirement for high crystallinity necessitates growth temperatures often beyond the thermal budget and glass temperature of common plastic substrates such as polyethylene terephthalate (PET) and restricts the compatibility of these TCOs for various applications [27].

2.2.3 Multicomponent TCOs

A breakthrough in the field came in 1996, when Hosono et al. proposed a blueprint for the design of new TCOs using heavy metal cations with the $(n-1)d^{10}ns^0$ electronic character, where n is the principal quantum number of the valence electrons of the atoms in their neutral state [28–31]. The theory proposed by Hosono et al. relies on large isotropic s -orbitals that comprise the CBM to form continuous conduction pathways in the material. As the s -orbital radii is larger than the intercation distance, strong conduction pathways exist for electrons even when the material is in a highly amorphous state [25, 32]. This is in contrast to covalent semiconductors such as Si, which rely on highly anisotropic sp^3 hybridised orbitals [25, 33]. Due to their highly anisotropic nature of the bonding orbitals any disorder introduced into the bonding matrix severely degrades carrier transport, which becomes dominated by hopping between localised tail states [4], as illustrated in Figure 2.2. An example of a TCO developed using this multicomponent oxide template is indium-zinc oxide (IZO). Even for samples grown at room temperature, IZO shows optical and electrical performance on a par with polycrystalline ITO grown at 400 °C [34]. A subtle but important improvement to IZO is the addition of Ga to form indium-gallium-zinc oxide (IGZO). Ga^{3+} has a strong ionic potential which allows it to bond strongly with O atoms preventing excessive free carrier generation which arises from oxygen vacancies in the material [4]. As the mobility of charge carriers is not limited by ionised impurity scattering the mobility may increase resulting in excellent mobilities of between (10-100) $cm^2/V\cdot s$ [35–37]. In addition, given the extra disorder in the material from the introduction of an additional cation, a variety of cation compositions can be achieved while maintaining the amorphous nature of the material circumventing the issue of grain boundary scattering that

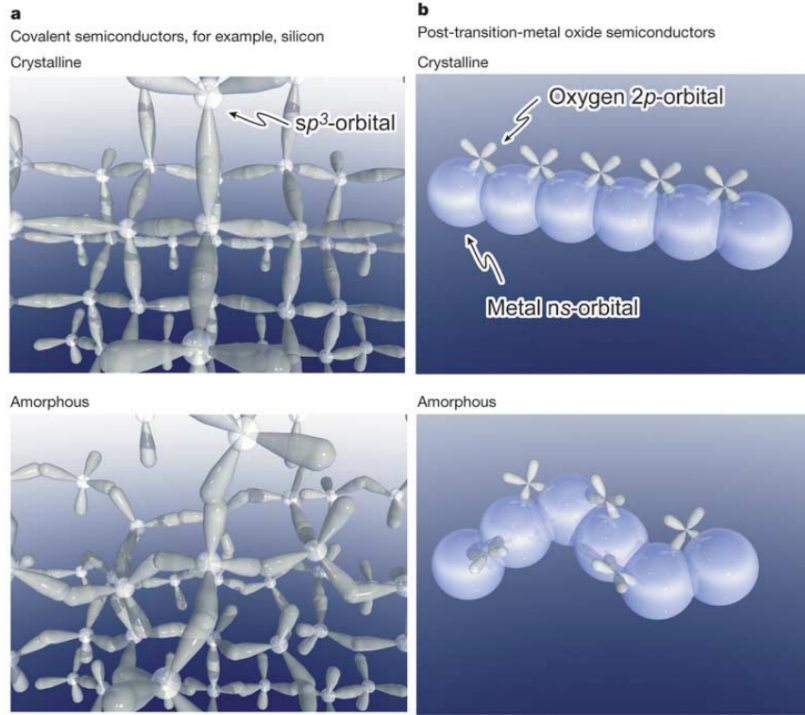


Figure 2.2: The highly anisotropic sp^3 hybridised orbitals in a:SiH leads localised states impeding electron transport. In contrast the $(n-1)d^{10}ns^0$ electronic character of materials suggested by Hosono et al. leads to strong conduction pathways even in an amorphous state. Figure reproduced from [25].

exists in polycrystalline samples. Moreover, as these multicomponent TCOs are being deposited as amorphous films they are compatible with a low thermal budget as well as a wider range of substrates making them more attractive for transparent flexible electronics.

2.2.4 Issues with indium

For quite some time ITO has been the industry standard in TCOs, with commercial polycrystalline ITO typically exhibiting conductivities of $\sigma = 5 \times 10^3$ S/cm, and a Figure of Merit of roughly $1.19 \times 10^{-2} \Omega^{-1}$ [22, 38, 39]. However the use of indium has many issues. Firstly, indium has a very low natural abundance in the Earth's crust (0.1 ppm) vs. Zn (132 ppm) [40, 41]. This is exasperated by the fact that indium does not exist as a sole mineral and therefore is only produced if it is recovered as a by-product from the refining of Zn and Pb

ores. Consequentially the unit price of indium can fluctuate significantly, which is not ideal as ITO is a key component in many TFT and solar cell devices. To compound this issue, there are no natural resources of In in the EU which results in researchers and manufacturers being reliant on imports and subjected to inflated sales prices. The summation of these factors led the European Union in 2020, to place In amongst a list raw materials of critical economic importance with a significant supply risk [42]. Although the EU judged the supply risk to In to be reduced in their most recent materials sustainability report [43], a long-term sustainable alternative would be an obvious benefit.

A second explanation for the desire to move on from ITO is the development of flexible electronics. PET, which is the nominal substrate of choice for flexible electronics, has a glass temperature of just 80 °C, far below the processing temperature for ITO which typically ranges from 200-600 °C [44]. Although there have been some improvements in the performance of ITO produced at lower temperatures, these are usually in the form of amorphous ITO which presents inferior electric properties ($\sigma = 1.5 - 2 \times 10^3$ S/cm) [3], to its polycrystalline counterpart ($\sigma = 5 - 10 \times 10^3$ S/cm) [24]. To add to this issue, ITO is well known to be a very brittle material. Irreversible cracks appear in polycrystalline ITO thin films at a bending angle of 36°, these films had a maximum bending angle of 60°, with the conductance dropping by 3 orders of magnitude across this range [3]. Amorphous ITO is known to be even more brittle than its polycrystalline counterpart [45]. In comparison, graphene is known to be able to operate as a flexible transparent conductor up to a bending angle of 138° [46].

Beyond a performance or cost concern, the final concern over the use of In comes from a health viewpoint. As the mining and utilisation of In is still a relatively recent development, there is a significant amount that remains unknown about the possible short and long term health risks associated with its use. This is exemplified in the contrast of what is considered the respiration exposure limit between the US Occupational Safety and Health Administration (recommended limit of 0.1 mg/m³, but no regulated limit) [47], and the Japanese equivalent (0.0003 mg/m³) [48], a 3 order of magnitude difference. Furthermore, indium lung disease is known to be a potentially fatal disease caused by the inhalation of indium particles [49], and even when the disease does not present, In workers show higher incidence of lung lesions, reduced diffusing capacity and in acute cases; emaciation, liver damage and an enlarged spleen [50]. To compound this issue it appears that the exposure route may have a considerable impact on the In lifetime in the body. With inhalation, there is similar levels of In in blood

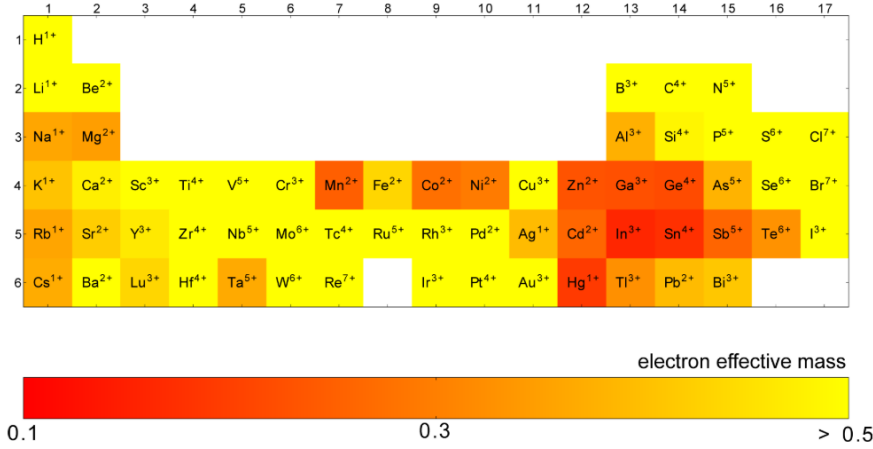


Figure 2.3: Heat-map of the effective mass of electrons at the CBM of binary oxides. Figure reproduced from Hautier et al. [8]

plasma in current workers as those with a median time since exposure of 4.6 years [51, 52].

2.2.5 In free alternatives

Finding an viable alternative to ITO has been an ongoing field of research for several decades. Computational studies are extremely useful in this regard as a large number of binary and ternary oxides can be modelled and the expected effective mass calculated. Although computational modelling rarely agrees perfectly with empirical data it does allows high throughput screening of material properties and thus is an invaluable tool in identifying materials of interest. A study of the effective masses of electrons in binary oxides as seen in Figure 2.3 finds that the highest electron mobilities are possessed by ZnO, SnO₂ and In₂O₃ [8]. While this study justifies the use of these binary oxides as host materials for doped TCOs it does not provide any guide for further exploration of binary oxide TCOs.

One of the forerunners as an alternative to ITO, is IGZO. As discussed previously, IGZO is a multicomponent oxide that can perform extremely well even when in an amorphous state. As-deposited IGZO grown on a PET plastic substrate at room temperature was shown to possess mobilities of 10 cm²/V·s, which is an order of magnitude greater than a-Si:H [25]. It has found success as a material used in TFTs [36, 37], as well as being used to detect harmful

gases [53–55]. However, gallium is also a rare element and is frequently used in other applications raising concerns over cost. Furthermore many of the health concerns regarding the toxicity of indium also carry over into gallium [56]. Another alternative to ITO that has been suggested is Al-doped zinc oxide (AZO), Al is readily and cheaply available which goes some way to resolve the issues facing ITO and IGZO. More importantly, RF sputtered AZO has showcased conductivities as high as $\sigma = 5 \times 10^3$ S/cm [38] which is extremely close to commercial polycrystalline ITO (6.6×10^3 S/cm) [24, 38]. However, Zn can see increased chemical activity depending on the oxidising strength of the deposition environment, and as a result large area AZO films see uneven distributions of electrical conductivity which limits their applications [57]. Furthermore, as the conductivity of AZO relies upon a high level of crystallinity this presents an issue for large area depositions where variations in crystalline grain size can impact the uniformity of material performance.

A recurring theme across high performance n-type TCOs is the presence of extrinsic dopants in a ZnO, SnO₂ or In₂O₃ host matrix. In order to focus on low-cost, common and abundant options I shall focus on ZnO and SnO₂. In the pure form these materials rely on intrinsic defects to generate charge carriers resulting in low conductivities (0.01-1 S/cm) in both ZnO and SnO₂ [58, 59]. While extrinsically doping these materials has proven very successful with materials such as GZO, AZO and FTO seeing use in industrial applications, another approach is to combine the binary oxides to form a ternary oxide. Zinc tin oxide is an excellent example of this. There are two crystalline forms of zinc tin oxide; the perovskite form ZnSnO₃ [60] and the inverse spinel phase Zn₂SnO₄ [61]. While these crystalline phases show transparencies > 80% in the visible range [62, 63], they require elevated growth temperatures and significant H₂ flows to generate charge carriers, and hence achieve conductivities of 102 S/cm [64]. An alternative option is to use the amorphous phase of zinc tin oxide (a-ZTO). Nanocrystalline and amorphous materials typically exhibit lower mobility due to increased ionised impurity scattering at grain boundaries, however using the multicomponent oxide theory [30, 31], a-ZTO can exhibit mobilities as high as 35 cm²/V·s in an amorphous form [65, 66]. The amorphous form has the added benefit of that due to the increased density of dangling bonds, the charge carrier concentration is much higher than the crystalline form [62, 67].

Furthermore, a-ZTO has been deposited using a wide variety of deposition techniques such as; RF magnetron sputtering [65, 68, 69], spray pyrolysis [70], mist-CVD [71], spin-coating [71], sol-gel, [74] and atomic layer deposition (ALD)

Species	σ (S/cm)	μ (cm ² /V·s)	E_g (eV)	T (°C)	Prep. method	Ref.
Zn _{0.22} SnO _{2.22}	445	35	3.7	500	RF MS	[65]
Zn _{0.20} SnO _{2.2}	220	18	>3.1	60	RF MS	[68]
ZnSnO ₃	-	20-50	3.3-3.9	600	RF MS	[69]
Zn _{0.61} SnO _{2.71}	304	10.5	-	450	SP	[70]
Zn _{0.72} SnO _{2.72}	-	14.6	3.01	350	mist-CVD	[71]
ZnSnO ₃	-	6.88	3.22	350	spin-coat	[71]
Zn _{0.5} SnO _{2.53}	0.14	15.7	>3.1	500	spin-coat	[72]
Zn _{0.5} SnO _{2.27}	0.1	3	2.8	450	PLD	[73]

Table 2.1: Comparison of the conductivity, electron mobility, band gap and treatment temperature of a-ZTO thin films prepared via differing growth techniques. Abbreviations: radio frequency magnetron sputtering (RF MS), spray-pyrolysis (SP), chemical vapour deposition (CVD), pulsed laser deposition (PLD).

[75]. As is shown in Table 2.1, these deposition methods exhibit a range of conductivities and charge carrier mobilities. This is partly due to the fact that as a-ZTO is an intrinsic semiconductor, it relies heavily upon oxygen vacancies and metal cation interstitials to generate charge carriers. This makes the material quite sensitive to the oxygen partial pressure during growth, the control of which can vary greatly between deposition techniques. In addition, a-ZTO is also sensitive to post-growth treatments such as annealing in an O₂ atmosphere, which can passify oxygen deficiencies, reducing the charge carrier density but increasing the Hall mobility of the material [65]. Conversely, annealing in a H₂ or N₂ atmosphere is seen to increase the charge carrier concentration in a thin film [65].

The optical and electrical properties of a-ZTO can also be controlled by the intercation ratio within the material. As ZnO has a lower band gap of 3.3 eV compared to SnO₂ 3.7 eV, it is expected to see some variance in the optical performance as the stoichiometries are varied [76]. A less intuitive result is the dependency of the electrical properties on the Zn/Sn ratio [77]. As shown in Figure 2.4, high charge carrier densities are observed at high Sn contents, while at high Zn concentrations the charge carrier mobility increases. This can partly explain the variation in performance of a-ZTO observed by researchers [2, 69, 72, 78, 79].

The electrical properties of a-ZTO are currently below the best performing TCO options such as ITO and AZO however it does possess a number of ad-

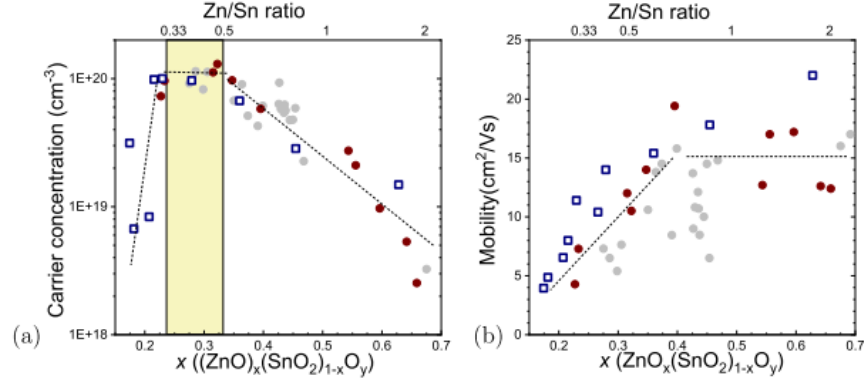


Figure 2.4: a) Carrier concentration vs Zn/Sn ratio, and b) Hall mobility vs Zn/Sn ratio. It is observed that a-ZTO films with high Sn content exhibit higher charge carrier densities while films with higher Zn concentrations showcase higher carrier mobilities. Figure reproduced from Zhussupbekova et al. [77].

advantages such as being composed solely of common and abundant materials [2], not requiring high deposition temperatures and a high chemical stability [68] which can affect the performance of TCOs such as AZO and GZO in particular [4]. This cation ratio dependency along with the sensitivity of the material to growth and post-growth conditions, allows a wide number of parameters to tune in order to optimise the performance of the material for a specific application. In fact, a-ZTO has already been implemented in a wide range of applications such as organic light emitting diodes (O-LEDs) [68], photovoltaic cells [80], gas sensors [81], and TFTs [82, 83].

Two areas in which the knowledge of a-ZTO is lacking are; how the optoelectronic performance of the material is dependent on the material thickness, and why the electrical performance of the material depends so strongly on the inter-cation ratio. The first issue is applicable to how a-ZTO will be used in various industrial applications, while the second issue has implications for optimising the electrical performance as a whole by modulating the Zn/Sn ratio within the films. Both are thus important for the continued development and improvement of the material and therefore shall be considered in Chapters 4 and 5.

2.3 P-type TCOs

2.3.1 Motivation and historical overview

While n-type TCOs are a well explored field with a wide variety of industrial applications the development of their p-type counterparts has lagged behind. Viable p-type TCOs would allow significant advancement in transparent electronics and allow greater functionality and lower power consumption in many applications.

Thin film transistors are a basic element of modern circuits and are used in a wide variety of transparent electronics to control basic units of pixels in systems such as flat panel displays, liquid crystal displays, and active matrix organic light emitting diodes (AMOLEDs) [84]. A significant progression in the conventional semiconductor industry came with the integration of complementary logic circuit design [84]. When n-type metal-oxide semiconductor transistors (NMOS) are combined with p-type metal-oxide semiconductor transistors (PMOS), they can form complementary metal-oxide semiconductor (CMOS) logic. CMOS technology offers lower power consumption, low waste heat generation as well as a high noise margin and therefore would allow significant advancement in the performance of transparent electronics if realised [85].

Another use of p-type transparent conducting oxides is p-n junctions. These are devices that combine n-type and p-type semiconductors to form a diode device. These p-n junctions have many applications in fields such as AC current rectification, surge protection, light emitting diodes as well as generating and receiving radio frequency signals [84]. Other applications include thermometers, photodetectors and radiometers [86]. A final highlighted application of p-type TCOs is for use in hole transport layers (HTL) in solar cell devices [87–89]. The need for society to divest from fossil fuel energy sources towards renewable and sustainable alternatives is well documented. Many countries including Ireland have signed up to the Paris Climate Agreement which states that emissions in each country should be reduced by approximately 50 % by 2030 [90]. Despite this, the energy demands of Ireland and the world continue to grow. One promising technology which already sees significant interest is solar cells. Their research and development has seen significant interest and growth over the past decade as researchers seek to improve their performance and efficiency. Conducting p-type oxides are often implemented in solar cells as hole transport layers as is illustrated in Figure 2.5 where their wide band gap, high work

P-type TCOs

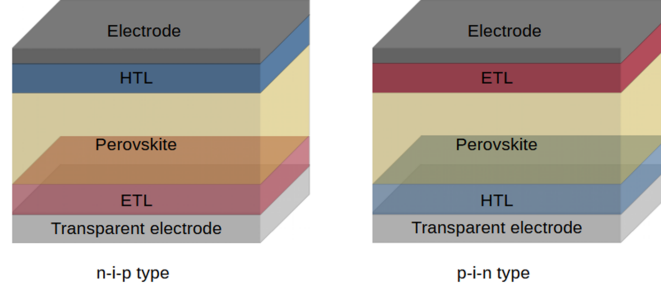


Figure 2.5: Schematic of n-i-p and p-i-n type perovskite solar cells. N-type TCOs such as ITO, SnO_2 or TiO_2 are typically used for the ETL or transparent electrode. Higher performing p-type TCOs are needed to reduce losses and carrier recombination effects [93].

function and good hole conduction is essential to the extraction and transport of holes created in the photoactive layer, particularly in p-i-n type devices [91, 92]. For satisfactory performance the p-type TCOs should have sufficient valence band structure to allow good hole mobility as well as optical transparency. The work function of the material should be aligned with the work function of the top contact as well the valence band maximum of the photoactive layer in order to suppress diffusion of charge and the loss of energy in the device. It is thus apparent that while high performance p-type TCOs have struggled to be developed thus far, the ongoing growth of optoelectronics in today's society in addition to the rising energy demands makes the research and development of viable p-type materials an area of great interest to many in the TCO community.

2.3.2 Doping binary oxides p-type

There have been many approaches to developing p-type TCOs. The first of which was to dope known TCO materials such as ZnO , SnO_2 , and In_2O_3 with acceptor impurities to generate electron "holes" (h) that may act as charge carriers. The success of this approach was quite limited however due to these TCO materials being intrinsically n-type. While the native defect concentration in these binary oxide TCOs may not be high enough to generate sufficient n-type conductivities, it is more thermodynamically favourable to generate hole killing traps than it is to allow a high hole concentration within the material

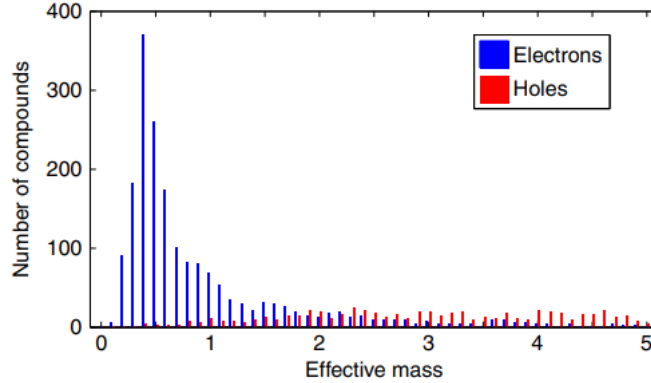


Figure 2.6: The distribution of effective masses of electrons (blue) and holes (red) in binary and ternary oxides as a multiple of an electron’s rest mass. Reproduced from Hautier et al. [99].

[94, 95]. Moreover in accordance with the selection criteria described in Section 2.1.3, in order to ensure high charge carrier mobility the valence band maximum of a material should be comprised of highly dispersive bands. However, the VBM in many binary oxides demonstrates highly localised behaviour due to the high electronegativity of the O anions [96–98]. This hole localisation leads to extremely high effective masses in many p-type TCOs, resulting in $m_h^* > m_e$ as is shown in Figure 2.6

2.3.3 Cu 3d¹⁰ based materials

Cu₂O

Cu₂O was first reported as a TCO by Bädecker in 1907 and over a century later it still remains relevant to ongoing research in p-type TCOs. The main attraction of this p-type metal oxide is a hole mobility up to 256 cm²/V·s and bandgap of 2.17 eV [84, 100]. In addition, Cu₂O has been prepared by a variety of growth methods such as PLD [101–103], ALD [104–106], and magnetron sputtering [100, 107, 108].

The high hole mobility in Cu₂O is attributed to the nature of the band structure near the VBM. In Cu₂O, the Cu⁺ ions possess a full 3d¹⁰ electronic configuration, with the energy level of Cu 3d¹⁰ orbital close to the O 2p⁶ orbitals. This leads to significant mixing between the orbitals and as a result a more dispersed valence band maximum with higher mobility is achieved [109, 110].

P-type TCOs

A theoretical hole effective mass of $0.24 m_e$ has been calculated [111], although experimental results has this figure slightly higher at $0.58 m_e$ and $0.69 m_e$ respectively [112].

Despite the high mobility reported for Cu_2O its overall performance as a TCO remains unsatisfactory. Its bandgap of 2.17 eV is lower than the 3.1 eV required for optical transparency meaning that thin films often exhibit a clear brown colour under visible light. A more serious issue however is its extremely low electrical conductivity. It is widely established that the main hole generating defect in Cu_2O is V_{Cu} [113, 114], with an estimated activation energy of 0.45 eV above the VB [115]. The concentration of these Cu vacancies has been shown to be highly dependent on O partial pressure during growth or post-growth annealing conditions [100, 116]. However as an ionic compound, Cu_2O favours the formation of self-trapped polarons through distorting the nearby crystal lattice of V_{Cu} over the formation of itinerant charge carriers [117]. As a result, Cu_2O films generally only report charge carrier densities and conductivities of $1.7 \times 10^{14} \text{ cm}^{-3}$, and 0.014 S/cm respectively [118]. A final consideration in the discussion of Cu_2O is the narrowness of the processing window to obtain pure Cu_2O without a parasitic CuO phase forming. Although CuO is also a p-type semiconductor, its presence would degrade the electrical performance of Cu_2O .

Delafossites CuMO_2

Following the limited success of the Cu_2O TCO, Hosono et al. developed a new approach for the design of novel p-type TCOs known as chemical modulation of the valence band (CMVB) [119]. This idea is based of the successful hybridisation that occurs between the fully occupied O 2p and Cu 3d orbitals. The delafossite structure is based on the chemical CuMO_2 formula, where M is a trivalent cation such as (B, Al, Cr, Ga, Sc, In or Y). The first delafossite TCO, CuAlO_2 , was designed by Kawazoe et al.. In its undoped state it shows a large optical bandgap (3.5 eV), corresponding to an average transparency of 70% in the visible range. Moreover, the addition of Al atoms has a serious impact on the conductivity with values as high as 1 S/cm being recorded [119]. However, while the Al cation contributes to conductivity through charge carrier generation it also causes serious degradation in the mobility of the material. This is attributed to the 3d Cu-O-Cu linkages in Cu_2O being interrupted and replaced by Cu-O-M-O-Cu links, resulting in strong anisotropy being observed between the ab-plane hole effective mass ($2.6m_e$) and the c-plane effective mass

($38.95m_e$) for CuAlO_2 [120]. Compared to CuAlO_2 , the delafossite CuCrO_2 shows improved electrical performance reaching conductivities as high as 220 S/cm when doped with Mg. However, the optical properties of CuCrO_2 remain an area to improve as it typically only sees transparencies as high as 30% [121]. An attempt to improve the transparency dropped the conductivity to 1 S/cm [122]. The main challenge delafossites face for performances similar to n-type TCOs is their low conductivities stemming from deep acceptor levels [123], coupled with a polaronic conduction [124, 125].

Spinels nd^6

Continuing the search for a viable p-type TCO, researchers began to improvise on the closed shell-O 2p hybridization theory Hosono et al. had put forward to develop a new family of materials, spinels. These transition metal oxides were based on transition metals with the nd^6 electronic configuration with a low spin ground state. This resembles the $3d^{10}$ closed shell electronic configuration present in delafossites. Spinels follow the formula ZnM_2O_4 where $M = \text{Co}^{3+}$, Rh^{3+} , Ir^{3+} [126]. In this configuration, the Zn atoms form ZnO tetrahedra while the corresponding M atoms form MO_2 octahedra. Based on absorption spectra ZnCo_2O_4 , ZnRh_2O_4 , ZnIr_2O_4 show band gaps of 2.26 eV, 2.74 eV, and 2.97 eV respectively [127]. However there remains some doubt over the magnitude of these figures as the band gap of ZnRh_2O_4 has been measured to be 2.1 eV by Mansourian-Hadavi et al. [128] and 1.2 eV by Singh et al. [129]. Of these spinel materials ZnCo_2O_4 is the most studied, showing conductivity values as high as 21 S/cm [130]. While the d^6 spinels show impressive conductivity for a p-type TCO the flat valence band maximum as well as a polaronic hopping conduction mechanism present in all the aforementioned materials represents a barrier to their further improvement [127]. This is exemplified by the extremely high effective mass $m^* = 18m_e$, and low hole mobility $\mu = 0.028 \text{ cm}^2/\text{V}\cdot\text{s}$ of ZnCo_2O_4 [131]. A further challenge spinels face is the high cost of the precious metals Rh and Ir, which constrains their inclusion in large scale industrial applications [132].

2.3.4 Oxychalcogenides

A consistent issue that Cu^+ based ternary oxides face as we have seen above is low charge carrier concentration coupled with a low hole mobility. As mentioned above, due to the low valence band dispersion that many transition metal

oxides possess the resulting hole mobility is low and unsatisfactory. An alternative approach that has seen some success is to partly or fully replace oxygen with other chalcogenides (Ch) elements, where Ch = S, Se and Te. A more dispersed valence band is expected from greater hybridization due to increasing covalency between the Cu 3d¹⁰ and Ch np⁶ orbitals in increasing order (O, S, Se and Te). An example of this approach is layered oxychalcogenides such as LaCuOS [133]. LaCuOS forms as a layered 2D material, consisting of alternating layers of [La₂O₂]²⁺ and [Cu₂S₂]²⁻ stacked along the c-axis. The LaO layers confine the CuS to 2D layers leading to quantum confinement and the expansion of the optical bandgap to approximately 3.1 eV [134]. Moreover, as the charge carriers are formed from Cu vacancies [135], they are extracted to [Cu₂S₂] layers and so are not scattered by charge carrier impurities [136]. This is shown in Mg-doped epitaxial film LaCuOSe which shows a p-type conductivity of 910 S/cm [135]. There is however several issues that oxychalcogenides face. Firstly, chalcogenides are well known for the toxicity and incompatibility with vacuum systems which makes dealing with them inside and outside the vacuum chamber problematic. Furthermore, the materials are also sensitive to atmospheric conditions. In addition, it is noted that the intrinsic charge carrier concentration in oxychalcogenide materials is typically quite low, therefore doping of LaCuOS via Mg²⁺ or Sr²⁺ on the La³⁺ site is necessary to raise the charge carrier concentration and conductivity from $2 \times 10^{15} \text{ cm}^{-3}$ and $6 \times 10^{-5} \text{ S/cm}$, to $2.7 \times 10^{20} \text{ cm}^{-3}$ and 20 S/cm [134, 137, 138]. It is also noted that despite the high conductivities achieved in Mg-doped LaCuSeO, due to the high charge carrier concentrations the materials shows no optical transparency [135]. Finally, while the mobility of the material improves due to the increased dispersion of the valence band maximum as one goes from S to Se and then Te, this is accompanied by a simultaneous decrease in the optical bandgap from 3.14, 2.80 to 2.40 eV respectively [139]. It is felt therefore that despite the promising hole mobilities and conductivities reported, these do not outweigh the additional expense of materials and cost in complexity of preparation when compared to the previously mentioned spinel materials.

2.4 Transparent Conducting Materials (TCMs)

Based on the success of the oxychalcogenides in increasing the mobility of the holes, and the difficulty of finding suitable dopants for oxides, researchers have

begun to look past oxides and now examine a wider variety of materials known as transparent conducting materials (TCMs). The most well researched of these materials are copper iodide and boron phosphide which have been known as transparent p-type materials since 1908 and 1957 respectively [140]. However, ternary chalcogenides such as CuAlS₂ [141, 142], and CuZS₂ [143, 144] have also seen attention due to the higher mobility they possess compared to oxide materials.

2.4.1 Copper Iodide

Of these candidates, CuI in particular, has seen a surge in popularity in recent times. There are number of phases of CuI that may form depending on the temperature and pressure of the system, below 643 K, γ -CuI which possesses a zincblende structure dominates [145, 146]. CuI possesses a theoretical direct bandgap of 3.203 eV [147], which has been measured experimentally as 3.118 eV [148], making it highly transparent to visible light.

The VBM of the material is comprised of I 5p and Cu 3p and 3d orbitals which leads to an anisotropic hole effective mass. This manifests as a light holes which possess an effective mass of $0.3 m_e$, and heavy holes along the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions with an effective mass of $2.1 m_e$ [148]. Cu vacancies have been calculated to have the lowest formation energy among native defects and thus are believed to control the charge carrier density of the material [149, 150]. These V_{Cu} , are most easily formed in I-rich growth conditions. Both the charge carrier concentration and hole mobility are found to depend strongly on the temperature of the system. This is attributed to anisotropic nature of the VBM leading to effectively two conductivity channels. The first channel has low hole mobility $\mu = 0.15 \text{ cm}^2/\text{V}\cdot\text{s}$ and respectable charge carrier concentration of $1.2 \times 10^{19} \text{ cm}^{-3}$ and dominates at temperatures below 50 K [151]. The second channel which dominates at room temperature exhibits impressive mobility for a p-type TCM ($\mu = 9 \text{ cm}^2/\text{V}\cdot\text{s}$) and carrier density of $1.2 \times 10^{18} \text{ cm}^{-3}$ [151].

The properties discussed thus far make CuI appear to be an attractive TCM candidate however the two main issues it faces are its difficulty with doping and its sensitivity to O incorporation. As both Cu and I atoms exist within the material in a +1 and -1 oxidation state respectively, this makes it difficult to find suitable dopant atoms to raise the charge carrier concentration to the 10^{20} cm^{-3} typically observed in n-type TCOs. In addition, CuI is extremely sensitive to O₂ exposure, with a significant O₂ incorporation within minutes of exposure to

atmospheric conditions. While O incorporation does add to the conductivity by producing more V_{Cu} within the crystal lattice [152], it also reduces the mobility due to ionised impurity scattering [151]. The challenge for CuI then is that it remains challenging to increase its charge density by two orders of magnitude to meet that of its n-type counterparts, while simultaneously the native charge carrier density is higher than preferable for a gate material for TFT applications.

2.4.2 Boron Phosphide

Boron Phosphide is currently used as a hardening material on aircraft wind-screens, however it has been known as a p-type conducting material for several decades [153]. A high throughput computational study on more than 30,000 materials highlighted it as a promising candidate TCM due to its extremely high hole mobility [154]. This hole mobility which has been computationally calculated to be as high as $900 \text{ cm}^2/\text{V}\cdot\text{s}$ is from the good overlap between the B 2p and P 3p bands leading to a dispersive valence band maximum [155]. In fact Shohnho et al. have reported p-type conductivities of 2600 S/cm and intrinsic charge carrier densities in the range of $1 \times 10^{17} - 1 \times 10^{19} \text{ cm}^{-3}$ [153]. To this point, as there are no known hole-killing defects that arise in the material and Be has been suggested as an effective dopant to raise the material's charge carrier concentration due to the low formation energy of Be_B defects and no self-compensation mechanisms predicted [139]. The optical properties of BP are the subject of some debate in the literature. Computational studies predict an indirect band gap at 2.26 eV and a direct bandgap at 4 eV [154], however the value of the direct band gap reported in experimental studies ranges from 2.2 to 6 eV [156–158].

The largest issue BP faces is its synthesis [156]. B is an extremely inert element, therefore to be able to react B and P, diborane and phosphine are typically used, however both of these chemicals are highly toxic [159]. Furthermore the dopant Be, suggested from high throughput computational studies is also known to be extremely toxic. Sputtering of B in a phosphine atmosphere, or alternatively co-sputtering from a P source has been suggested however this introduces other practical challenges such as having a phosphine gas line or the reaction of the P sputtering target with water or air.

2.5 Correlated metals as TCOs

An approach that has gained traction over the past number of years is the use of correlated metals as TCOs. Although they possess low carrier mobilities as is typical for correlated metals, their metal-like charge carrier densities enables them to achieve extremely high conductivities [160]. Correlated systems have been known for several decades, they describe materials that are predicted to be conductors by Band Theory but in fact behave as insulators. CoO and NiO are both examples of this. Both materials possess half-filled d-orbitals and as such the Fermi level lies within the 3d band thus implying the materials should behave like metals. In contrast to this, CoO is one of the strongest insulators presently known [161]. The defining characteristic of these correlated systems is that their electrons can no longer be described as non-interacting entities, instead each electron has a complex effect on the behaviour of its neighbours. Correlated materials can be further separated into a number of subcategories such as spin Peierls, Mott-Hubbard insulators and high temperature superconductors. As this work is based on exploiting Mott-Hubbard insulators and correlated metals, I shall focus on them. The effect of strong electron correlation can be understood by examining the band structure of a correlated metal, shown in Figure 2.7. The Coulomb repulsion between electrons (U) leads to a split in the d-band. The strength of this splitting is generally observed to increase across rows, and decrease down the columns of the periodic table. The strength of the electron correlation in a system is quantified by a renormalisation factor Z_k , where

$$Z_k = \frac{U}{W} = \frac{m_{band}^*}{m^*} \quad (2.10)$$

where W is the bandwidth of the occupied O 2p and metallic d states [162, 163]. As the electron correlation also acts to deviate the mobility of the system away from the band effective mass of non-interacting electrons, m_{band}^* , Z_k can also be expressed in terms of this. The renormalisation factor may take values $0 < Z_k < 1$, where $Z_k = 0$ represents a Mott insulator where all charge carriers are localised and $Z_k = 1$ represents a non-correlated system where the effective mass of charge carriers is fully represented by the band structure value [164]. One concern that correlated systems face due to their extremely high charge carrier concentration is the encroachment of the reflection edge into the visible light range which occurs at 1.75 eV. The screened plasma energy $\hbar\omega_p$, written in full in Eq. 2.6, describes the energy at which the reflection edge lies. It can be

Correlated metals as TCOs

seen that $\hbar\omega_p \propto \frac{n}{m^*}$. In this regard, the enhanced effective mass that correlated metals exhibit from electron correlation is to their benefit. The high effective mass acts to counteract the high charge carrier concentration and shifts $\hbar\omega_p$ below 1.75 eV, enabling optical transparency in the visible region [165].

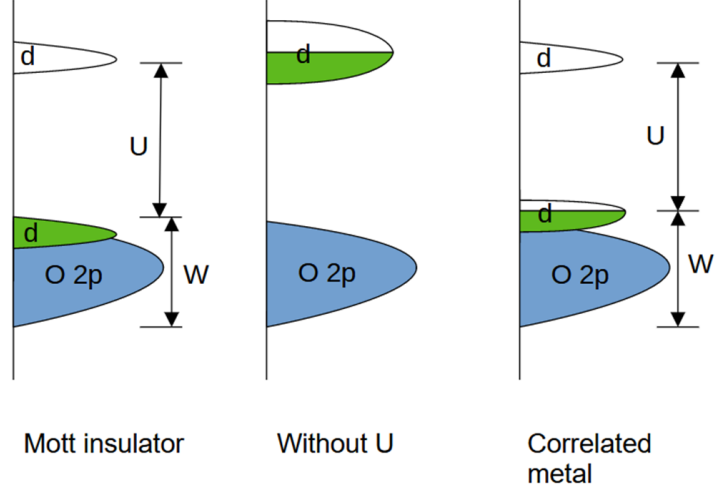


Figure 2.7: Schematic of valence band modification due to electron correlation illustrating the Coulomb repulsion (U) and occupied bandwidth (W) terms.

The n-type correlated materials CaVO_3 , and SrVO_3 have previously been examined as prospective n-type TCOs. Zhang et al. report conductivities as high as of 3.5×10^4 S/cm for a 45 nm film of SrVO_3 , and 2.6×10^4 S/cm for a 38 nm film of CaVO_3 [165]. This is represented in Figure 2.8 where the n-type correlated systems SrVO_3 (20 nm film) and CaVO_3 (38nm) have higher conductivities than epitaxially grown ITO (500 nm film) [165]. One of the shortcomings of these materials is their relatively poor optical performance as n-type TCOs, however due to their extremely high conductivities this can be addressed by reducing the thickness of the films. Zhang et al. [165] report that as the film thickness of SrVO_3 is reduced from 45 nm to 4 nm the optical transmittance in the visible range increases from 60 % to 75 %, while the conductivity drops only by a factor of two. These n-type correlated systems offer therefore a low-cost alternative to In based n-type TCOs [166].

Correlated metals have also been suggested as p-type TCOs, and are known as p-type metals. There are a number of candidate materials such as doped NiO and Co_3O_4 but the two that show the most promise are doped Cr_2O_3 , and V_2O_3 .

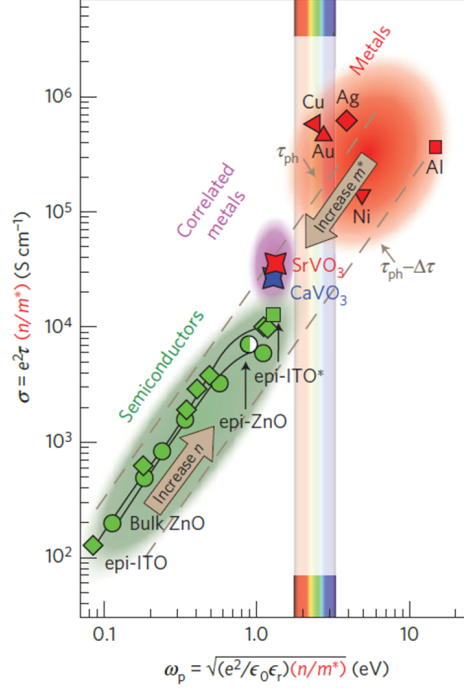


Figure 2.8: Experimental data showing the balancing of plasma frequency and conductivity in well known metals, n-type TCOs and correlated n-type systems. Green circles represent bulk crystalline ZnO, with green rhombuses representing 500 nm epitaxial ITO. Adapted from Zhang et al. [165].

Cr_2O_3 is an antiferromagnetic insulator with a Néel temperature $T_N = 307$ K. Its structure is well characterised, and is seen to adopt the corundum structure with a rhombohedral primitive unit cell, with the unit cell parameters $a = 0.4958$ nm and $c = 1.3594$ nm [167]. Although there have been some reports of native p-type conductivity pure Cr_2O_3 is generally considered a complete Mott insulator, with a $Z_k \approx 0$ [168–170]. Due to a strong U value there is a large energetic splitting of the 3d band. Typical of a Mott insulator, the CBM is predominately comprised of empty Cr 3d orbitals while the VBM is a combination of full Cr 3d states hybridised with O 2p orbitals. The material has a direct band gap which has been measured experimentally to be $E_g \approx 3.4$ eV, and is in strong agreement with computational reports. To overcome its insulating properties Cr_2O_3 is often doped with elements such as Mg [171–174], Ni [171, 175], and Li [171, 176] or co-doped with Mg and N in order to introduce itinerant charge carriers.

Previous studies on a 150 nm Mg and N co-doped film, report conductivity values of as 0.33 S/cm, coupled with 65% transmittance in the visible region [177]. The main challenges that Cr_2O_3 faces is its conduction mechanism which comprised of the small-polaron hopping of holes resulting in mobilities as low as $\mu \approx 1 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ [178]. Recently researchers working on Cr_2O_3 studied alloying the material with S, in accordance with the CMVB method developed by Hosono et al. in an attempt to raise the mobility of the material [119, 179].

A more promising p-type correlated metal is V_2O_3 . V_2O_3 exists in a number of phases, namely; a corundum structure with a rhombohedral primitive unit cell which is observed under ambient conditions and behaves as a paramagnetic metal. Upon cooling, the material undergoes a phase transition at $\approx 170 \text{ K}$ to a monoclinic structure which behaves as a antiferromagnetic insulator [170, 180]. In recent years, a third V_2O_3 phase has been discovered which also forms under ambient conditions in a bixbyite structure [181, 182]. This bixbyite phase has a 0.07 eV higher enthalpy of formation per formula unit than the corundum phase and thus is considered metastable [183]. At room temperature and in the V^{3+} oxidation state, the V 3d bands are split into two-fold degenerate e_g bands and three-fold degenerate t_{2g} due to the crystal field. Furthermore, due to the trigonal distortion due to the rhombohedral lattice, the t_{2g} bands are further split into a low lying doubly degenerate e_g^π band a non-degenerate a_{1g} band with a 0.3 eV energy difference [168]. This e_g^π is partially filled by V valence electrons resulting in the E_F lying within the valence band and the p-type conductivity that is observed in the material. Typical of a correlated metal the material sees strong conductivity, with charge carrier concentration typically $>10^{22} \text{ cm}^{-3}$ resulting in conductivities ranging from 400-2122 S/cm [184].

Regarding its optical performance, V_2O_3 sees a strong interband absorption onset at 3.6 eV which occurs as charge carriers are promoted from O 2p bands to V 3d e_g bands [184]. The reflection edge or plasma energy ($\hbar\omega_p$) of V_2O_3 has been measured using ellipsometry as 0.97 eV, which is agreement with previous measurement of V_2O_3 single crystals which have a $\hbar\omega_p = 1$ [184, 185]. The largest shortcoming V_2O_3 possesses as a p-type TCO is the absorption it sees in the visible range due to V d-d transitions. As there is no change in orbital angular momentum in these transitions they are forbidden, yet they remain a limitation of the optical transparency of the material.

Doping of V_2O_3 with Ti, and in particular Cr is a well established practise [187–189]. The effect of this doping is to slightly increase the transition temper-

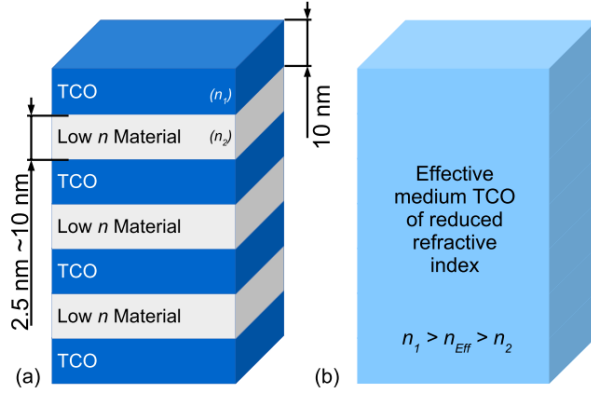


Figure 2.9: Schematic of a nanolaminate structure where a TCO and a lower electron density n material are combined to tune the refractive index of the composite material. Reproduced from Caffrey et al. [186].

ature of the paramagnetic to antiferromagnetic insulator phase transition [190]. As the utilisation of V_2O_3 as a TCO is a relatively novel concept, effective dopants are still not well known. Sarmadian et al. investigated Mg, Sc and Y as substitutional dopants in the bixbyite phase of the material, and predicted Mg to act as a shallow acceptor in the system [191].

An alternative approach to improving the TCO performance of V_2O_3 is the use of nanolaminates. Nanolaminates refer to repeating pseudo-2D layers of alternating materials, a schematic of this structure is shown in Figure 2.9. Nanolaminates have been previously shown to be able to effectively tune a wide variety of material properties such as refractive index [186], band gap [192], oxidation state [193] and thermoelectric properties [194, 195]. To tune the refractive index, individual layers with thicknesses far below the wavelength of the incident light are stacked. In this regime, known as the long-wavelength limit, the incident light will interact with the refractive index of the composite material rather than those of the individual layers [196]. To my knowledge, a nanolaminate approach has not yet been applied to improve the performance of V_2O_3 thin films, however given its effectiveness in modulating the optical properties of other TCOs it may offer an attractive route to the improvement in electrical performance of V_2O_3 films.

Despite the shortcomings in its optical performance it is clear that V_2O_3 is a material with high potential as a p-type TCO. With $\hbar\omega_p \approx 0.97$, there is scope to further improve the conductivity of the material either by doping the

material or by increasing the renormalisation factor in order to decrease the hole effective mass. Thus it shall be a focus of the later work of this thesis.

Chapter 3

Methodology

3.1 Thin film synthesis

The predominant growth technique used in this work is radio frequency (RF) magnetron sputtering, in the following paragraphs I will explain the basis of operation for DC sputtering, then magnetron sputtering and finally RF magnetron sputtering. As samples were deposited in a reactive and non-reactive sputtering environment both of these approaches shall be described and explained.

3.1.1 Sputtering

Sputtering is typically used in high vacuum conditions as it allows for the deposition of high purity elements and compounds, with a high deposition rate and typically low surface roughness. This ability to produce high quality films makes sputtering a favoured deposition technique for research applications [64, 197, 198], while the high reproducibility and throughput aspects mean it sees significant use for depositing large area surface coatings in a wide variety of industrial environments [199].

Prior to any sample depositions a bulk cylindrical disc of the desired material is prepared, hereafter this shall be referred to as the "sputtering target". The sputtering process can be described as the energetic bombardment of the sputtering target with gas ions. Ar gas is typically used for this purpose as it is inert and is relatively cheap compared to other noble gases. Ar gas is introduced into the vacuum chamber, where it is ionised by a strong DC electric field in order to form a plasma. These Ar^+ ions are then accelerated towards the sputtering

target. In a mechanism that is analogous to a cue ball striking a pyramid of billiard balls, the energetic bombardment of the target with Ar^+ ions produces a plume of sputtered atoms from the sputtering target. Secondary electrons are also produced in the bombardment process through inelastic collisions of Ar^+ with the sputtering target. The secondary electrons are accelerated under the electric field and upon collision with a neutral gas atom may impart their kinetic energy or cause an ionisation event, creating further ions for the sputtering process. These secondary electrons thus play a vital role in sputtering process as they sustain the plasma energetically as well as enriching the plasma by generating gas ions. The plume of sputtered atoms will coalesce on a substrate resulting in a growth of a thin film. There is insufficient time and space for a thorough discussion on substrates here, nonetheless the choice of thin film substrate can have significant impact on the growth mode and characteristics of a thin film.

The main drawback of sputtering as a deposition technique is the low levels of Ar gas ionisation which leads to a low sputter rate and the need for a high deposition pressure [199]. This high deposition pressure can result in an uncontrolled plasma, and the resputtering of the material that has already condensed on the substrate, further slowing the deposition rate [199].

3.1.2 Magnetron sputtering

Magnetron sputtering is a modification of sputtering developed to address the aforementioned issue of low Ar ionisation. In a conventional glow discharge electrons are lost to recombination at the walls of the chamber. However, in magnetron sputtering a magnetron is introduced behind the sputtering target orientated such that one pole lies in the centre of the target while the other pole lies along the edge of the target. The magnetic field causes the secondary electrons produced in ion bombardment to follow circular trajectories close to the target surface, as illustrated in Figure 3.1. The circular trajectories of the secondary electrons increases the ionisation rate of Ar gas atoms, thus increasing the gas ionisation efficiency and thereby increasing the ion current density arriving at the sputtering target [200]. This increased ion current density increases the bombardment rate of the sputtering target allowing an increase in the deposition rate of a thin film. Moreover, the increased gas ionisation efficiency permits a reduction in the gas pressure of the system which in turn decreases the scattering rate of sputtered atoms and increases the deposition

rate of a thin film. For these reasons DC magnetron sputtering is extremely popular for thin film depositions for industrial applications.

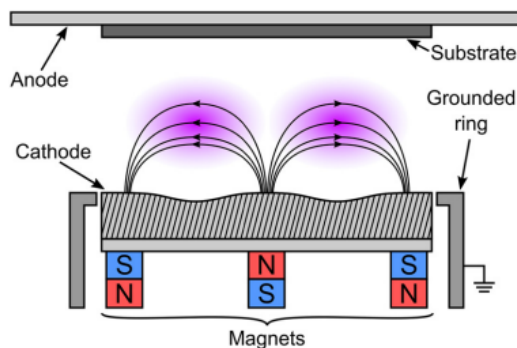


Figure 3.1: Electrons are trapped by the magnetic field lines introduced by the magnetron which leads to higher ionisation rates near the surface of the sputtering target. Figure adapted from Gudmundsson et al. [201].

However, there are some disadvantages to magnetron sputtering that should also be discussed, primarily the amount of the sputtering target that is wasted during use. Due to the circular trajectories of the secondary electrons, the plasma is heavily concentrated along these magnetic field lines resulting in a toroidal shaped region of the sputtering target, colloquially referred to as the "racetrack", being preferentially sputtered. Once the material in the racetrack has been sputtered away the sputtering target must be replaced, however as the racetrack presents as only a fraction of the total area of the sputtering target a large amount of the sputtering target is wasted which is far from ideal from an industrial point of view. There are several modifications to magnetron sputtering that are available to rectify this issue such as alterable magnetic arrays [202], and varying the sputtering target shape [203] however they are beyond the scope of this work.

3.1.3 RF Magnetron sputtering

Most sputtering for industrial applications takes place using DC biases, however in instances where it is desired to deposit a non-conductive material the application of a unidirectional bias can cause issues. A positive charge build-up will occur at the surface of the sputtering target which may result in arcing between the sputtering target and walls of the chamber. A common solution to

this issue is radio frequency (RF) power being supplied to the sputtering target in the form of a high frequency AC capacitively coupled source. The logic of this approach is that the charge accumulated by ion bombardment during one half cycle is neutralised by the electron bombardment in the next half cycle. Radio frequencies between 5-30 MHz are possible, however, 13.56 MHz is the typical frequency used as this is the frequency allotted to deposition and film growths by international communication authorities [200]. The high frequency switching of the bias accelerates both the high velocity electrons and low velocity ions towards the sputtering target in alternating cycles. The electrons have a much

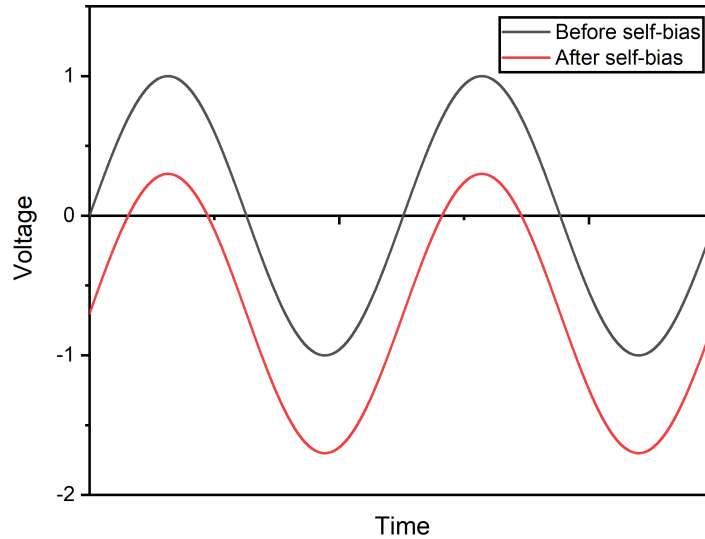


Figure 3.2: Alternating bias is applied to the sputtering target. Due to the lower inertia of the electrons the target self-biases to a negative bias thus increasing the period of time ions are attracted to the sputtering target.

lower inertia than the ions, and so for a given voltage applied by the generator a much larger electron current will arrive at the sputtering target than ion current. This large electron current acts to shift the median voltage at the target to a negative bias, commonly referred to as self-biasing [200]. The effect of this self-biasing is to extend the lifetime of the negative bias of the sputtering target relative to the positive as is shown in Figure 3.2. Thus the ions present in the plasma are attracted to the sputtering target for a greater period of time thus increasing the sputtering rate of the system. Using this approach RF sputtering allows a continuous and sustainable approach to sputtering insulating

materials [200, 204, 205]. Moreover, due to the positive bias applied by the AC electric field there is an increased concentration of oscillating electrons close to the target surface which serves to increase the ionisation rate of gas atoms in the plasma allowing for lower gas pressures and higher deposition rates.

While there are several advantages to RF sputtering it rarely sees use in industrial applications. This mainly due to RF systems being more expensive, while generally having a lower deposition rate than DC sputtering systems [204]. For this reason industrial applications typically sputter using conductive metal targets as they are less expensive and less brittle than compound targets, however in research laboratories where these factors are less of a concern RF sputtering sees significant use.

3.1.4 Reactive sputtering

So far we have considered cases where the sputtering target is comprised of the desired material for sample growth, however there are cases where one would like to change the chemical composition or oxidation state of the sputtered material. This process, known as reactive sputtering, is achieved by introducing additional gases to the chamber during the sputtering process which may react at the target surface to form a new compound at the substrate. Because reactive sputtering requires a reactive gas atmosphere, in instances of high partial pressures it is possible to observe complete oxidation of the sputtering target surface. This is colloquially referred to as target poisoning, and creates a hysteresis loop with the deposition rate observed in the chamber [206]. This is illustrated in Figure 3.3.

The hysteresis effect comes from the rate of formation of a compound layer on the target surface

1. A - B. Referred to as the metal region, in this region the sputtering rate is high, while some compound may form on the target surface it is quickly sputtered away.
2. B - C. Point B is referred to as the oxide point. At this point the rate of compound of formation exceeds the sputter rate from the target surface, and due to the increased bonding energy of a compound, the deposition rate drop dramatically.
3. C - D. Referred to as the compound region, in this region despite the reduction in the reactive gas partial pressure, the deposition rate remains

low as the compound formation rate at the target surface remains high.

4. D - A. When the reactive gas pressure drops sufficiently low enough, the rate of sputtering from the target surface exceeds the rate of compound formation as the target surface returns to its metallic state.

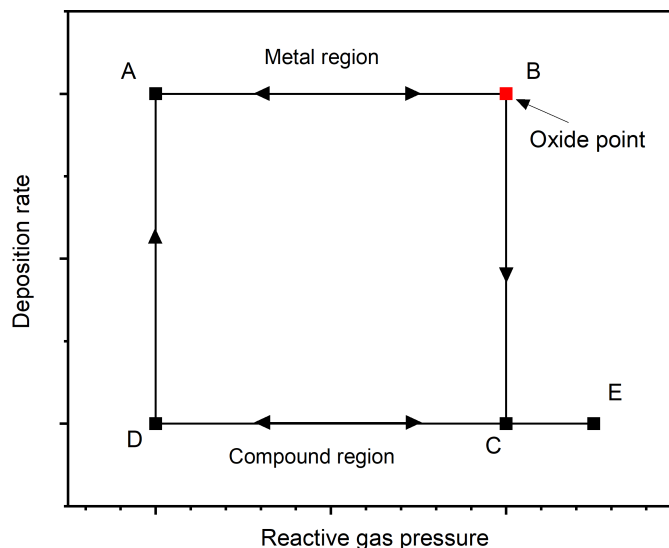


Figure 3.3: Reactive sputtering hysteresis loop. Once the reactive gas pressure reaches the oxide point the sputtering rate will drop dramatically, and will only recover if the reactive gas pressure drops to point D.

As previously mentioned it is typically unfavoured in industrial applications to use RF sputtering due to the increase cost and the comparatively slow deposition rate. As a result, in instances where it is desired to grow a non-conductive material reactive sputtering is typically used. An additional advantage of reactive sputtering is that it allows greater control of the oxidation state of the deposited film when compared to non-reactive sputtering of oxide targets. However, the hysteresis behaviour observed between the deposition rate and reactive gas partial pressure can add significant complication to thin film depositions. Low reactive gas partial pressures can result in the growth of sub-stoichiometric films. Meanwhile high reactive gas partial pressures, that may be close to the oxide point, can result in large variations in the sputter rate as any small perturbation to the deposition conditions may cause the target to go into the compound region. This potential for large fluctuations in growth conditions is far

from ideal, especially in attempts to grow stoichiometric films with a high degree of accuracy and consistency as is necessary for the growth of bilayers which is discussed in Chapter 6.

3.1.5 Structure of the deposition chamber

The growth chamber used to produce the vast majority of samples and work presented in this thesis is shown pictured in Figure 3.4a, while a schematic of the chamber is shown in Figure 3.4b. The magnetron sputtering cathodes produced by AJA International were planar with fixed magnetic arrays. These are compatible with cylindrical sputtering targets of 5.08 cm diameter and 0.32 cm thickness. As is shown in Figure 3.4b, one magnetron was placed vertically, while the other was placed on an adjacent flange at angle of 50 ° to the surface normal of sample.

A rotating sample stage ensured an equal growth rate of the thin films across the substrates, this is particularly important for depositions from the magnetron canted at an angle of 50°. Both magnetrons were equipped with shutters, which were utilised to expose or close off a sputtering target. The main purpose of this was to allow the pre-sputtering of sputtering targets while keeping the sample substrate pristine. The sample stage was equipped with a SiC heating element produced by UHV Design. This SiC heater allowed a maximum heating temperature of 800 °C, beyond which the element would begin to oxidise and performance would decrease rapidly. The temperature of the heater was monitored using a thermocouple placed at the bottom of the heater. The spatial separation between the heater and sample holder meant there was a thermal lag between the temperature of the heater and sample. To overcome this issue, upon the heater reaching the desired deposition temperature the chamber was allowed to thermally equilibrate for one hour before thin film depositions begun. The main deposition chamber has a base pressure of 1×10^{-5} mbar, obtained by a turbo pump and rotary roughing pump. The pressure of the main chamber during depositions was controlled using a mass flow controller to restrict the Ar pressure. Similarly, in order to facilitate reactive sputtering the chamber was connected with independent N₂, and O₂ gas lines each with their own mass flow controllers.

In instances where an *in vacuo* transfer was desired a vacuum suitcase was connected to the loadlock. This permitted the transfer of samples between vacuum chambers without exposure to atmospheric conditions. The base pressure of the

Thin film synthesis

vacuum suitcase was 2×10^{-10} mbar. In order to improve electrical contact with the sample for X-ray photoelectron spectroscopy (XPS) and scanning tunnelling microscopy (STM) measurements, prior to sample growth, gold contacts were deposited on the four corners of the 1×1 cm² substrates. Additionally, as the magnetron growth chamber and STM are in different buildings, after growth samples were transferred to the STM using a "vacuum suitcase". The vacuum suitcase was connected to the STM preparation chamber, thus enabling sample transfer under UHV conditions.

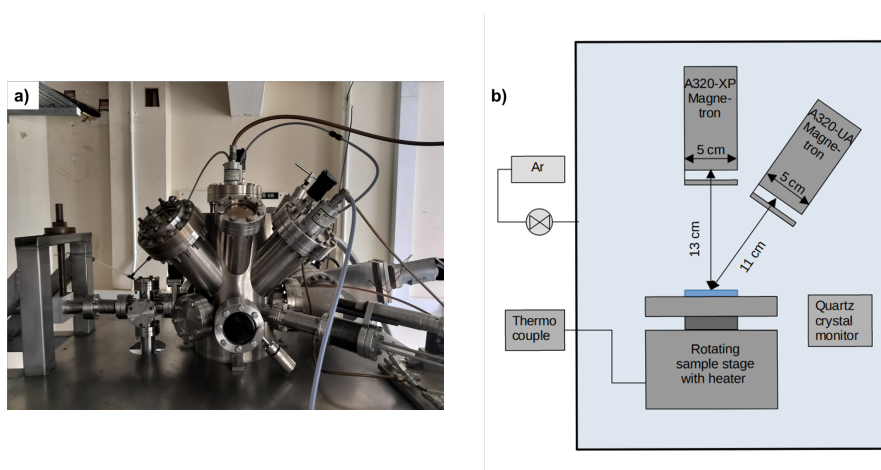


Figure 3.4: a) Image and b) schematic of the RF magnetron sputtering system used for sample growths. Dual cathodes equipped with shutters allowed for dual or alternating depositions. A rotating sample stage ensured equal deposition of sputter material across the sample.

3.1.6 Spray pyrolysis

While the majority of the thin films that are discussed in this work were prepared via RF magnetron sputtering, in Chapter 5 a number of sample were prepared via spray pyrolysis. For this reason it is appropriate to briefly cover this technique.

Spray pyrolysis is a low-cost, high speed growth technique which although is considered more aggressive than RF magnetron sputtering, has strong potential to upscale for industrial scale applications. The process involves mixing precursors, comprised of metal salts dissolved in solvents, and spraying them



Figure 3.5: Image of the interior of the spray pyrolysis chamber used for growths of zinc-tin oxide samples

through an atomizer onto the heated surface of a chosen substrate. The precursors are then evaporated leaving behind a thin film [207]. Control over the stoichiometry in films is achieved by careful choice of the type of metal salt, the choice of solvent and the ratio of precursors in the mixture. The selection of the best performing precursor components depends on a number of factors such as; metal salt solubility, precursor chemical compatibility, and rate-of-formation of unwanted by-products during growth [207]. As there is a large variation in these deposition parameters, the optimisation of spray pyrolysis films is quite an involved process.

Spray pyrolysis synthesis in this work was performed using a custom built spray pyrolysis deposition chamber comprised of a large Abbess 18 Cube stainless steel chamber equipped with an atomizer nozzle (PNR Air assisted ultrasonic atomiser, model MAD 0331 B1BA). The distance from the tip of the nozzle to the substrate is 29 cm [208]. The optimal position for the substrate during growth was established from empirical growth trials. Substrates were heated using a hotplate of area 10×10 cm, which possessed a small temperature gradient across the surface area. A thermocouple was attached directly to the heater in order to provide accurate temperature readings. In order to

control the heating to a desired temperature, a proportional-integral-derivative (PID) was utilised which also allowed the current temperature of the heater to be read. In this growth chamber, both compressed air and nitrogen are available as carrier gases, with their flow modulated by mass flow controllers. Additionally, the internal O₂ concentration within the growth chamber could be varied between 0-21 %, and is monitored using an O₂ sensor a distance of 35 cm from the atomizer [208].

3.2 Optical characterisation

Characterising the optical properties is an important step in evaluating the potential of any TCO. To achieve this transmission and reflectance measurements were run in the UV-visible spectral range of 1.5 - 3.1 eV. The system used was a PerkinElmer Lambda 650S UV-vis spectrophotometer equipped with an integrating sphere, small spot kit, and dual tungsten and deuterium lamps to probe the spectral range from 1.5 - 5.8 eV. The integrating sphere is comprised of a spherical measuring chamber with photodetector and walls coated with highly reflective paint such that any light that enters the chambers will be reflected without loss until it reaches the detector. This serves to improve the signal-to-noise ratio of the system. The small spot kit is used to focus the beam to an area of 1×1 cm², to match the dimensions of the samples and again increase the signal-to-noise ratio.

The absorption of a film can be expressed as in Eq. 3.1

$$A = 1 - (T + R) \quad (3.1)$$

Where A is the absorption of the film, T is the transmittance and R the reflectance. However this fails to include the thickness dependency of absorption and thus make it difficult to compare films of varying thicknesses and compositions. Instead the absorption coefficient shown in Eq. 3.2 is typically used

$$\alpha = \frac{-\ln(T + R)}{t} \quad (3.2)$$

where α is the energy-dependent absorption coefficient of the material and t is the thickness of the thin film. A spectrum of the variation in the absorption coefficient with incident photon energy can be used to extract the optical bandgap of materials. These spectra, known as Tauc plots, were first proposed by Tauc

Transition	γ
Direct allowed	1/2
Direct forbidden	3/2
Indirect allowed	2
Indirect forbidden	3

Table 3.1: Tauc plot coefficients

in the late 1960's for the estimation of bandgaps in amorphous semiconductors such as amorphous Si and Ge [209, 210]. The method was later developed and expanded upon by Davis and Mott [211], and today is widely applied to calculate the bandgap from optical absorption data. The Tauc method is based off the assumption that the energy-dependent absorption coefficient can be expressed by

$$(\alpha \cdot h\nu)^{1/\gamma} = B(h\nu - E_g^{Opt}) \quad (3.3)$$

where h is Planck's constant, ν is the frequency of light, γ is a constant dependent upon the nature of the electronic transition, B is a constant, and E_g^{Opt} is the optical bandgap. The full range of values γ may take are given in Table 3.1. An example of a Tauc plot is shown in Figure 3.6. Due to the relatively large optical bandgap in amorphous zinc tin oxide the absorption coefficient remains near zero until well into the UV region of the light spectrum. A linear extrapolation is drawn from the point of onset of absorption, and the optical bandgap is estimated as the point that this extrapolation crosses the abscissa, marked as a black square.

It is worth noting that while the Tauc method is commonly applied to a range of materials and systems there is little consensus as to which properties the electronic structure of material must possess for the Tauc method to be appropriate [212]. This can lead to ambiguity in how the Tauc method should be applied to define the bandgap of a material, particularly for transition metal oxides such as NiO, Fe₃O₄, and Co₃O₄ which can see discrepancies as large as 2 eV for their reported optical band gap [212]. In addition, the Tauc method assumes perfectly parabolic bands which may not be always be accurate. Moreover, amorphous materials often exhibit significant sub-band gap states, known as tail states as the valence band maximum and conduction band minimum bleed into the band gap. In UV-vis spectrophotometry these are often observed as the presence of Urbach tails in Tauc plots. These tail states can lead to a rise in absorption below the formal bandgap and blur the point at which linearity occurs, this

shall be discussed further in Chapter 4.

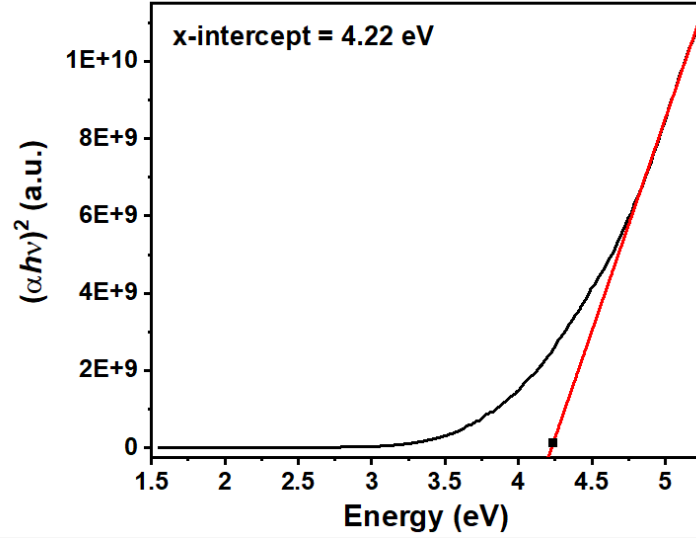


Figure 3.6: A Tauc plot of a direct allowed transition in amorphous zinc tin oxide

3.3 Electrical characterisation

Electrical measurements were performed in this work using the Hall effect. The Hall effect is the response of charge carriers to an external magnetic field applied perpendicular to the direction of current flow. While the conductivity of a film may be calculated using a simple van der Pauw configuration, shown in Figure 3.8, by introducing the Hall effect one may also measure the Hall mobility of the material. Furthermore, provided one has knowledge of the film thickness, the charge carrier concentration can also be estimated, and by observing the slope of the associated Hall voltage plots the semiconductor type (n-type or p-type) may be determined.

When an external magnetic field is applied perpendicular to the current the charge carriers experience a Lorentz force F_L which is represented in Eq.3.4

$$F_L = q(v \times B) \quad (3.4)$$

where q is the fundamental charge of an electron, v is the velocity of the

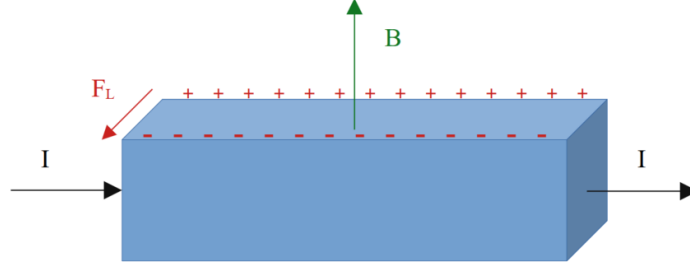


Figure 3.7: The Lorentz force (F_L) caused by the external magnetic field (B) being applied perpendicular to flow of current (I) causes a transverse motion in the charge carriers. This deflection leads to a build up of charge on one side of the material and a potential difference known as the Hall voltage (V_H) forming.

charge carrier and B is the strength of magnetic field applied. The Lorentz force leads to a deflection in the path of the charge carriers until the charge carriers are concentrated enough to repel the addition of any additional charge carriers. This build up of charge leads to a transverse electric field, and a potential difference across the sample known as the Hall potential

$$V_H = \frac{IB}{n_c q t} = IB \mu_H R_{Sh} \quad (3.5)$$

Where I is the current flow in the system, n_c is the number of charge carriers, t is the thickness of the films, μ_H is the Hall mobility and R_{Sh} is the sheet resistance of the film. Rearranging this formula gives

$$\mu_H = \frac{V_H}{IB R_{Sh}} \quad (3.6)$$

Therefore by applying a known magnetic field, the mobility of a material can be obtained by measuring the Hall voltage and sheet resistance. In this work, the sheet resistance (R_{Sh}) was measured using a four-point-probe method in the van-der-Pauw configuration (illustrated in Figure 3.8). In this method, a current is applied across two adjacent contacts, for the sake of convenience we shall pick contacts A and B (I_{AB}). While this current is applied, the voltage across points C and D is recorded (V_{CD}). We can then define the vertical sheet

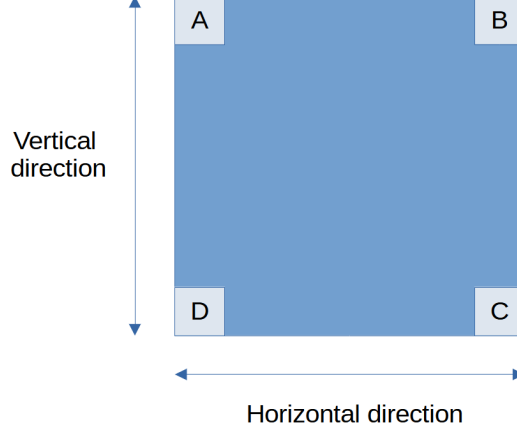


Figure 3.8: The van der Pauw configuration used to contact samples for electrical characterisation

resistance, $R_{AB,CD}$, as

$$R_{AB,CD} = \frac{V_{CD}}{I_{AB}} \quad (3.7)$$

To minimise the effects of any inhomogeneities that may exist within the sample and obtain a more accurate vertical sheet resistance, a current is applied between points C and D (I_{CD}) while the voltage between points A and B is recorded (V_{AB}). Inputting these values into Eq. 3.7 gives the value $R_{CD,AB}$. To minimise the effect of inhomogeneities further, the polarity of the current applied across points A and B, and C and D is reversed, giving the values $R_{BA,DC}$, and $R_{DC,BA}$. The R_{Sh} in the vertical direction (R_{Vert}), can therefore be calculated as

$$R_{Vert} = \frac{R_{AB-CD} + R_{CD-AB} + R_{BA-DC} + R_{DC-BA}}{4} \quad (3.8)$$

An equivalent equation can be derived for R_{Hor} , the sheet resistance in the horizontal direction. R_{Vert} and R_{Hor} can then be combined using the van der Pauw formula (Eq. 3.9) to calculate the R_{Sh} of the material as whole.

$$e^{-\frac{\pi R_{Vert}}{R_{Sh}}} + e^{-\frac{\pi R_{Hor}}{R_{Sh}}} = 1 \quad (3.9)$$

Thus by measuring the parameters R_{Vert} and R_{Hor} , the R_{Sh} of a material

can be calculated even without the sample thickness. To measure the Hall voltage, current and voltage were measured across opposing contacts of the sample, I_{AC} and I_{BD} respectively, while a magnetic field was applied perpendicular to the surface normal of the thin film. To reduce error terms in Hall voltage calculations the direction of the applied magnetic field is switched and the polarity of the applied current I_{AC} is reversed during measurements. Samples in this work were measured in the van der Pauw configuration using a combination of silver wire and silver adhesive to contact the sample. Contacts were manually made by transferring silver paint to the film using a wooden toothpick and quickly attaching a silver wire before the paint dried. The contacts were made as small as possible on the surface of the film so as to minimise error in measurements. An 800mT electromagnet was used to apply the external magnetic field to the sample, allowing a $0.1 \text{ cm}^2/\text{V}\cdot\text{s}$ resolution.

3.4 X-ray characterisation

3.4.1 X-ray diffraction

X-ray diffraction is a technique used to determine the crystalline composition and orientation of a material. X-rays incident upon a material may elastically scatter from core electrons of atoms as the X-ray impinges upon the crystal lattice. Diffraction is a form of scattering, where the incident beam is reflected back from the material at angle of θ , as illustrated in Figure 3.9. Therefore, θ can also be defined as the angle made when the incident and diffracted path of X-rays is bisected by the plane vector of the atoms. Furthermore, the total change in angle of the beam is 2θ . Constructive interference will occur for X-rays diffracted off consecutive atomic layers when the path difference they have travelled, $2d_{hkl} \sin \theta$, is an integer multiple of the X-ray wavelength. This constructive interference is observed as an increase in the intensity of X-rays diffracted through a given value of 2θ . This relationship is summarised in Bragg's law of diffraction shown in Eq. 3.10

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.10)$$

where n is the order of the diffraction, λ is the wavelength of the beam of incident X-rays, and θ is the angle of the incident beam with respect to the interlayer spacing d_{hkl} . As interlayer spacing may depend upon the orientation

X-ray characterisation

of the material being examined, the Miller indices (h, k, l) are used to denote the crystallographic plane or reflex being probed.

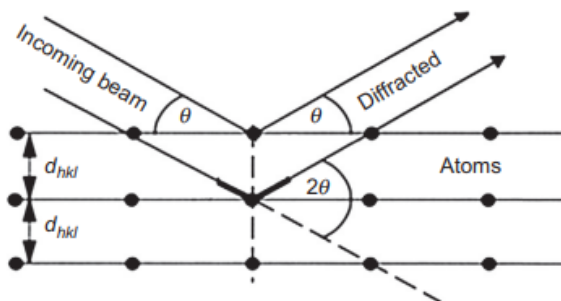


Figure 3.9: When the path difference between consecutive diffracted X-ray beams is integer multiples of $2d \sin \theta$ constructive interference will occur. Figure adapted from [213].

In most modern XRD systems, X-rays are generated when electrons produced via thermionic emission from a W filament, are accelerated using a high voltage towards a Cu or Mo anode. Upon collision with the anode, the high kinetic energy of the electrons may be converted to form X-rays. The X-rays generated can be monochromated to reduce the bandwidth of wavelengths incident upon the sample. The monochromator is comprised of Ge crystals constructed such that they fulfil the Bragg condition at one specific wavelength. By restricting the range of conditions that may fulfil the Bragg condition higher resolution diffraction peaks can be obtained. Moreover, as passing through the monochromator is dependent not only on the wavelength of the X-ray but also upon its direction. This directional dependence collimates the beam and further improves the resolution as any angular divergence of the beam incident on the sample is translated to the detector. While monochromators can offer higher resolution spectra, one disadvantage of their use is a significant reduction in the intensity of the incident X-ray beam. Consequentially to obtain comparable signal-to-noise ratios, scans must be run over a long period of time. The majority of XRD work presented in this thesis took place on the D8 Discover instrument with a monochromated Cu source with wavelength $\lambda=0.1506$ nm. However, polycrystalline and amorphous samples were run on the D8 Advance system equipped with an unmonochromated Mo source. Due to the lack of monochromation both the $K\alpha_1$ and $K\alpha_2$ peaks are present which broadens the observed peaks, however the increase in X-ray intensity is beneficial for poly-

crystalline samples which can suffer from a lower reflected signal.

3.4.2 Grazing Incidence XRD

Grazing Incidence XRD (GIXRD) is a modification of standard XRD usually implemented to maximise the signal in polycrystalline thin films [214]. The penetration depth of X-rays in most materials is relatively high ($> 1 \mu\text{m}$), thus in low scattering materials such as polycrystalline or amorphous films, the 2θ signal collected may be dominated by signal from the substrate. By maintaining the X-ray source at low angles, one can increase the path the incident beam travels through the sample, thus increasing the signal received. In order to fulfil the Bragg condition the detector arm is swept through a larger range of 2θ positions. It is worth noting that GIXRD can struggle to examine highly textured materials such as polycrystalline samples due to the increased levels of signal lost through surface scattering effects.

3.4.3 X-ray Reflectometry

X-ray Reflectometry is a technique used throughout this thesis to obtain the thickness of thin films. Similar to XRD, this technique relies upon measuring the intensity of X-rays produced via interference effects, in this case when they are reflected from interfaces that lie within a thin film [215, 216]. In air, the refractive index is generally taken to be unity. As seen in Eq. 3.11, because the refractive index of the thin film being examined $> n_{\text{air}}$, total external reflection is observed until the incident beam of X-rays reaches a certain critical angle.

$$\sin \theta_C = \frac{n_f}{n_i} \quad (3.11)$$

Where θ_C is the critical angle, n_i is the refractive index of the initial medium and n_f the refractive index of the final medium.

Above the critical angle the intensity of the reflected signal decreases, with a form that is dependent on the structural properties of the sample. The observed oscillations are typically referred to as Kiessig fringes and their frequency and magnitude depend on the thickness of the film and the density difference between film and substrate [215]. Higher levels of roughness in the film leads to increased scattering of the incident X-rays and thus a faster damping of the XRR signal. The roughness therefore can be modelled as the rate of extinction of the XRR signal. In addition, as refractive indices can be related to the density of a

X-ray characterisation

material, one can use the critical angle to model the density of the thin film. As XRR relies solely on the electron density of a material, a significant advantage it possesses is that it is completely independent of the crystal structure or defects present in a sample [217]. There does exist however an upper limit on the film thicknesses that XRR can measure. For the Bruker D8 Discover used in this work this limit is 100 nm. Beyond this thickness, the period of Kiessig fringe oscillation exceeds the angular resolution of the instrument and no X-ray reflection is observed. Additionally, beyond this point the coherence length of laboratory X-ray sources becomes insufficient and more powerful and coherent X-ray sources become necessary.

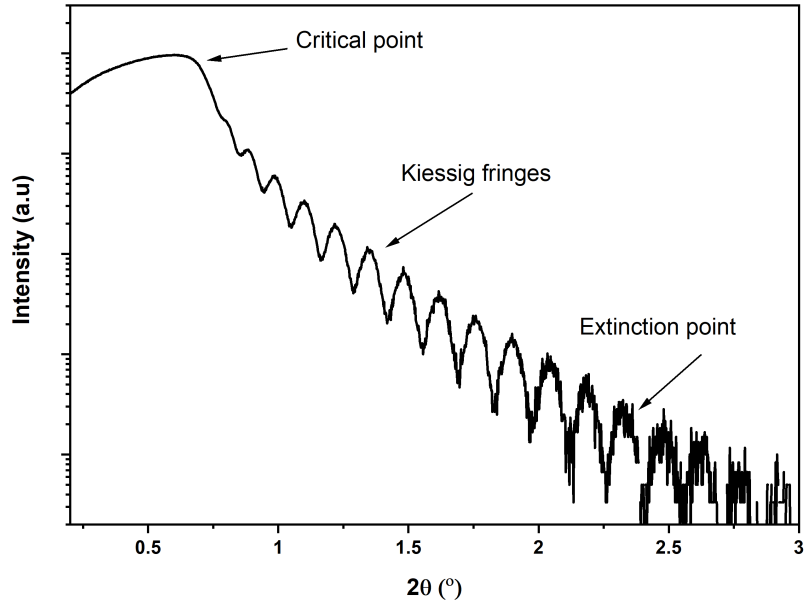


Figure 3.10: An example of an XRR plot used to calculate film thickness as the frequency of Kiessig fringe oscillation is correlated to the film thickness.

3.4.4 X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a technique used to identify and verify the elemental and chemical composition of thin films. XPS is based on the photoelectric effect first theorised by Einstein in 1907. Photons have quantised energies depending on the frequency of their oscillation (ν) as shown

in Eq. 3.12.

$$E = h\nu \quad (3.12)$$

where E is the energy of the photon, and h is Planck's constant. When a photon of sufficient energy strikes a material it may excite an electron to a higher energy level or out of the atom entirely. This effect is demonstrated in Figure 3.11. Electrons emitted in this process are called photoelectrons. Any excess energy the photon may possess is transferred to the photoelectron in the form of kinetic energy such that

$$h\nu = E_K + \Phi + E_B \quad (3.13)$$

where E_K is the kinetic energy of the photoelectron, Φ is the work function of the material and E_B is the binding energy of the core level electron in the atom.

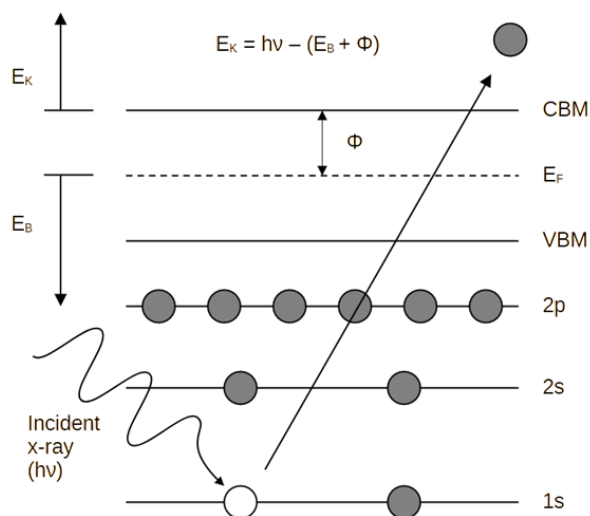


Figure 3.11: Illustration of the photoemission process

In order to generate X-rays for XPS, a thoriated tungsten filament is heated to produce electrons via thermionic emission. The electrons are then accelerated towards an anode by a potential difference of 10-15 kV. As the high kinetic energy electrons bombard the anode, typically composed of Al, an X-ray emission line spectrum is produced. This line spectrum can be subsequently monochromated using quartz crystals and Bragg's laws of diffraction described in Eq. 3.10 to select the Al $K\alpha$ line at 1486.7 eV [218]. When the sample is exposed to this X-ray irradiation photoelectrons are produced. The photoelectrons pass

X-ray characterisation

through a dual electrostatic lens system before reaching a HemiSpherical Analyser (HSA). The first electrostatic lens selects the analysis area of the sample and specifies the angular acceptance of the detector. The second electrostatic lens retards the photoelectrons through the use of a lens voltage. The HSA serves to function as a filter, only allowing electrons with the correct kinetic energy, which corresponds to the chosen pass energy to reach the detector. It is comprised of two concentric hemispheres of radii R_1 , and R_2 respectively. The inner sphere is negatively biased (V_1), while the outer sphere is positively biased (V_2) with respect to V the median equipotential between the two spheres. Consequentially, there exists an inverse square field between the two spheres. The pass energy (E_p) is defined as the energy of a photoelectron that travels through the HSA along the equipotential plane V [219], it can also be defined through Eq. 3.14 where

$$E_p = \frac{e(V_2 - V_1)}{\frac{R_2}{R_1} - \frac{R_1}{R_2}} \quad (3.14)$$

The resolution of XPS spectra depends upon the entrance and exits slits chosen, the acceptance angle of incoming electrons and the pass energy selected. Typical pass energy values range between 20-50 eV, with lower pass energies allowing high resolution XPS spectra. However, a balance must be struck as reducing the pass energy also decreases the intensity of the signal collected. Usually the XPS is run in constant analyser energy mode, where the pass energy of the HSA is held constant while the retarding potential of the second electrostatic lens is varied thereby allowing the measurement of a specified range of kinetic energies. The measured kinetic energy can be related to the photoelectron binding energy using Eq. 3.15, and as the binding energies of photoelectrons are characteristic of the elements present, XPS may thus be used to examine the elemental compositions of films [220].

$$E_K = h\nu - (\Phi + E_B) \quad (3.15)$$

In addition to elemental identification, XPS can also give information on the chemical state of elements within a sample. This can be seen as a shift in the E_B of a core level peak position, usually referred to as a chemical shift. This perturbation in the E_B is due to the Coulomb interaction that occurs due to an electronegativity difference when two atoms are in close proximity of each other, such as being bonded [220].

The intensity of the incoming photoelectrons relies upon a number of factors

such as the elemental concentration, source current, monochromator alignment, detector efficiency and detector focus. In addition, it also relies upon the relative sensitivity factor (RSF) of a particular atomic orbital. The RSF is an indicator of how easy it is to excite a specific core electron from a particular element relative to a C 1s orbital which is defined to have a RSF = 1 [220]. Therefore as the source current, monochromator alignment, detector efficiency and focus all remain constant throughout a particular scan, one can use the RSF to compare the concentration of elements within a sample

$$\frac{N_A}{N_B} = \frac{\frac{I_A}{S_A E_K^{0.7} \lambda_{IMFPA}}}{\frac{I_B}{S_B E_K^{0.7} \lambda_{IMFPB}}} \quad (3.16)$$

where $\frac{N_A}{N_B}$ is the concentration of element A relative to the concentration of element B. I_A and I_B represent the intensity of the photoelectron signal from A, and B respectively. Similarly, S_A and S_B are the photoionisation cross-sections of elements A and B. $E_K^{0.7}$ takes into account the difference in escape depths for electrons of a given E_K for elements A and B. And finally, λ_{IMFPA} , and λ_{IMFPB} are the inelastic mean free paths in elements A and B for that photoelectron kinetic energy and thus relate to the sampling depth.

Although XPS is an extremely powerful technique it does have some limitations. Firstly, XPS assumes a perfectly homogeneous distribution of elements. Therefore if the distribution of elements is uneven, the observed spectra may not be an accurate representation of the overall elemental composition of the material. Additionally, XPS relies on measuring the kinetic energy of emitted photoelectrons to convert to binding energy and thus identify the elements present samples in a sample. Within this principle lies a requirement that electrons may only be elastically scattered before leaving the material. Due to this requirement XPS is restricted to being a surface sensitive technique [221], as a photoelectron may only travel a finite path before energy loss interactions take place [222]. The average path length a photoelectron may travel before an inelastic collision occurs is referred to as the inelastic mean free path (λ_{IMFP}). The inelastic mean free path is element specific and depends on the energy of the incident photon however for most laboratory XPS sources the λ_{IMFP} is < 10 nm. For examining the elemental depth profile of a material XPS is typically combined with sputter and annealing cycles.

In this work an Omicron MultiProbe XPS system equipped with a monochromatic Al K α source (XM 1000, 1486.7 eV) and hemispherical electron energy

analyser (EA125) was used to verify elemental compositions. The instrument has a base pressure of 5×10^{-11} mbar, and an instrumental resolution of 0.6 eV for a 20 eV pass energy and slit settings of 4.5 mm. For XPS on a-ZTO, a pass energy of 50 eV was typically used which corresponds to 1.0 eV instrumental energy resolution. Although there is a drop in energy resolution, a-ZTO presents broad core level peaks, and a higher pass energy allows a higher intensity signal to be collected. Routine operation consisted of running a spectrum over all available energies to obtain a survey spectrum, before subsequent scans focusing on core level orbitals.

3.5 Synchrotron X-ray characterisation

3.5.1 X-ray Absorption Spectroscopy

As previously discussed XPS is a technique based on the principle of photoemission. X-rays incident on a material may excite a photoelectron from a core energy level, which is then used to examine the elemental and chemical character of the material. One drawback of XPS however is the limitations of laboratory X-ray emission sources, which are limited to the soft X-ray region such as 1486.7 eV for Al which is a common XPS X-ray source. X-ray absorption spectroscopy (XAS) is another X-ray spectroscopy technique which allows one to obtain chemical and bonding information from a material. XAS is based on analysing the modulation of the X-ray absorption coefficient $\mu(E)$. The oscillations in μ at and above the absorption edge are sensitive to the types and distances of atoms neighbouring the absorbing atom. Although XAS requires a synchrotron light source it presents a number of advantages when compared to XPS. Firstly, the intensity of the incident light beam is far higher than what is available with XPS in a laboratory setting, allowing one to scan faster due to an improved signal-to-noise ratio. Secondly, while laboratory X-ray sources are limited to producing soft X-rays, synchrotron facilities allow the selection of a much broader range of X-ray energies, well into the hard X-ray region. Finally, while in laboratory X-ray sources the incident X-ray beam has a fixed energy, in synchrotron facilities this energy can be tuned, allowing one to probe a far greater range of atomic core levels. In this work I shall discuss and present results using both X-ray absorption near edge structure (XANES) and extended X-ray Absorption Fine Structure (EXAFS) techniques. The summation of both of these techniques is commonly referred to as XAS or alternatively X-ray absorption fine structure

(XAFS). Both XANES and EXAFS are based on the same physical principle, the modulation of μ with X-ray energy, however as they focus on separate parts of the XAS spectrum they can provide different information.

As described in Eq. 3.13, when an X-ray is incident upon a material, photoemission may occur if the X-ray energy is greater than the binding energy of an electron in a core level of the atom. Any excess in energy is given to the photoelectron in the form of kinetic energy. If the incident X-ray does not have sufficient energy to excite a photoelectron, then the electron will not be perturbed from its well defined quantum state and the X-ray will not be absorbed. When the photon energy is equal to the binding energy of an electron in a core level a sharp jump in μ is observed. This is typically referred to as an absorption edge, which corresponds to the promotion of an electron to the continuum. Following the absorption event, the atom is defined to be in an excited state with a core hole. The atom may exist in this excited state for a finite period before decay processes occur, these may either take the form of fluorescence or Auger electron emission.

The measurement of $\mu(E)$ is conducted using the Beer-Lambert law which states

$$I = I_0 e^{-\mu t} \quad (3.17)$$

where I_0 is the intensity of the incident X-ray beam, I is the intensity of the beam after passing through the sample and t is the thickness of the sample. Rearranging this one gets the form typically used to describe μ .

$$\mu(E) = \ln\left(\frac{I_0}{I}\right) \quad (3.18)$$

Thus by measuring the intensity of the incident and transmitted X-ray beam the energy dependent X-ray absorption coefficient may be measured.

3.5.2 X-ray Absorption Near Edge Structure

XANES measures the variation in μ as the incident beam energy is swept from below the binding energy of a core level electron in the material to approximately 30 eV beyond the absorption edge. Although XANES is typically a more qualitative technique than quantitative, it is extremely sensitive as a probe of the local chemical and oxidation state of a material. XANES relies on the fact that there is a finite number of chemical environments that an atom may exist in, and the XANES spectra of these different chemical environments are consistent

within a functional group and easily distinguishable from one another. This is illustrated in Figure 3.12. The observed changes in spectra are due to changes in electron density that occur during bonding, which have a knock-on effect on the binding energy of core level electrons. A XANES spectrum can be divided

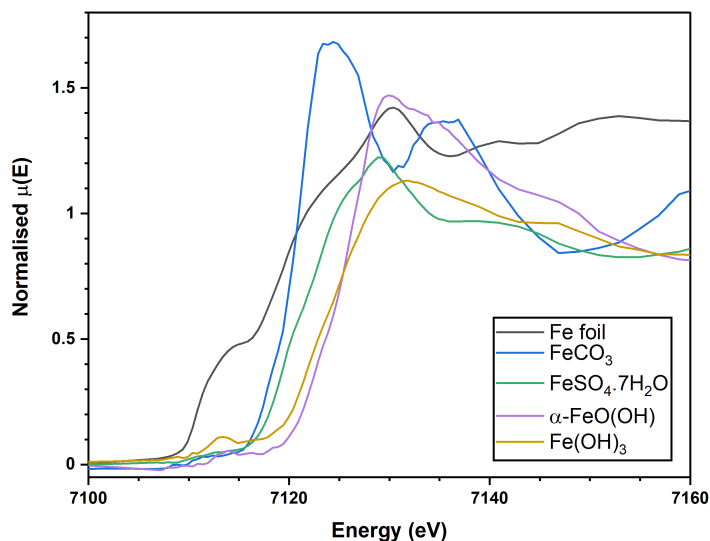


Figure 3.12: The XANES spectra of the Fe K-edge illustrating the effect of different oxidation states and functional groups. Reproduced from Newville [223].

into three main areas of interest

1. Pre-edge region - Features in the pre-edge region are based on promotions from core-levels to available bound excited states. These low intensity features are typically electric quadrupole rather than strongly allowed dipole transitions, for example $1s \rightarrow 3d$, or $1s \rightarrow 4d$ transitions. Therefore, the intensity of pre-edge features typically decreases as the population of the d-orbital increases. As a result, pre-edge features are a useful guide to the oxidation state of transition metals.
2. Absorption edge - The XANES peak shape and position are highly reliant on the chemical environment of the absorbing atom as is shown in Figure 3.12. Often the differences in XANES lineshapes can be quite subtle in which case $d\mu/dE$ is examined.
3. Post-edge region - Analysis of the post-edge region typically extends up to

30 eV beyond the absorption edge. Fitting of the post-edge features can be quite complicated however it is possible to use a combination of principle component analysis (PCA) and linear combination analysis (LCA). These analysis techniques can allow one to deconvolute and estimate the number and relative concentration of functionalised groups in a given spectrum.

3.5.3 Extended X-ray Absorption Fine Structure

Extended X-ray absorption fine structure (EXAFS) treats the μ signal as it extends far above the absorption edge, and involves sampling the configuration of neighbouring atoms that surround the absorbing atom. When a photoexcitation occurs, the photoelectron is ejected from the absorbing atom and may scatter off the electrons of neighbouring atoms. As the absorption coefficient relies on whether there is an available unfilled electronic state at the location of the absorbing atom, the presence of electron scattered back from the neighbouring atom will alter μ [223]. Thus EXAFS allows one to examine the scattering paths and neighbouring atoms that surround atoms of the chosen absorption edge. μ is typically described using Eq.3.19

$$\mu(E) = \mu_0(E) + \chi(E) \quad (3.19)$$

Where μ_0 is the absorption spectra expected for a single isolated atom, and $\chi(E)$ is *the* EXAFS term. This can be rearranged to

$$\chi(E) = \frac{\mu - \mu_0}{\Delta\mu} \quad (3.20)$$

Where $\Delta\mu$ is the step edge jump as shown in Figure 3.13. As EXAFS relies upon the scattering of the photoelectron from neighbouring atoms, and this is most easily understood by considering the wave-nature of the photoelectron, it is common to convert $\chi(E)$ from energy space to k -space where k is the wave number of the photoelectron, given by

$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}} \quad (3.21)$$

Where m is the mass of the photoelectron, E is the energy of the incident X-ray, E_0 is the absorption edge energy and $\hbar$ is the reduced Planck constant. The primary quantity used in EXAFS analysis is $\chi(k)$. When this signal is

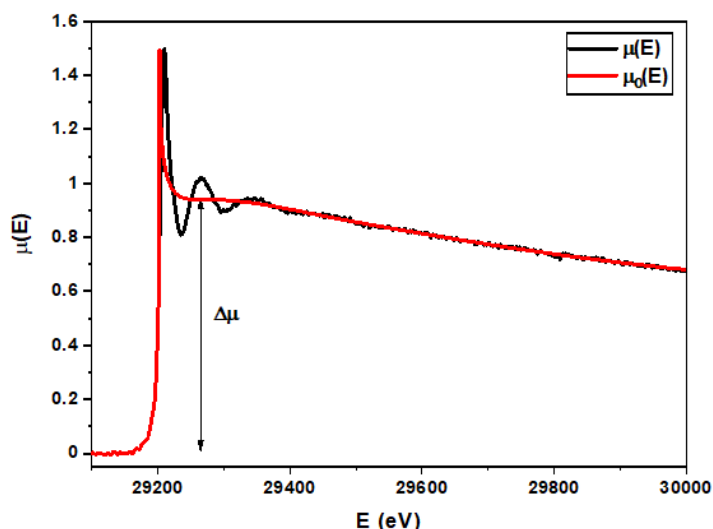


Figure 3.13: The extended μ signal shown along with the estimated signal from a single isolated atom μ_0 at the Sn K-edge.

plotted against the photoelectron wavenumber, k , a clear oscillatory function is observed. However, typically the $\chi(k)$ signal decays quite rapidly with k , therefore it is common procedure to multiply $\chi(k)$ by k^2 , or k^3 so as to extend the EXAFS signal. As mentioned, the $\chi(k)k^2$ signal possesses a clear oscillatory nature, that is comprised of one or more frequencies. The frequencies that appear in $\chi(k)k^2$ spectra correspond to different near neighbour coordination shells that each scatter the photoelectron along a different path. This can be observed by applying a Fourier transform to the $\chi(k)k^2$ signal, thus converting the signal back in real (R) space, where the $\chi(R)$ peaks correspond to the configuration of atoms that surround the average absorbing atom.

3.5.4 XAS data analysis

In XANES analysis it is standard procedure to normalise the spectra such that the absorption coefficient varies between 0 and 1. This is achieved by subtracting a pre-edge and post-edge function from the μ signal so the post-edge region has an intensity of approximately 1. In this work the pre-edge function used was a first order Victoreen function [223, 224], while the post-edge function was a constant.

In EXAFS analysis, subsequent to absorption coefficient normalisation, the bare

atom absorption coefficient (μ_0) is modelled. This can either be achieved by using a MBACK function developed by Weng et al. [225], or by using a spline function to model μ_0 . This bare atom contribution is subtracted from the μ spectra, to obtain a signal that solely depends on the interference of the scattered photoelectron. The signal is then converted into k space. A k weighting of k^2 was considered appropriate and was applied across all samples. A Kaiser-Bessel window function was then applied to the $\chi(k)k^2$ signal to remove additional noise from the spectra before, finally, a fast Fourier transform (FFT) was performed on the signal to obtain a $\chi(R)$ spectrum.

Instrumentation

Synchrotron sources provide a highly collimated and intense beam of X-rays with a range of energies. For XAS measurements it is important to be able to tune the wavelength of X-rays incident upon the sample. This is usually achieved in the hard X-ray region above 3 keV, using a double crystal monochromator comprised of two parallel and near perfect Si (111) crystals. The first crystal is centered on the incident X-ray beam and using Bragg's law of diffraction (Eq. 3.10) is rotated to reflect one particular wavelength of light. Due to the near perfect Si crystal, the reflected beam shows a very small energy spread with a high reflectivity coefficient ($\approx 100\%$). The diffracted beam then hits the second Si crystal which has the same lattice spacing as the first. The second crystal is orientated such that it is parallel to the first, so that it intercepts the reflected beam and re-diffracts it so that it is parallel to the incident beam. In this method, the wavelength of X-rays may be easily selected by rotating the set of Si (111) crystals through a single axis.

One challenge that synchrotrons face is the stability in the wavelength of the X-rays. The angular change needed to produce a different X-ray wavelength can be of the order of $1 \times 10^{-4}^\circ$, which can be difficult to maintain due to mechanical drift over time. Another issue is temperature drift, as there can be over 1 kW of power passing through an area the size of a few mm^2 [223]. This amount of power may cause the production of a significant amount of heat in the Si crystals which may cause the wavelength to drift as the temperature rises. In this work, both XANES and EXAFS was performed at the BALDER beam-line at the MAX IV synchrotron facility in Lund, Sweden. XAS was carried out at room temperature at the Zn and Sn K-edges, which occur at 9.66 and 29.2 keV respectively. The XANES and EXAFS spectra measured at the Sn

Microscopic characterisation

edge were collected using a transmission configuration, while XANES data at the Zn edge was collected using a PIPS detector in fluorescence detection mode. Multiple scans were recorded for a given spectra and subsequently merged in order to improve the signal-to-noise ratio.

FEFF fitting

FEFF is an ab initio calculation software developed by Bruce Mattis and John Rehr, to model EXAFS spectra [226, 227]. It can be used to extract bonding parameters from $\chi(R)$ spectra such as bond type, bond distance and coordination number. The version of FEFF software used in this work was FEFF8. FEFF works by modelling the crystal structure of a material as selected from a crystallographic database [228]. It then simulates a $\chi(k)k^2$ and $\chi(R)$ spectra for this crystal structure and then aims to fit the observed spectra to the calculated spectra using the EXAFS equation (Eq. 3.22)

$$\chi(k) = S_0^2 \sum_j \frac{N_j f_j(k)}{k R_j^2} e^{-2k^2 \sigma_j^2} e^{-2R_j/\lambda(k)} \sin(2k R_j + \delta_j(k)) \quad (3.22)$$

where j indicates shells of like atoms, S_0^2 is the passive electron reduction factor, N_j is the coordination number of an atom in the j th shell, k is the photoelectron wavenumber, R_j is the distance to the neighbouring atom, σ_j^2 is the Debye Waller factor and $\lambda(k)$ is the electron mean free path. There is also an induced scattering amplitude $f_j(k)$ and phase shift $\delta_j(k)$ which are dependent on the atomic number of the scattering atom.

3.6 Microscopic characterisation

3.6.1 Scanning Tunneling Microscopy

Scanning tunneling microscopy (STM) was first developed by Gerd Binnig and Heinrich Rohrer in 1981, and they later received a Nobel prize for their work in 1986. STM is based upon the concept of quantum tunneling between a biased probe and an atomically clean, conductive surface of a sample. An atomically sharp tip is held extremely close to the surface of a sample, then a bias (V) is applied to the tip which allows electrons to quantum tunnel from the tip of the

probe to the surface of the sample or vice versa.

$$I \propto e^{-kz} \quad (3.23)$$

where I is the tunneling current, k is a constant, and z is the distance between the probe and sample surface. As seen from relationship 3.23, the tunneling current is exponentially dependent on the distance between the tip and the sample, therefore STM can be used to map the topography of a surface.

STM is typically operated in either constant current mode (CCM) or constant height mode (CHM). In constant height mode, the height of the tip above the surface of the sample is held constant. As the tunneling current relies heavily on the distance between the tip and sample, CHM can be used to scan the surface topology for atomic steps or other morphological features. Conversely, in constant current mode, the tunneling current is held constant as the tip is rastered over the surface of the sample. Using a feedback loop to control and record the tip height, the tunneling current is held constant and the topography of the sample may be traced out. As electrons tunnel from the tip of the probe to the sample, STM is continuously probing the electronic structure of a sample. Therefore STM can also be used to detect different chemical species on a surface due to changes in the measured electronic structure of the sample.

3.6.2 Scanning Tunnelling Spectroscopy

Scanning Tunnelling Spectroscopy (STS) is a technique closely related to STM. In this technique instead of the tip being rastered across the surface of a sample, the tip position and height is held constant while the tip bias is swept from a positive to negative voltage (V). By recording the tunneling current (I), the density of states in the valence band and conduction band can be probed, and by examining the resulting dI/dV plot, the fundamental bandgap of the material at that point can be estimated. Often in STS a grid measurement system is implemented, whereby the bandgap of the material is measured at multiple points on the grid, these can then be averaged to estimate the bandgap of the whole sample.

In this work a commercial Createc low-temperature STM, with base pressure of 3×10^{-11} mbar, was utilised to examine samples in both STM and STS modes. Measurements were conducted in CCM mode at a temperature of 77 K. Single-crystalline W-tips with a (001) orientation were used, which were elec-

trochemically etched in NaOH solution.

3.6.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a useful technique for examining the morphology of materials far below the resolution limit of light based microscopes. As such SEM was used in this work to examine the morphology of thin films grown by magnetron sputtering.

In SEM, an electron beam is produced either by thermionic or field emission from an electron gun. The electron beam is then collimated and accelerated down the column of the microscope by a potential difference in the range of 5-30 kV. In this column a series of electromagnetic lenses focus the electron beam to a point which can then be rastered across the surface of the sample. The electron beam interacts with the sample producing a range of signals each offering differing information. The main signals in SEM are the secondary electron (SE) signal, the back scattered electrons (BSE) signal, and energy dispersive X-ray spectroscopy (EDX). Secondary electrons are produced by inelastic scattering processes that arise between the electron beam and the material. Due to the edge effect, where the intensity of the SE signal increases around edges in the sample, the SE signal is extremely useful for characterising the topography of a material. The BSE signal is produced by the elastic scattering of electrons in the electron beam from atoms in the material. As the cross section for Rutherford scattering increases with atomic Z-number, the BSE signal can be useful for examining the distribution of elements within the sample. Finally, EDX spectroscopy is a technique that is available in SEM imaging however because it was used far more frequently with scanning transmission electron microscopy (STEM), it shall be discussed in Section 3.6.4.

The two main limitations of SEM are the requirement for samples to be conductive, and the resolving power of the technique. While the former can be resolved by sputter coating the specimen with C or Au, the latter proves to be a more fundamental issue. The Rayleigh criterion, described in Eq. 3.24, states that the maximum resolution that may be achieved by a microscope depends on the wavelength of the particle used for imaging.

$$\theta_{min} = 1.22 \frac{\lambda}{D} \quad (3.24)$$

where θ is the angular resolution in radians, λ is the wavelength of light, and

D is the diameter of the circular aperture. This explains why scanning electron microscopes, by using high energy electrons for imaging, allow higher resolving power than light microscopes. Scanning electron microscopes typically have a maximum accelerating voltage of 30 kV, however, the main limitation to the resolving power of the instrument is aberrations in the electron beam. While electromagnetic lenses in the electron column attempt to focus the beam and remove these aberrations, due to the electron nature of the beam some aberrations in the beam shape will always be present. Therefore, the maximum resolution of a SEM depends on a number of operating parameters such as beam size, chosen accelerating voltage and type of signal collected, but is typically in range of 1-20 nm.

SEM images were taken using a Zeiss Gemini Ultra SEM. Prior to imaging, samples would be ultra-sonicated in acetone and isopropyl alcohol to remove any surface contaminants. Samples were then placed on SEM imaging stubs and grounded using silver paint to reduce charging effects during imaging due to a non-conductive substrate. Microscopy work was typically done using a low beam energy (5-10 kV) to reduce charging effects and maximise surface contrast for SE imaging.

3.6.4 Scanning Transmission Electron Microscopy

The first transmission electron microscopy (TEM) was developed in 1931 by Max Knoll and Ernst Ruska. For this work, Ruska later shared the Nobel Prize in physics with Gerd Binnig and Heinrich Rohrer in 1986. TEM has seen a rise in popularity over the past 2-3 decades due to the higher spatial resolution it offers over SEM. The increased accelerating voltages used in the electron column of transmission electron microscopes, typically in the range of 80-300 kV, enable nanometre level resolution imaging. Scanning transmission electron microscopy (STEM) is a modification to TEM where a condenser lens is added to the column before the electron beam reaches the sample. This changes the electron beam from a parallel illumination of the sample, to a point that can be rastered across the sample. STEM has seen increased popularity over TEM in recent years due to the increased spatial resolution it offers which when combined with techniques such as EDX, electron energy-loss spectroscopy (EELS) and 4D-STEM make it a powerful technique for local chemical and structural analysis.

The interaction of the electron beam as it passes through the sample in STEM allows for a different range of signals than are available in SEM. These

are namely bright field (BF) imaging, annular dark field (ADF) imaging, high angle annular dark field (HAADF) imaging, diffraction as well as EDX and EELS. For succinctness I shall focus on HAADF, EDX and EELS techniques as these were the techniques used in this work. The HAADF signal used for imaging, relies on inelastically scattered electrons typically scattered between an angle of 50-200 mrad from the central axis. As the electron cross-section increases with Z-number, higher atomic number elements will scatter strongly and appear brighter in HAADF imaging. An advantage of HAADF imaging when compared to TEM, is the ease of interpretation of images as multiple scatterings do not take place due to the high angle of collection, as well as allowing one to ignore the interference of electrons. One limitation of HAADF imaging however is its insensitivity to lighter elements due to the weak elastic and inelastic scattering at high angles from light elements. For this application ADF is typically used as it shows a much higher signal-to-noise ratio for lighter elements.

An important factor in any electron microscopy is aberration control and minimisation. Although theoretical calculations state that the resolving power of many STEM microscopes should be in the picometer scale, due to imperfections in the electromagnetic lenses used to focus the electron beam, aberrations are introduced which limit the possible resolving power of the microscope. Low order aberrations have a large impact on the shape of the electron beam. While the lowest order aberrations can be reduced by correctly focusing the electron beam to the correct height of the sample, higher order aberrations still remain and limit the resolving power of the microscope. In some sophisticated systems aberration corrected software is introduced which analyses the shape of the incident beam and may control the electromagnetic lenses to reduce aberrations present and increase the imaging resolution.

STEM work in this thesis was carried out on a FEI Titan G2 80-200 ChemiSTEM, equipped with a Schottky type FEI X-FEG electron gun, a Cs probe corrector, an in-column Super-X EDX unit with a dual electron energy-loss spectroscopy (EELS) detector.

3.6.5 Energy-Dispersive X-ray Spectroscopy

Energy-dispersive X-ray spectroscopy (EDX) is an extremely useful tool in electron microscopy as it allows simultaneous high resolution imaging and elemental space mapping. The technique is based on the excitation of core-level electrons

as the electron beam interacts with the sample. As electrons in the electron beam collide inelastically with atoms of the sample they may excite a core level electron, in the process creating an electron hole. The atom in this excited state is unstable, and the core hole has a finite lifetime before an electron from a higher energy level will fall down to replace the core-level population, with the difference in energy between the two energy levels being released as an X-ray. As the energy difference between core energy levels is characteristic of individual elements and their atomic structure, by measuring the energy of the emitted X-rays EDX can be used as a tool for elemental identification.

While EDX is extremely useful for live elemental mapping it does have limitations, particularly in detecting light elements with a Z-number < 11 . This is due these elements producing very low energy X-rays which are prone to strong absorption by the sample. Moreover, it is not possible to accurately calculate the amount of oxygen in a sample, which given the prevalence of oxide materials across many fields is problematic. While O content can be estimated by calculating the ratio of cations in an area and relating this to the expected coordination of the cations, this approach cannot be verified as stoichiometric information is not available from EDX.

3.6.6 Electron Energy Loss Spectroscopy

Electron energy loss spectroscopy (EELS) is a technique used during electron microscopy that can provide chemical and physical characterisation on the elements present. As has been previously discussed in Section 3.6.5 as the electron beam passes through the sample it may lose energy due to inelastic processes. In EDX, one is focused on the signal produced by the atoms from these interactions, in EELS one considers the losses to the electron beam from these inelastic collisions. There are two regions that are considered in EELS; core-loss EELS, where the electron beam excites core level electrons, and low-loss EELS which gives information on plasmons and small excitations that exist within the materials. Core-loss EELS can be used to collect information on the chemical and oxidation state of the elements present with extremely high spatial resolution. Meanwhile, low loss EELS provides information on the plasmons that are present in a material, which can be correlated to the bandgap of a material. The identification of these plasmons can be a useful tool for confirming the chemical stoichiometry present in a sample. While EELS can be a powerful tool, it too has limitations. Low-loss EELS detectors typically have a resolution of 1-2 eV

which makes the identification of any smaller shifts in the bandgap quite difficult. Similarly, while it is possible to observe shifts in chemical and oxidation state with core loss EELS these shifts are often far smaller than the large shifts between chemical states seen in XPS, thus making it a less effective than XPS for probing chemical and oxidation state changes. The dual EELS detector used in this work allowed the simultaneous measurement of both low-loss and core loss peaks.

Chapter 4

Band gap variation in amorphous zinc tin oxide thin films

In the previous chapters I have examined the fundamental properties and principle of operation of TCOs. I have explored the properties that define a high performance TCO and identified issues with the current industrial forerunner in $\text{In}_2\text{O}_3:\text{Sn}$ (ITO), as well as explaining the motivation for the considerable effort that has been spent to find a suitable alternative. In this chapter I shall explore a promising alternative candidate in amorphous zinc-tin oxide (a-ZTO). In this study I shall explore how the behaviour of a-ZTO varies with thickness in the low thickness regime and specifically how this relates to its optical and electrical performance.

4.1 Introduction

A promising alternative to IGZO is zinc tin oxide (ZTO). While ZTO is available in a number of forms including the crystalline ZnSnO_3 , and Zn_2SnO_4 , in this thesis I shall focus on its amorphous form (a-ZTO). a-ZTO shows low than 10 % absorption in the visible light region, and conductivities as high as 445 S/cm [65]. a-ZTO has also been produced by a wide variety of deposition techniques such as magnetron sputtering [78], ALD [76, 229], PLD [73], and CVD [230,

Deposition

231]. The chosen deposition method can have a large impact on the observed optoelectronic properties. This is because as an intrinsic semiconductor the optical and electrical properties of a-ZTO are strongly tied to the concentration of oxygen vacancies and metal and hydrogen interstitials in the film [4]. Thus small differences in growth compositions and conditions can affect the formation of defects and local structures that control charge carrier generation [232]. Previous studies have explored this modulation in optoelectronic properties with film composition, and have shown that charge carrier concentration and electron mobility can be tuned based on the Zn/Sn ratio [70, 77, 233].

However one area that has been overlooked is investigating how the optoelectronic properties of this TCO material vary as a function of the thin film thickness. This is pivotal as while a-ZTO has already been included in a number of devices and applications, if it is to see widespread use, a well grounded understanding of its optical and electrical behaviour is essential. In this chapter, I begin by examining the physical structure and chemical composition of magnetron sputtered a-ZTO thin films using SEM, XRD and XPS. Following this, the electrical and optical performance of the a-ZTO films are characterised as a function of the film thickness. Finally, an in-situ STS study is carried out to verify the presence of an observed blueshift in the band gap of the material.

4.2 Deposition

Samples of amorphous zinc thin oxide were grown via non-reactive RF magnetron sputtering from the cathode directly perpendicular to the plane of the substrate. Thin films were deposited from a single custom made ZTO sputtered target produced by Kurt J. Lesker, with a preset cation ratio of 30% Zn: 70% Sn as from a previous study this cation ratio was found to produce films with the highest conductivity values [77]. Prior to a deposition commencing a presputter of the sputtering target was performed for 10 minutes to remove any contaminants from the surface of the sputtering target. During depositions a power of 30 W was applied to the sputtering target, resulting in a power density of 1.48 W/cm^2 , and a deposition rate of approximately 2 nm/minute. This growth rate was calculated from a single thin film which was grown and its thickness measured via XRR and fitted in the Bruker Leptos software. The base pressure of the growth chamber was 1×10^{-5} mbar. During depositions a pure Ar gas flow of 30 SCCM was added to the main chamber, resulting in a pressure of $1 \times$

10^{-3} mbar during growths. A deposition temperature of 300 °C was chosen for this study as preliminary optimisation indicated that it corresponded with the best electrical properties in the a-ZTO thin films. Once the target temperature was reached with the SiC heater, the system was left for one hour in order to thermally equilibrate.

Samples were grown on quartz glass, of area 1×1 cm² for basic electrical, optical and morphological measurements. As STM, STS and XPS are all surface sensitive techniques an *in-vacuo* transfer from the magnetron to the STM and XPS instruments was performed using the vacuum suitcase as detailed in Section 3.1.5 and [234]. This enabled a pristine surface to be measured. Because of the *in-vacuo* nature, routine sample preparation for XPS and STM was not possible. For this reason, an alternative sample holder that would be compatible with both XPS and STM systems was devised, this is represented in Figure 4.1. In addition, in order to enhance the electrical contact with the sample, prior to sample growth gold contacts were deposited using a shadow mask at each of the 4 corners of the quartz substrate. Due to the comprehensive nature of the measurement, STS analysis was conducted on only two samples, which were selected for their extreme thicknesses.

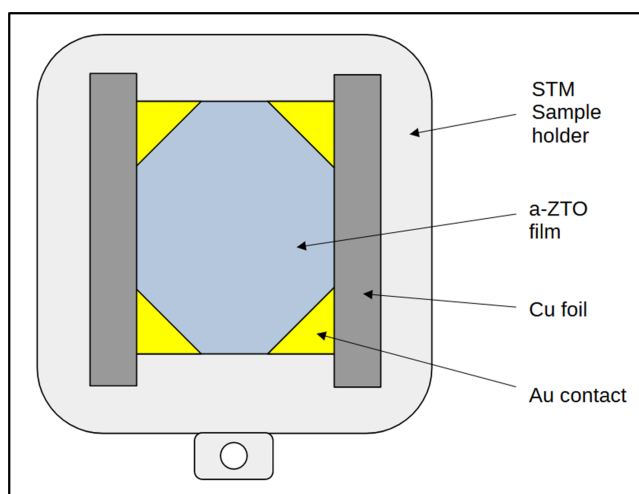


Figure 4.1: An illustration of the sample holder used for *in-vacuo* transfers to the STM and XPS instruments.

4.3 Physical characterisation

An accurate characterisation of the morphology of the a-ZTO thin films was imperative to understand the behaviour of the material at low thicknesses. To this end, several techniques such as XRR, XRD, SEM and XPS were employed to investigate the physical and chemical composition of the thin films.

The growth rate in magnetron sputtering is dependent on a number of factors including applied power, gas pressure, and substrate temperature. Although the growth rate had previously been calibrated for the deposition conditions used, the thickness of each of the samples in this study was verified using XRR measurements and fitting in the Bruker Leptos software. Figure 4.2, shows a representative spectra and fit for a 57 nm thick film. In total, six samples were produced ranging in thickness from 3, 6, 9, 12, 24, and 57 nm. All films show a low roughness of approximately 0.8 nm, which is observed by a clear XRR signal reaching as far as 3° .

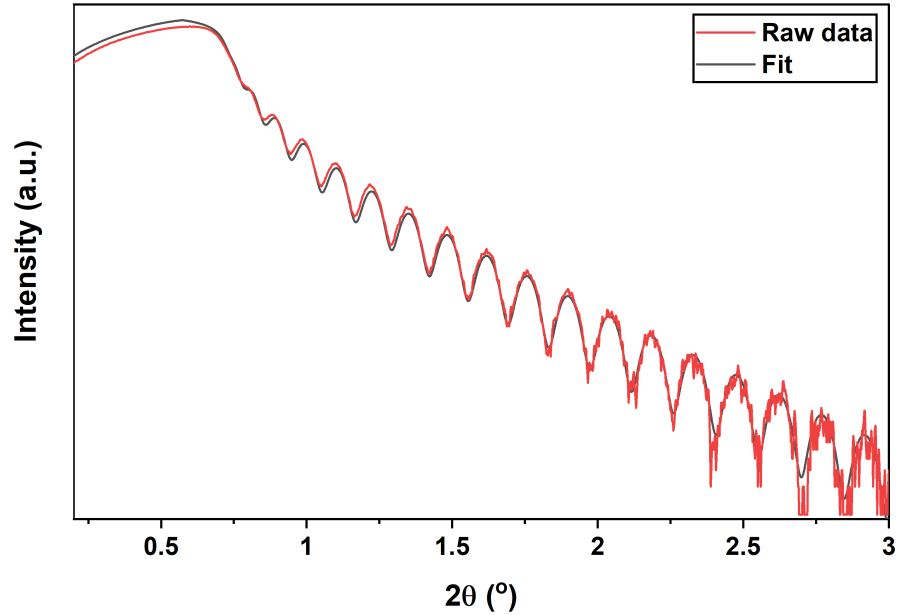


Figure 4.2: XRR data and fit on a 57 nm a-ZTO thin film. The extension of the extinction point out to 3° indicates low roughness in the films as expected for amorphous structures.

To characterise the local bonding structure of the zinc tin oxide thin films XRD was performed. ZTO is known to exist as several polymorphs including

the perovskite structure ZnSnO_3 , and as the inverse spinel form ZnSn_2O_4 , which can affect the charge carrier properties as well as the material's band gap [235, 236]. XRD measurements were taken in the grazing incidence configuration on the Bruker D8 Advanced using an unmonochromated Mo $K\alpha$ source at 40 kV and 40 mA through a 0.1 mm slit. The range of 2θ angles swept was from 10-70 °, while the source angle was kept at 1.5 ° throughout the scan in order to increase the X-ray path length through the sample and reduce the diffracted signal from the substrate. The only peak observed in the spectra is a single broad peak centred at 17.9 °, which is attributed to the quartz sample holders used for XRD. The GIXRD spectra confirm the amorphous nature of the

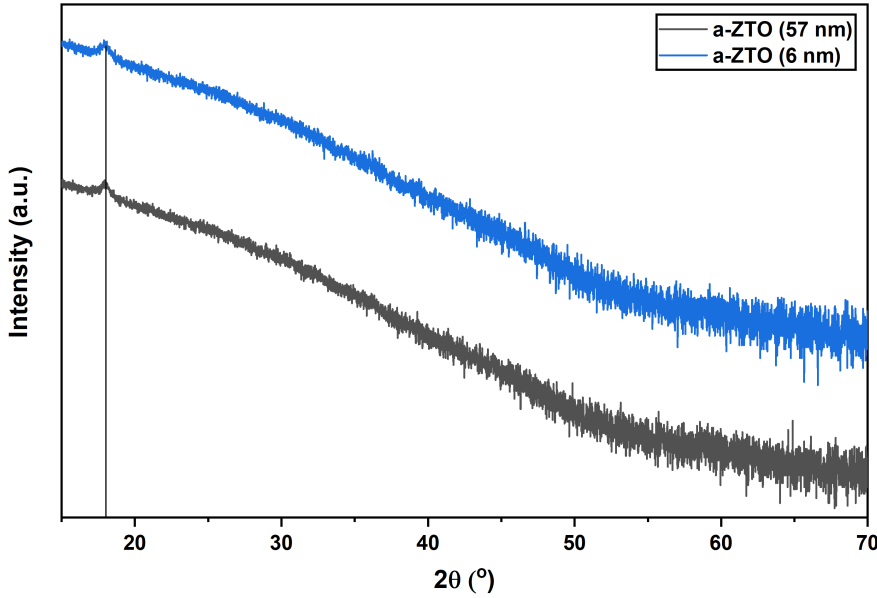


Figure 4.3: Grazing incidence X-ray diffraction shows that the a-ZTO thin films remain amorphous over the thickness regime examined, for visual clarity the spectra are vertically offset. A single broad peak is visible at 17.9 ° which is attributed to the quartz sample holder used.

ZTO thin films, and indicate that the films remain amorphous over the length scales investigated. As the constructive interference needed for XRD requires a repeating unit cell, the amorphous nature of the ZTO thin films prevents structural information such as bond length and grain size from being derived from XRD.

Following the examination of the thickness and crystalline nature of the

Physical characterisation

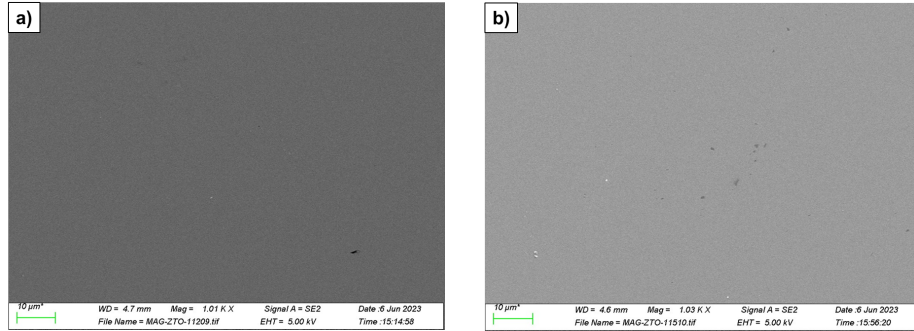


Figure 4.4: SEM imaging of a) high thickness (57 nm) and b) low thickness (6 nm) films. Both films indicate a smooth continuous surface that is free from grain boundaries or terraces.

thin films, SEM was employed to explore whether any morphological differences existed between the samples. SEM images presented in Figures 4.4a and 4.4b show the a-ZTO films are flat and amorphous with no indications of dislocations, grain boundaries or islanding. It is notable that the a-ZTO films remain smooth and continuous even in the low thickness 6 nm sample. This can be compared to spray pyrolysis grown a-ZTO which sees large macroscale changes in the structure of thin films based on the precursors used [70]. The main topological features that are observable in both samples are the small bright and dark artefacts which I identify as small droplets of silver paint that have landed on the sample surface during the sample preparation process. Furthermore, the SEM imaging is in agreement with the Leptos fitting from XRR data that the a-ZTO films possess low surface roughness.

In order to examine the elemental composition of the thin films an XPS study was performed. Two samples of a-ZTO were grown via non-reactive RF magnetron sputtering, these had thickness of 6 nm and 57 nm respectively, and represented the extremes of the thickness range examined. For the 57 nm film, an *in-vacuo* sample transfer was performed from the growth chamber to the Omicron Multiprobe XPS system using a vacuum suitcase with a base pressure of 2×10^{-10} mbar. An *in-vacuo* sample transfer was attempted for the 6 nm sample, however in the transfer process this sample inadvertently became exposed to atmospheric conditions. A survey spectrum as well core level spectra of the Zn 2p_{3/2}, Sn 3p_{3/2} and O 1s regions were recorded with 50 eV pass energy, resulting in instrumental resolution of 1.0 eV. In the survey

spectra, shown in Figure 8.1a of the Appendix, both samples show the expected core level and Auger peaks that are characteristic of the presence of Zn, Sn and O. An additional C 1s signal is observed in the 6 nm a-ZTO sample, which is attributed to adventitious C bonded to the surface of the film due to exposure to atmosphere. The effects of this air exposure can be noted from the lower peak intensity of the 6 nm in the measured core level spectra. No attempt was made to sputter clean the surface adhered carbon and hydrogen species from air exposure, as this may have a distorting effect due to surface band bending and preferred oxygen removal of Ar ion etching in vacuum [237].

As the stoichiometric ratio of the sputtering target does not always transfer directly to the stoichiometric ratio of the deposited thin films, core level spectra of the Zn 2p_{3/2} and Sn 3p_{3/2} peaks were analysed and quantified using the Casa XPS software. These are shown in Figures 4.5a and 4.5b respectively. Due to the amorphous nature of a-ZTO and the stable oxidation states of Zn²⁺ and Sn⁴⁺ cations this simplified the fitting process. Note, Sn can also exist in a Sn²⁺ oxidation state, however this form is not stable and SnO readily oxidises to SnO₂. Peak components were selected from the Casa XPS elemental library based on the peak position, and using Gaussian/Lorentzian (GL) line shapes and Shirley backgrounds. The fitting parameters are displayed in Table 4.1. The Zn/Sn composition was determined by comparing the cross sectional areas of the Zn 2p_{3/2} and Sn 3p_{3/2} peaks respectively. In this work, the Zn/Sn ratio of the sputtering target 30/70, resulted in a measured Zn/Sn ratio of 20.2/79.8 in the 57 nm film, and 17.5/82.5 in the 6 nm film exposed to atmosphere. This deviance from the expected Zn/Sn ratio may be due to inhomogeneities in the composition of the sputtering target or the preferential sputtering of Sn atoms. Nonetheless, while this Zn/Sn ratio is found to differ from the expected value it is found to be consistent across the range of thicknesses examined.

The Sn 3p_{3/2} peak in the *in-vacuo* transferred film shows an approximately 0.5 eV shift from the reference value for SnO₂ of 716.00 eV [238], while the Zn 2p_{3/2} peak is shifted 0.4 eV from the reference value of ZnO of 1022.30 eV [239]. Furthermore, in both samples it is observed that the Zn 2p_{3/2} peak is broader than the same peak measured for crystalline ZnO which has a FWHM of 1.61 eV at 20 eV pass energy [240]. This peak broadness in both of the cation peaks is attributed to the amorphous nature of the thin films. Because of this amorphous nature, a range of chemical environments exist within the films, which in turn gives rise to a range of chemical site dependent binding energies broadening the core peak full width at half maximum (FWHM). Therefore higher resolution

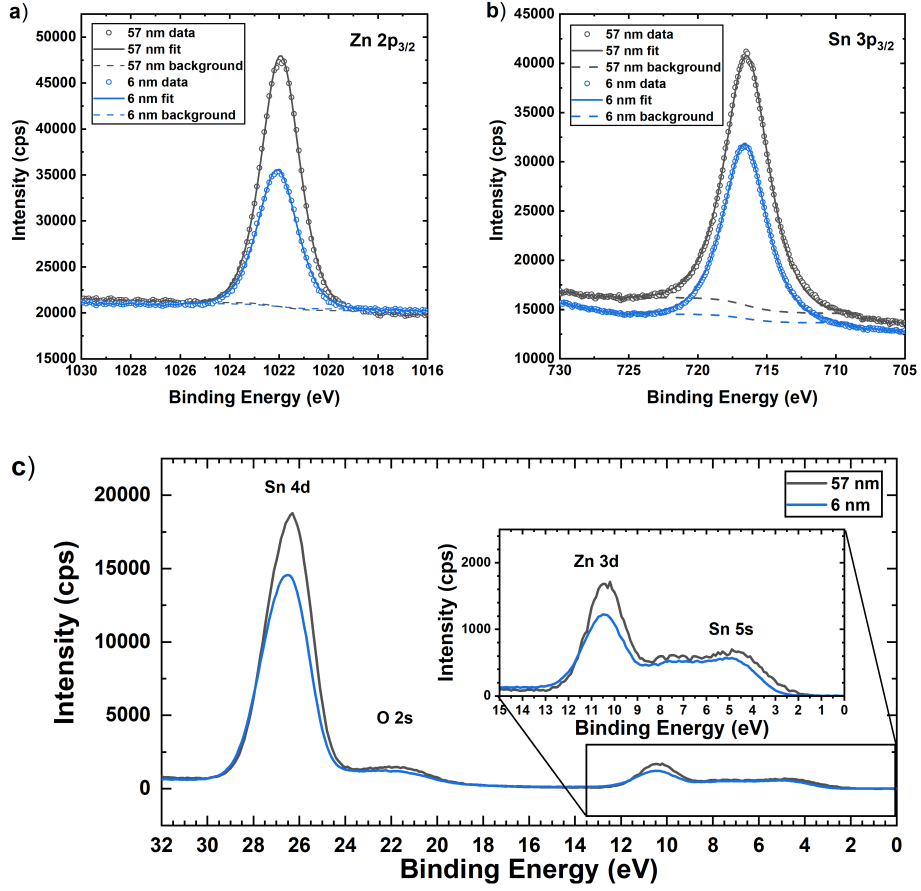


Figure 4.5: a) XPS spectra of the Zn 2p_{3/2} core level peak in both a 57 nm and 6 nm sample. b) Core level scan of the Sn 3p_{3/2} peak in a 57 nm and 6 nm film. The Zn 2p_{3/2} peak was fitted with a GL value of 57, and Sn 3p_{3/2} peak with a GL value of 70. The peak positions and residual of the fits are given in Table 4.1. c) Normalised XPS spectra of the valence band maximum region.

Sample	Peak	Peak position (eV)	FWHM (eV)	Area (%)
57 nm	Zn 2p _{3/2}	1021.9	1.81	7.5
57 nm	Sn 3p _{3/2}	716.5	3.71	29.6
6 nm	Zn 2p _{3/2}	1022.1	1.87	5.3
6 nm	Sn 3p _{3/2}	716.6	3.66	24.9

Table 4.1: XPS fitting parameters of Zn 2p_{3/2} and Sn 3p_{3/2} peaks in a-ZTO for a high and low thickness film.

measurements obtained at lower pass energy or narrower slits will not reduce the FWHM of the observed peak [237]. A 0.2 eV shift to higher binding energy is observable in the Zn 2p_{3/2} spectrum of the 6 nm film. This shift may be due to the adsorption of adventitious C and hydroxides on the surface of the film, however the small scale of shift indicates that the a-ZTO films are stable under atmospheric conditions. In the O 1s spectrum shown in Figure 8.1b in the Appendix, the effect of atmospheric exposure is observed by the presence of a doublet peak and an increase in the FWHM. In addition, in Figure 4.5c a shift of approximately 0.6 eV is seen between the VBM of 57 nm and 6 nm film, however the different intensity levels of the spectra make an exact comparison difficult. The implications of this shift shall be discussed in Section 4.5.

4.4 Electrical measurements

The conductivity, charge carrier conductivity and Hall mobility of the thin films was measured via the Hall effect described in Section 3.3. The 1×1 cm² sample geometry of the sample allowed the use of the van der Pauw configuration for these measurements. Silver wires adhered to each corner of the square samples using silver paint allowed stable electrical contact to be made with the sample. The Hall voltage was measured at multiple magnetic fields using an electromagnetic that can vary its field between -300 to 800 mT. The films showed excellent conductivities, with the highest value noted in the 12 nm sample (394 ± 39) S/cm. However, it is observed that below 12 nm, the a-ZTO exhibit a decrease in both Hall mobility and charge carrier density. This drop in the charge carrier density is attributed to a decrease in concentration of charge carrier generating defects such as O vacancies and cation interstitials at lower thicknesses. It is interesting to note the charge carrier concentration sees a drop at higher thicknesses as well. It is difficult to comment with confidence on the mechanism that might be causing this effect but if a-ZTO is to be a viable candidate for industrial applications this behaviour of the charge carrier concentration at higher thicknesses is indubitably something that should be more closely examined. The observed drop in Hall mobility can be understood if one considers the charge transport network as a percolation system. Above percolation threshold thickness the isotropic Zn 4s and Sn 5s orbitals that make up the CBM create a 3D charge transport network leading to high mobilities in the highly amorphous state [25]. However below a thickness of 12 nm, the 3D nature of the charge

transport network rapidly degrades leading to the sharp drop in Hall mobility.

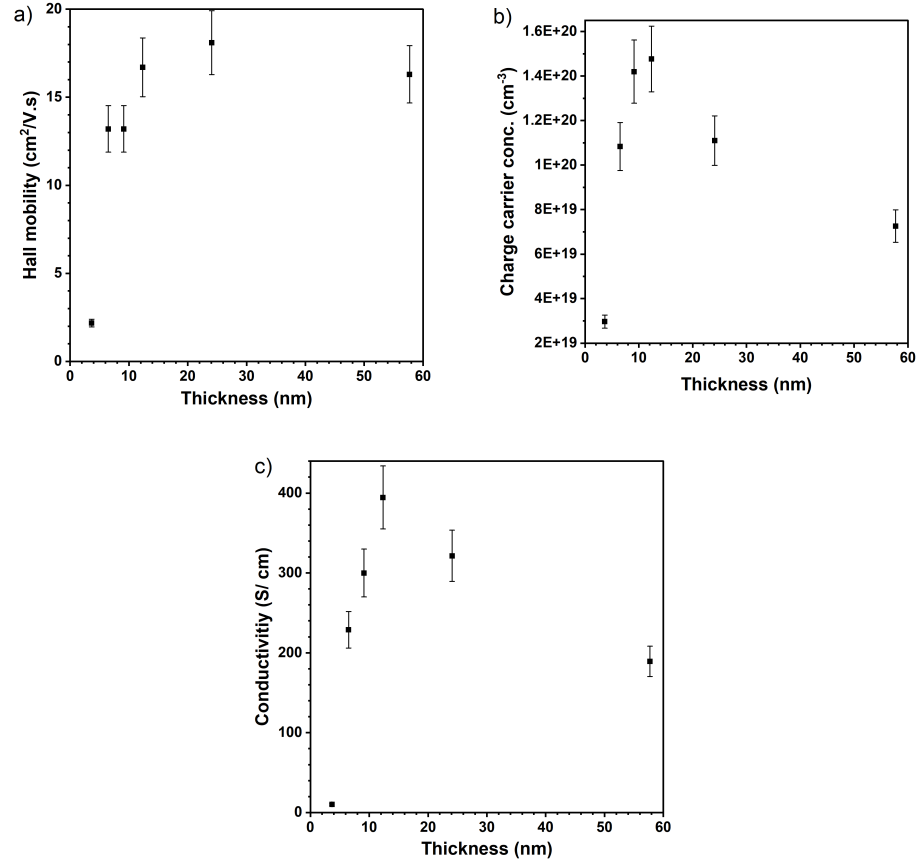


Figure 4.6: The variance of a) Hall mobility, b) charge carrier concentration and c) conductivity in a-ZTO as a function of thickness. A decrease in both the Hall mobility and the charge carrier concentration is observed below 12 nm which contributes to a sharp drop in the films' conductivity. Data is collated in Table 4.2.

4.5 Optical measurements

The optical band gap of the amorphous ZTO thin films was measured using the Tauc method as described in Section 3.2. Transmittance and reflectance spectra were taken in the 230-800 nm range using a PerkinElmer Lambda 650S spectrophotometer fitted with a small spot kit and integrating sphere. Figure

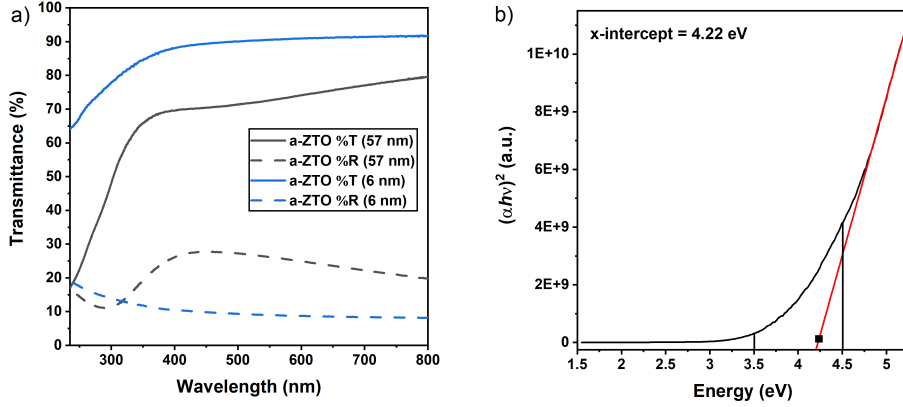


Figure 4.7: a) Overlying transmission and reflectance spectra for a high thickness (57 nm) and low thickness (6 nm) a-ZTO sample. b) Tauc plot of a direct allowed transition for a 24 nm thick film, due to the high density of subgap states the point of linearity becomes blurred, see (3.5-4.5) eV.

4.7b shows a Tauc plot from a 24 nm thin film modelled as a direct allowed transition ($\gamma = 1/2$).

Before discussing the results of the Tauc plot it is worth highlighting the limitations of such plots in cases of high subgap density of states (DOS), a prominent feature of amorphous TCOs. A high density of subgap states is a well known consequence of the disorder of amorphous materials. Such subgap states can introduce error into Tauc diagrams by blurring the point at which the absorption edge becomes linear. This occurs as the subgap DOS creates a low slope increase region, see (3.5 - 4.5) eV in Figure 4.7b. In this work, care is taken to ensure that measurements are obtained from the linear region at higher energies to avoid this broad onset. In addition there can also be the introduction of a "turn down" region as error is introduced by the transmission spectra saturating at higher energy. By working with films of sub-100 nm thickness, the films in use see significant (10-20%) transmission even at higher energy, see Figure 4.7a, thus avoiding these issues in this work. Figure 4.8 shows the calculated band gaps for the range of thickness of a-ZTO explored, these are then tabulated in Table 4.2. The FoM^G calculated from these films is lower than the value for ITO, which typically is in the range of $4 \Omega^{-1}$ [12], however the films overall do compare well with other a-ZTO films shown in Table 2.1. Additionally, a clear blueshift, the increase in the value of the optical band

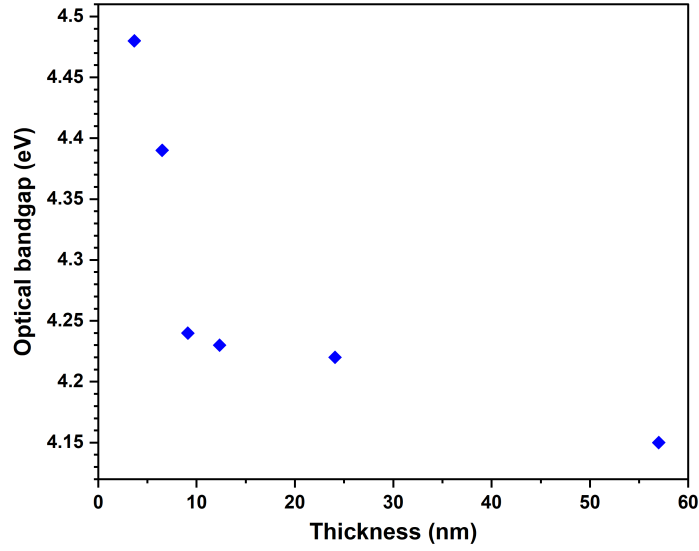


Figure 4.8: A blueshift in the optical band gap of a-ZTO thin films is observed with reduced thickness. Exact band gap figures are available in Table 4.2.

gap (E_g) with reduction in thickness, is observed. XPS analysis indicated an apparent 0.6 eV shift in the VBM of the 6 nm film which may be the cause of this 0.33 eV band gap blueshift, however there is a number of physical mechanisms that should be considered.

The Moss-Burstein shift is a common occurrence in TCO materials. Charge carriers will preferentially populate the lowest available energy state in the CB. As the charge carrier density increases new charge carriers must be excited to higher energies leading to an effective widening of the optical band gap. [6, 7] The observed behaviour however indicates the charge carrier concentration decreases as the thickness is reduced, see Figure 4.6b, thus carrier density related Moss-Burstein shifts can be ruled out as the cause of this blueshift. Another mechanism to consider is quantum confinement. Quantum confinement is an effect that occurs when charge carriers (electrons or holes) are confined in one or more dimensions. Electrons typically behave as free particles when the dimensions of the defining structure are very large when compared to the electron *de Broglie wavelength*. At this scale, electron energy levels can be treated as continuous bands. However, when the dimensionality of the system is reduced such as in thin films (2D), nanowires (1D) or quantum dots (0D) these energy levels cease to act as continuous bands and instead become discrete [241]. This

Scanning Tunnelling Spectroscopy

Sample (nm)	σ (S/cm)	μ_{Hall} (cm ² /V·s)	n (cm ⁻³)	avg. T (%)	E_g (eV)	FoM ^G (Ω ⁻¹)
56.7	189 ± 19	16.3 ± 1.6	(7.3±0.7)×10 ¹⁹	72.7	4.15	0.31 ± 0.03
24.1	321 ± 32	18.1 ± 1.8	(1.1±0.1)×10 ²⁰	83.0	4.22	1.11 ± 0.11
12.3	394 ± 40	16.7 ± 1.7	(1.4±0.1)×10 ²⁰	88.1	4.23	1.74 ± 0.17
9.1	300 ± 30	13.2 ± 1.3	(1.5±0.1)×10 ²⁰	89.3	4.24	1.03 ± 0.10
6.4	229 ± 23	13.2 ± 1.3	(1.1±0.1)×10 ²⁰	90.2	4.39	1.02 ± 0.10
3.7	10 ± 1	2.2 ± 0.2	(3.0±0.3)×10 ¹⁹	90.9	4.48	0.06 ± 0.01

Table 4.2: The electrical and optical properties of a-ZTO films as thickness is varied.

change in band structure has knock on implications for key properties such as optical band gap [242–244], conduction state (semiconductor, semimetal etc.) [245, 246], and photoluminescence [247]. In 2D transition metal dichalcogenides such as PtSe₂, a rise in band gap due to quantum confinement is commonly observed [245, 248]. Quantum confinement effects have also been predicted computationally for crystalline oxide systems such as SrTiO₃, BaTiO₃, KTaO₃ [243, 244]. Recently, quantum confinement resulting in a blueshift in optical data has also been observed experimentally in polycrystalline TCOs such as In₂O₃ [249] and ZnO [250, 251].

Labram et al. describe that a thin film of thickness L can be thought of as an infinite quantum well (IQW). The energy of conduction band states available to electrons confined to an infinite quantum well can be described by Eq. 4.1

$$E_n = E_{xy} + \frac{n^2 h^2}{8m^* L^2} \quad (4.1)$$

where E_{xy} is the energy associated with the electron in the unconfined xy -plane, n is a positive integer, h is the Planck constant, m^* is the effective mass of electrons in the semiconductor, and L is the thickness of the quantum well in the z -direction where the z -direction is defined as parallel to the surface normal [251]. One can clearly see that as the thickness of the films L decreases, the energy of the CBM ($n=1$) increases resulting in a blueshift in the energy required to excite an electron to the conduction band. The 0.6 eV shift in the VBM observed in Figure 4.5c, would ostensibly indicate that the VBM of the 6 nm film recedes to a lower value. This would disagree with the expected behaviour if quantum confinement was occurring, where the valence band structure is expected to be fixed and the change is primarily located in the CB.

4.6 STS measurements

While the Tauc method is a well-used approach for determining the band gap of TCOs, as previously discussed it contains within it a number of assumptions about the nature of the material and the its band gap. Thus in order to support that the changes being observed are real and not just an aspect of the fitting method, the band gap was also measured by alternative means. It is possible to measure the band gap of materials using electron energy loss spectroscopy (EELS) in the low-loss region. However the energy resolution of many EELS detectors is approximately 0.4-0.5 eV and thus would not be small enough to resolve the observed shift. While higher resolution systems are possible through monochromated electron sources these instruments are extremely costly and were not available. Additionally, sample preparation for EELS is destructive and very time consuming. A more appropriate method to resolve both the valence band (VB) and CB edges is scanning tunneling spectroscopy (STS) [252]. STS offers localised and non-destructive measurements that can therefore be utilised to punctiliously define the electronic band gap of a material.

It is important to note that STM/STS, which involves the tunnelling of electrons from the tip to surface or vice-versa, probes the surface and the tip. Tunnelling will only occur if there are available states in both the tip and surface. Therefore, assuming a metallic tip, tunneling will commence once the CBM and VBM energy relative to Fermi level is overcome. The localized measurement capability of STS means that it can probe the electronic structure of materials at the nanoscale, allowing for a detailed understanding of inhomogeneities and local variations in electronic properties that might be missed by bulk measurement techniques. STS therefore makes for an attractive methodology to further investigate this band gap blueshift.

A 6 nm and 57 nm film were grown as described above, and transferred *in-vacuo* to the STM. The STM and STS measurements were conducted in UHV with a base pressure of 3×10^{-11} mbar. STM images and STS spectra were recorded at a temperature of 77 K in constant current mode. Single-crystalline W-tips with a (001) orientation were used, which were electrochemically etched in NaOH solution. The tunneling bias was applied to the sample.

STM images of the 6 nm sample, in Figure 4.9a and 4.9b show a continuous surface void of any preferential growth directions or anti-islands, this is in agreement with SEM analysis (see Figures 4.4a and 4.4b). Root mean square (RMS) roughness values were calculated for both STM regions, these were found to be

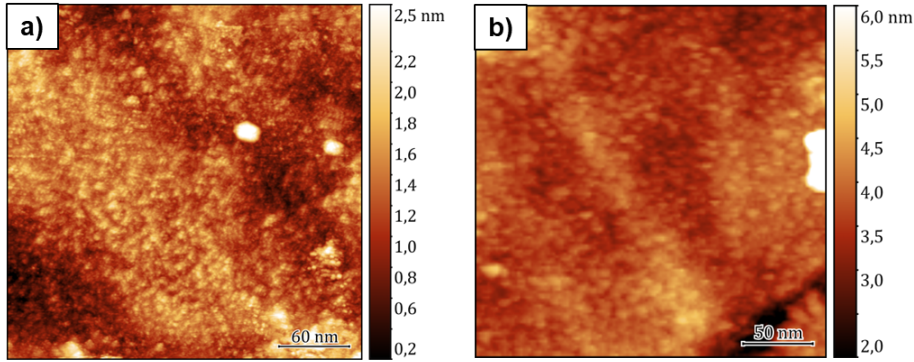


Figure 4.9: STM images of a 6 nm thin film a) 300 nm $\times$ 300 nm area, and b) 250 nm $\times$ 250 nm area, show a smooth and continuous surface with RMS roughness values of 337.5 pm, and 543.6 pm respectively.

337.5 pm for Figure 4.9a, and 543.6 pm for Figure 4.9b. These figures match, to the same order of magnitude, XRR fitting which estimates the roughness of the a-ZTO films to be 0.8 nm.

Through STS the electronic band gap at a single point of the thin film was measured. These dI/dV curves were then built up to create a series of heat-maps of the band gap in the thin films. Figures 4.10c and 4.10d are the averaged dI/dV curves for a heat-map, and are included as visual representation of the STS measurement process. A blueshift was observed between the average electronic band gap of the 57 nm film (2.56 ± 0.27 eV), and 6 nm film (3.04 ± 0.25 eV). This is due to a discernible shift in the position of the CB in the 6 nm sample. It is noted that both samples show a surface with a large dispersion of band gap values. Therefore in order to portray a more accurate representation of the band gap variation across the sample, interpolated band gap heat-maps for the 57 nm, and 6 nm film are shown in Figures 4.10a and 4.10b respectively. This dispersion in band gap values is due, in part, to the extremely localised nature of STS measurements (usually sub-nanometer) vs. the length scale of the pixel in the grid scan (6 nm). The grid pixel may represent an area at least an order of magnitude larger than the area of measurement resulting in this ostensibly large variation in band gap value from pixel to pixel. Another factor is the amorphous nature of the sample in question. The composition of the samples is not perfectly homogeneous, which may result in small clusters of ZnO, and SnO₂ as well as higher order O polymorphs forming [70, 253]. To

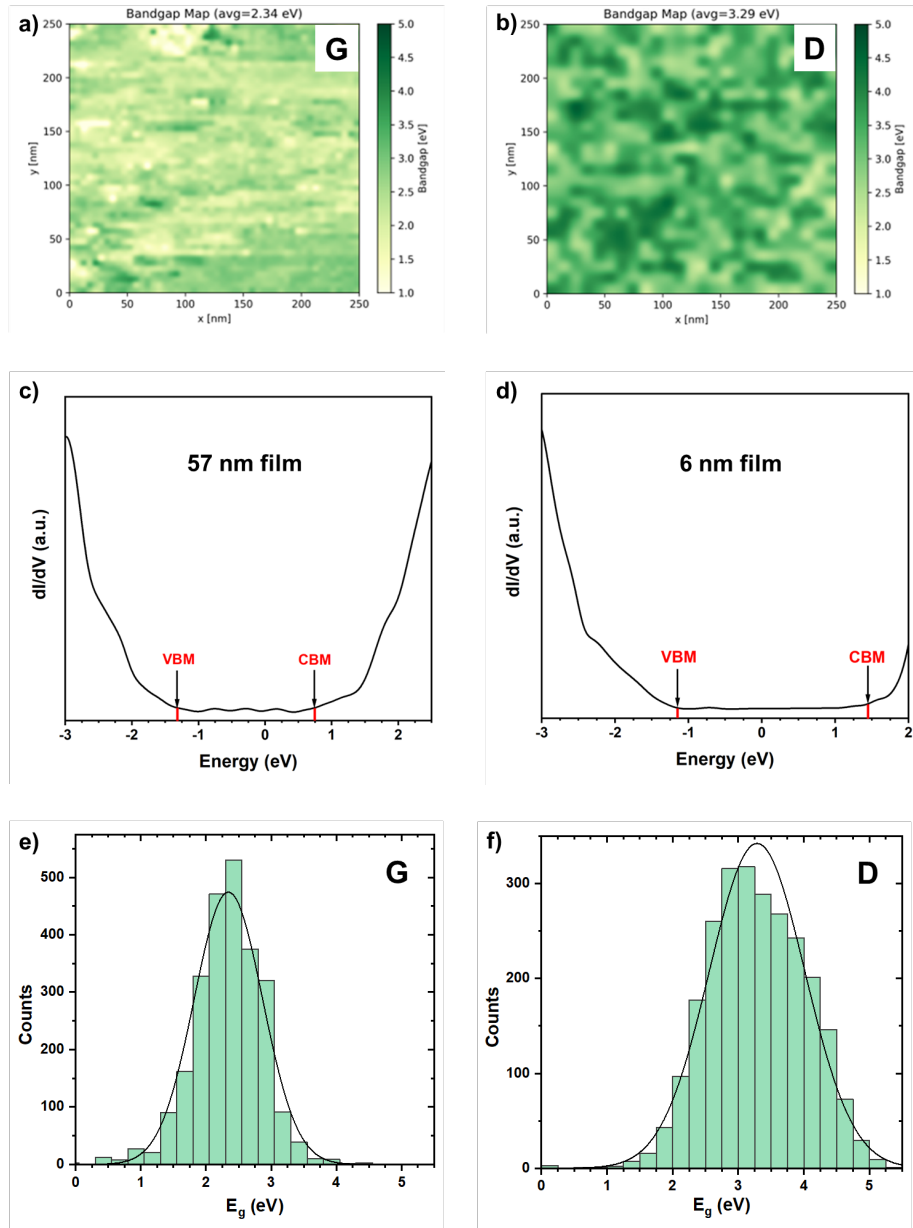


Figure 4.10: Figures a), and b) show interpolated STS grid spectra of a 57 nm, and 6 nm film respectively. Figures c) and d) are the averaged dI/dV curves from a band gap heat-map for a 57 nm, and 6 nm film respectively. Red drop lines have been added as a visual guide to illustrate the method of band gap estimation. Figures e) and f) are the corresponding histograms of Figures 4.10a and 4.10b, showing the range and frequency of band gap values recorded. A Gaussian curve has been overlaid on both plots.

demonstrate the distribution of the band gap values recorded in each band gap heat-map, histograms of the band gap values measured in each pixel are shown in Figures 4.10e and 4.10f. A discussion of the remaining band gap heat-maps, as well as statistical values such as the mean, median, standard deviation and kurtosis of the plots is available in the Appendix.

One must be cautious in comparing the exact band gap figures from UV-vis measurements and STS as they are based on entirely different methodologies. In STS one measures the highest lying occupied states in the VB and the lowest lying unoccupied states in the CB. In an amorphous thin film, it is extremely likely that these are tail states. However, when estimating the band gap from UV-vis spectrophotometry and the Tauc method, it is these tail states that one takes care to avoid. With these considerations taken into account, one can state that STS agrees with the observation of a blueshift in the band gap for a reduction of film thickness in a-ZTO.

4.7 Conclusion

To summarise, in this chapter an investigation into the optical and electrical properties of a-ZTO was performed as the thickness of the material was varied. First, high quality a-ZTO thin films were grown that demonstrated excellent as-grown conductivities up to 394 S/cm. These figures are quite competitive compared to those presented in Table 2.1 especially for such low thickness films. Furthermore, although the film conductivities are below the record conductivity of 445 S/cm published by Rucavado et al. [65], the films presented are without any post-growth treatment typically used to improve the conductivity of a-ZTO thin films, such as annealing in O₂ or H₂ atmospheres. Through XPS and XRD spectra, and SEM imaging, it was observed that the chemical and structural properties remain consistent throughout the thickness region examined. A significant drop in the material's electron mobility is seen below a thickness of 10 nm which I attribute to the degradation of the 3D conduction network beyond the percolation threshold of the material. Furthermore an increase in the band gap with reducing thickness is reported for a-ZTO. Below 10 nm, a significant blueshift of 0.33 eV in the optical band gap is observed. The presence and scale of the shift was confirmed via STS measurements (0.48 ± 0.26) eV. While the two techniques are based on differing principles and therefore do not measure the same total gap, the shift in both cases is found to be consistent. The mecha-

nism responsible for this band gap blueshift remains unclear. A 0.6 eV decrease in the VBM of the 6 nm was observed via XPS, however STS measurements indicate that the shift is primarily located in the CB as would be consistent with quantum confinement and the IQW model outlined above [251]. Further experimental work is required to definitively answer what is the cause of this blueshift, and this shall be given consideration in Chapter 7.

In the following chapter I shall examine the chemical and bonding environment of a-ZTO as the intercation ratio of Zn:Sn is varied in order to elucidate the effect that changing the intercation ratio on the behaviour and properties of the material.

Chapter 5

Investigating the local bonding structure of amorphous zinc tin oxide by X-ray absorption spectroscopy

In the previous chapter I examined the structural, optical and electrical properties of a-ZTO as the thickness of the thin films was varied. In this study I observed a blueshift in the band gap of the material which has implications for a-ZTO's inclusion in solar cell devices where band gap matching is vital to effectively extract charges from the active material. However a potentially more pressing issue in a-ZTO is the effect that varying the composition, specifically the cation ratio (Zn:Sn) has on the material's performance. In this chapter I shall use a combination of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy to explore the effect that varying the cation composition has on the local chemical and bonding environments.

5.1 Introduction

However, one issue that a-ZTO faces is the variance in its electrical and optical performance that it sees when it is prepared via different growth methods at nominally similar growth compositions [77]. As an amorphous intrinsic semiconductor, the mechanisms that governs its charge carrier concentration and carrier mobility are complex. Previous studies have investigated these properties and found that as the material is thermally stable and free from nanoscopic voids charge carriers are generated from point defects, namely oxygen deficiencies and metal cation clusters [232, 254, 255]. Subsequent investigations from Zhussupbekova et al. researched the role that film composition and cation ratio plays in the charge carrier concentration, electron mobility and absorption coefficient [70, 77]. They conclude that there are two conduction regimes that exist, namely a high Sn content region which sees a high charge carriers and an equal cation concentration region which sees high electron mobility. However, it remains unclear exactly how the cation ratio affects the formation of the point defects which control these electrical properties. The authors note however that the two conduction regimes coincide with the compositions of the theoretically predicted ZnSn_2O_5 and ZnSn_3O_7 [77, 256, 257]. It is hypothesised therefore that if these polymorphs do exist they may alter the formation energies of various defects within the material which may result in the observed variation in conductivity with cation composition. Clarity around the local bonding structure in a-ZTO would help researchers clarify how the doping mechanisms that occur within the material are affected as the material composition is varied. This in turn would provide a blueprint for the optimisation of the dopants and optoelectronic properties of a-ZTO for various applications.

In this chapter I employ a combination of X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the Zn and Sn K-edges to study the effect of changing the intercation ratio on local bond structure and physical properties of a-ZTO films grown by magnetron sputtering and spray pyrolysis. Both XANES and EXAFS examine the modulation of the X-ray absorption coefficient (μ) with incident X-ray photon energy. In XANES this is typically used to give information on the chemical environment and oxidation state of the absorbing atom, while in EXAFS, in collaboration with FEFF8 ab-initio fitting software it can be correlated to the local bonding environment of the absorbing atom. In this work I shall focus on XANES and EXAFS performed at the Zn and Sn K-edges which occur at 9.66 and 29.2 keV

respectively.

5.2 Deposition

In this chapter, samples of amorphous zinc-tin oxide were produced via non-reactive RF magnetron sputtering and spray pyrolysis. In order to obtain sufficient signal from XAS measurements, a-ZTO samples were grown to an approximate thickness of 100 nm. Prior to any deposition occurring a target presputter was performed for 10 minutes in order to clean the surface of the sputtering target. This was performed with the sputtering target shutter closed in order to preserve a pristine substrate. Sputter depositions were performed using two custom ZTO targets prepared by Kurt J. Lesker on quartz glass substrates of area $1 \times 1 \text{ cm}^2$ in a pure Ar atmosphere. These custom ZTO targets had a preset Zn:Sn cation ratio of 30/70 (MAG1), and 50/50 (MAG3). A power density of 1.48 W/cm^2 was applied to the MAG1 target, while a power density of 2.07 W/cm^2 was applied to the MAG3 target, in both cases achieving a deposition rate of 2 nm/ minute. The thickness of these films was measured and fitted using XRR and the Bruker Leptos software. A combination of both targets was used to achieve a 40/60 ratio (MAG2), with a deposition rate of 4 nm/ minute. A reference sample of SnO_2 was also prepared via RF magnetron sputtering using a SnO_2 target obtained from Kurt J. Lesker. The base pressure of the deposition chamber used for sample growth is $1 \times 10^{-5} \text{ mbar}$, which was raised to $1 \times 10^{-3} \text{ mbar}$ during depositions due to the addition of an Ar gas flow of 30 SCCM used to form the sputtering plasma. A deposition temperature of 300°C was used for sputter deposited films as this corresponded with previous studies on amorphous zinc tin oxide. Upon the SiC heater reaching the desired temperature the system was left for one hour in order to allow it to reach thermal equilibrium.

In addition to a-ZTO grown via magnetron sputtering, a number of a-ZTO samples were grown via spray pyrolysis. Four different combinations of precursors with Zn/Sn solution ratios of 50/50 were studied: Zinc acetate dehydrate + tin (II) 2-ethylehexanoate (SP1), Zinc acetylacetonate hydrate + tin (II) 2-ethylehexanoate (SP2), Zinc acetylacetonate hydrate + tin chloride (SP3) and Zinc chloride + tin (II) 2-ethylehexanoate (SP4). As the chemical precursors may decompose and evaporate at different temperatures, the composition of the films was later verified by XPS and these results are presented in Table 5.1.

Physical characterisation

All films were deposited on standard microscope glass slides (Thermo Scientific 2.5×5 cm, 1 mm thick) at a heater temperature of 450 °C. The precursor solution was sprayed at a rate of 1.7 ml/ min using a mixture of compressed air and nitrogen (95% N₂: 5%O₂) with a gas flow of 17 l/ min. A full and complete description of the system used is available in previously published work [70, 208].

5.3 Physical characterisation

Prior to XAS analysis the basic physical and structural properties of the films were characterised. This was done using a combination of XRD, and XPS as well as electrical and optical measurements. The range of a-ZTO cation compositions investigated was chosen to match the high charge carrier and high mobility regimes previously observed in a-ZTO [77]. In addition, samples of a-ZTO with matching cation compositions and prepared via spray pyrolysis were also examined, as spray pyrolysis presents different growth mechanisms than magnetron sputtering. Moreover, due to the variety of precursors used in spray pyrolysis growth it was assumed that would have an impact on the XANES spectra observed.

As the sputtering target or precursor ratio does not always directly transfer to the deposited thin films, XPS was used in order to confirm the Zn/Sn ratio of the thin films discussed in this chapter. Thus the focus of this XPS presented in this chapter is mainly on the cation peak ratios however a survey spectrum and O 1s core level spectrum for sample MAG1 are available in the Appendix as Figures 8.4a and 8.5 respectively. As before, XPS spectra were taken on an Omicron Multiprobe XPS system equipped with a monochromatic Al K α source (XM 1000, 1486.7 eV). The instrument has a base pressure of 5×10^{-11} mbar, and a pass energy of 50 eV was used to obtain an instrumental resolution of 1.0 eV for survey and core level spectra. Magnetron samples were transferred from the growth chamber *in vacuo* using a vacuum suitcase with a base pressure of 2×10^{-10} mbar, further details are available in previously published work [70, 234]. Spray pyrolysis grown samples were transferred in air and subsequently sputtered clean. An Ar ion gun was operated at a voltage of 750 V, with a sputter current of approximately 6 μ A and a chamber pressure of 1×10^{-5} mbar for 10 minutes. These sputtering parameters were chosen as it was found to effectively remove surface adsorbates without significantly damaging the sample surface [70]. Survey spectra of the spray pyrolysis grown samples are available

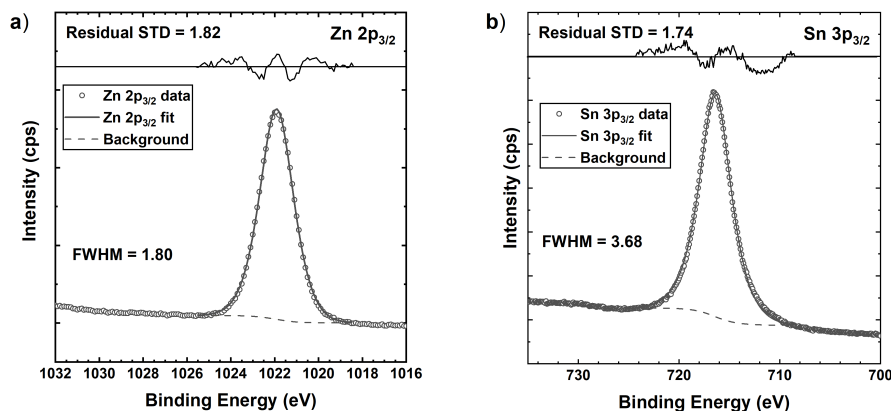


Figure 5.1: XPS was used to quantify the Zn/Sn ratio in each of the films studied. Shown are representative spectra from sample MAG1 of the a) Zn $2p_{3/2}$ and b) Sn $3p_{3/2}$ core levels. The Zn $2p_{3/2}$ peak was fitted with a GL value of 57, and Sn $3p_{3/2}$ peak with a GL value of 70. Peak positions and FWHM for each of the samples are shown in Table 5.1.

as Figure 8.4b in the Appendix.

As in Chapter 4, the spectra of Zn $2p_{3/2}$ and Sn $3p_{3/2}$ regions present broad core level peaks. This peak broadness is attributed to the range of chemical environments that the atoms experience due to the amorphous nature of the films. The Zn/Sn composition was calculated by comparing the peak areas corresponding to the Zn $2p_{3/2}$ and Sn $3p_{3/2}$ peaks in Casa XPS software. Peak areas were calculated using Gaussian/Lorentzian line shapes in association with a Shirley background function. Specifically, the Zn $2p_{3/2}$ peak was fitted with a GL value of 57, and Sn $3p_{3/2}$ peak with a GL value of 70. The cation peak positions and calculated Zn/Sn ratio of the films are presented in Table 5.1. All samples showed a shift in the Sn $3p_{3/2}$ peak position towards higher binding energy when compared to the value of 716.00 eV from crystalline SnO₂ [238]. Meanwhile, the position of the Zn $2p_{3/2}$ peak, specifically the a-ZTO films grown by spray pyrolysis, matches more closely to the value of reference ZnO of 1022.30 eV [239].

XRD is commonly used to verify the crystal structure and calculate lattice parameters of a material. Thus to in order to verify that the ZTO films were amorphous, grazing incidence X-ray diffraction (GIXRD) measurements were performed with a Bruker D8 Advance X-ray diffractometer using an un-

Physical characterisation

Sample name	Film Zn/Sn ratio (%)	Zn 2p _{3/2} peak position (eV)	FWHM (eV)	Sn 3p _{3/2} peak position (eV)	FWHM (eV)
MAG1	20:80	1021.9	1.80	716.5	3.68
MAG2	27:73	1022.0	1.82	716.4	3.83
MAG3	41:59	1022.1	1.74	716.5	3.65
SP1	31:69	1022.3	1.53	716.4	3.76
SP2	43:57	1022.5	1.52	716.8	3.77
SP3	31:69	1022.3	1.53	716.4	3.83
SP4	23:77	1022.3	1.71	716.7	3.70

Table 5.1: XPS fitting parameters used to estimate the Zn:Sn ratio in the a-ZTO thin films. All Zn spectra were fitted with a Gaussian/Lorentzian line shape of value 57, while Sn spectra were fitted with a Gaussian/Lorentzian line shape value of 70.

monochromated Cu K $_{\alpha}$ source (1.54 Å) at 40 kV and 40 mA through a 0.1 mm slit at an angle of (15-70) °. The corresponding spectra are shown in Figure 5.2. The only observable peak in these spectra occurs at 17.9 °, which is attributed to the quartz sample holder used during measurements. I conclude from this XRD analysis that despite the variation in cation ratio and starting precursors used, all of the ZTO show an amorphous structure. All of the a-ZTO films present an amorphous signal. The only peak observable in the spectra is a single broad peak which I attribute to the quartz sample holder used during measurements.

To characterise the optical properties of the a-ZTO thin films, transmittance and reflectance measurements were taken in the 230-800 nm range using a PerkinElmer Lambda 650S. Due to the borosilicate glass substrates used during the spray pyrolysis growth process, the spray pyrolysis samples were not compatible with UV-vis characterisation, as the substrates see significant absorption beyond 355 nm. For this reason, optical characterisation in this work focuses on RF magnetron sputtered a-ZTO. It is observed that the absorption of the a-ZTO, calculated by combining the transmittance and reflectance measurements, remains below 5% in the visible light range. Upon reaching 400 nm, the absorption drops due to the onset of optical excitation of charge carriers to the conduction band minimum. This can be represented in the Tauc plots shown in Figure 5.3b, which are modelled as direct allowed transitions. It is interesting to note a slight blueshift in the bandgap of the a-ZTO films increasing Sn cation concentration. This is agreement with previous UV-vis spectra on a-ZTO [70]. There are two plausible explanations for this shift; firstly, the Moss-Burstein

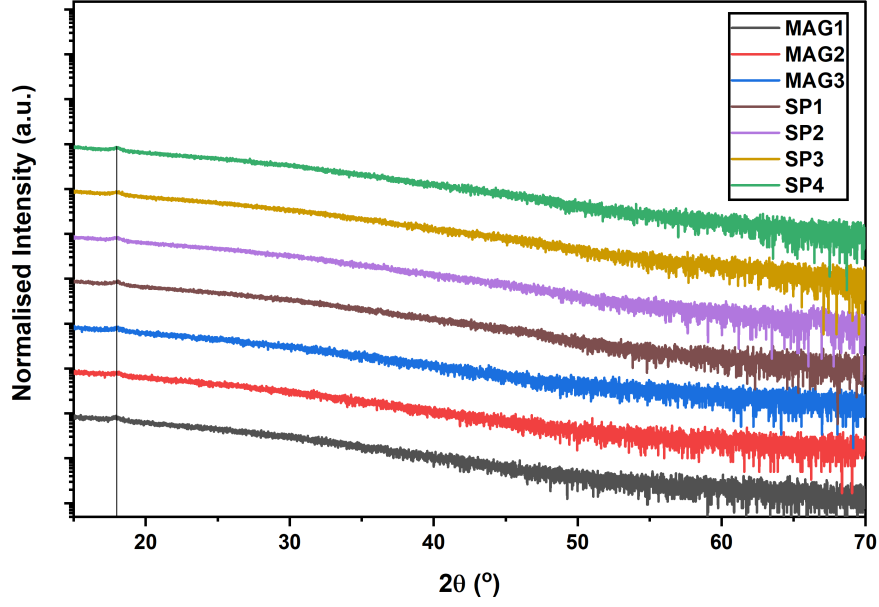


Figure 5.2: Grazing incidence X-ray diffraction shows no crystallinity in the samples between 15-70 °. For clarity the spectra have been vertically offset. A single broad peak is observed at 17.9 ° which is attributed to the quartz sample holder used to record spectra.

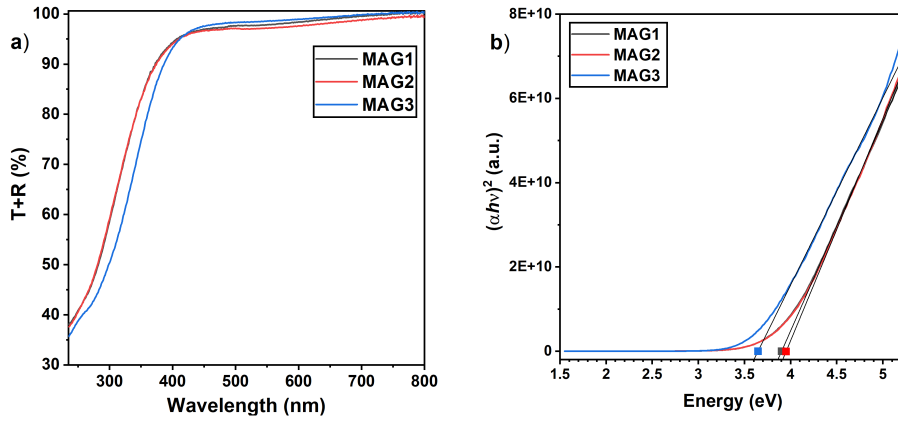


Figure 5.3: a) The absorption of the a-ZTO is plotted and can be expressed as $A = 1 - (T + R)$. b) Overlaid Tauc plots for RF magnetron sputtered a-ZTO thin films, a blueshift is observed with increasing Sn concentration

XANES at Zn K-edge

effect, where due to the increased charge carrier density observed at high Sn concentrations (see Table 5.2), an increase in the optical band gap is observed. An alternative explanation is that as ZnO has a lower band gap than SnO₂, when increasing the Zn content in the a-ZTO films one might expect the band gap value of a-ZTO to converge towards that of pure ZnO.

Sample name	Film Zn/Sn ratio (%)	σ (S/cm)	μ_{Hall} (cm ² /V·s)	n (cm ⁻³)	E_g (eV)
MAG1	20:80	228 ± 23	17.4 ± 1.7	$(8.2 \pm 0.8) \times 10^{19}$	3.9
MAG2	27:73	131 ± 13	16.0 ± 1.6	$(5.1 \pm 0.5) \times 10^{19}$	3.9
MAG3	41:59	76 ± 8	19.5 ± 2.0	$(2.4 \pm 0.2) \times 10^{19}$	3.6
SP1	31:69	73 ± 7	6.9 ± 0.7	$(6.6 \pm 0.7) \times 10^{19}$	-
SP2	43:57	180 ± 18	8.2 ± 0.9	$(1.4 \pm 0.1) \times 10^{20}$	-
SP3	31:69	24 ± 2	3.2 ± 0.4	$(4.7 \pm 0.5) \times 10^{19}$	-
SP4	23:77	304 ± 30	10.2 ± 1.1	$(1.9 \pm 0.2) \times 10^{20}$	-

Table 5.2: Electrical and optical properties of a-ZTO films as cation ratio is varied. Films grown via spray pyrolysis see a greater variation in electrical properties as there may be large macroscale changes in morphology between samples.

The conductivity, Hall mobility and charge carrier concentrations of the samples were measured using a four-point probe arrangement and an 800 mT electromagnet. Electrical connections in the van der Pauw configuration were made using silver wires that adhered to each corner of the sample with silver paint. The properties of the thin films are summarised in Table 5.2, notably it is seen that by controlling the cation ratio, properties such as charge carrier concentration (n) and Hall mobility (μ_{Hall}) can be varied. More specifically it is observed that at higher Zn ratios, the a-ZTO films show higher electron mobilities while at increased Sn content the films show a higher charge carrier density. This behaviour is in agreement with previous studies on ZTO, which in addition show that the bandgap of the material can also be tuned via the intercation ratio [77]. A greater variation in the electrical properties of the spray pyrolysis grown samples is observed. This is attributed to macroscale changes in the structure of the films due to the more aggressive nature of the growth technique and the different precursors used during growth [70].

5.4 XANES at Zn K-edge

To probe changes in the local chemical and bonding environment as the cation ratio was varied, X-ray absorption spectroscopy was measured and normalised at the Zn and Sn K-edges respectively. Crucially both XANES and EXAFS are independent of the crystalline nature of the material, making them well-suited to examine the bonding structure of a-ZTO thin films. XAS was performed at the BALDER beam-line at the MAX IV synchrotron facility in Lund, Sweden. The Zn K-edge at 9.66 keV and the Sn K-edge at 29.2 keV were chosen for this study as the K-edge transitions are more sensitive to changes in coordination and local geometry required for local bond arrangement studies. XANES data at the Zn K-edge was collected using a passivated implanted planar silicon (PIPS) detector in fluorescence detection mode between 9560 and 9810 eV. The necessary wavelength was selected using a Si{111} double crystal monochromator. Multiple scans were recorded for a given spectra and subsequently merged in order to improve the signal to noise ratio. XANES data was analysed using the Larix software created by Matthew Newville [223]. In order to normalise the X-ray absorbance factor ($\mu(E)$) to vary between 0 and 1, XAS spectra were fitted with a first order Victoreen pre-edge function and a polynomial post-edge function. XANES data was treated with a FFT smoothing filter with a box size of 5.

XANES relies on there being a finite number of chemical environments that an atom may exist in, and the XANES spectra of these different chemical environments are consistent within a functional group and easily distinguishable from one another. The Zn K-edge captures transitions from the Zn 1s orbital to empty Zn 4p orbitals in the conduction band. The XANES spectra of magnetron grown samples are depicted in Figure 5.4. The spectra are characterised by a relatively broad main peak at 9668 eV. This peak broadness is due to the amorphous structure of the thin films and is characteristic of a-ZTO [75, 258]. It is interesting to note that the peak shape remains consistent across all magnetron grown samples, with no shift in the main absorption edge. As differences in $\mu(E)$ can often be subtle and difficult to discern, the first derivative $d\mu/dE$, shown inset in Figure 5.4, was also examined to more closely evaluate any possible changes in line shape. A doublet peak with a subtle shift of 0.4 eV towards higher binding energy as the Sn cation concentration is increased is observed.

For comparison to the magnetron grown ZTO, samples of a-ZTO prepared via spray pyrolysis were also examined and shown in Figure 5.5. Spray py-

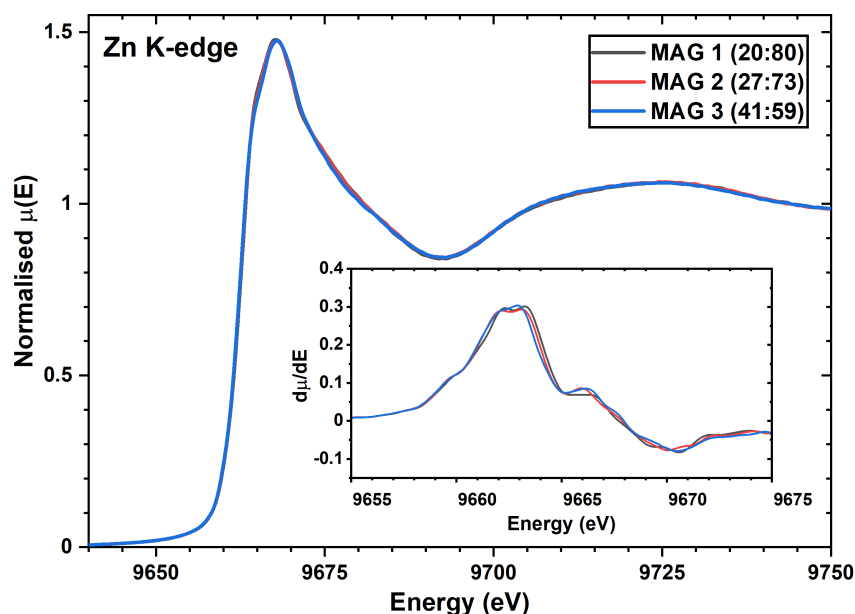


Figure 5.4: Normalised XANES spectra at the Zn K-edge of magnetron grown a-ZTO, and inset the first derivative, $d\mu/dE$, of the XANES spectra. The Zn:Sn ratio of the films is given in parentheses in the legend.

rolysis being a chemical vapour deposition method displays different growth mechanisms compared to magnetron sputtering, thus ZTO prepared using this technique may serve as a suitable comparison to any changes observed in magnetron grown a-ZTO. At this point it is worth noting that the XANES spectra of sample SP1 at the Zn and Sn K-edges were quite similar to the line shapes of MAG1 and SP4. Therefore for the avoidance of overlap and confusion in figures as well as clarity of discussion it was left out of Figures 5.5 and 5.7. However, as I felt it was still relevant to the general study of the effect chemical precursor has on the bonding environment it is included in Section 3.5.3. There are clear differences between the spectra of spray grown a-ZTO, most noticeable in the spectrum of SP3 at point A, where the shoulder at 9665 eV is typical of crystalline ZnO [75, 259], and point C. The $d\mu/dE$ of spray grown samples is shown in Figure 5.5 with a magnetron grown sample included for visual reference. The most noticeable changes are seen in SP3, where the even doublet present in magnetron grown a-ZTO is lost and replaced with a dominant peak at 9662 eV. One notes a similar shift in maximum peak intensity (towards 9662 eV) in SP2 and SP4, which may suggest a shift to a more crystalline ZnO environment.

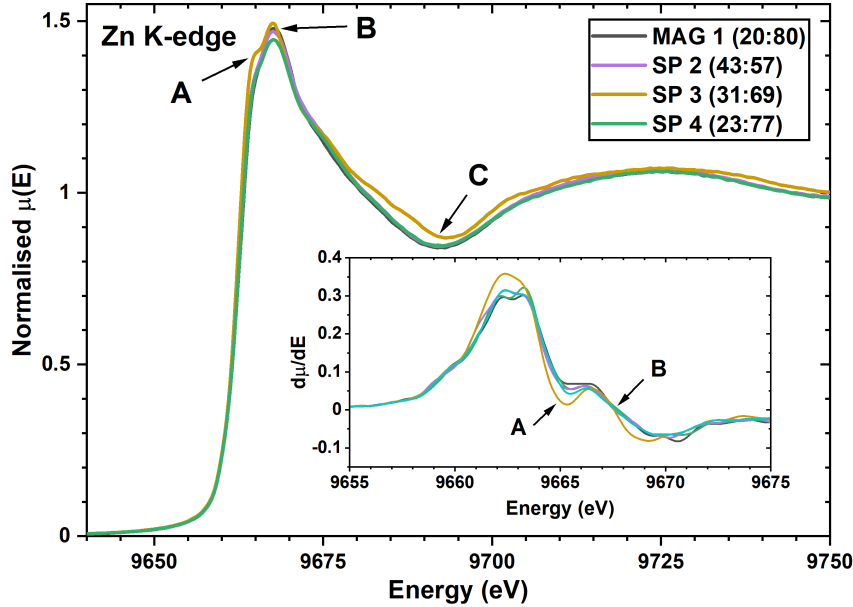


Figure 5.5: Normalised XANES spectra at the Zn K-edge for spray pyrolysis grown a-ZTO and inset the $d\mu/dE$ of the XANES spectra. Small variations are noticeable in the line shape of spray pyrolysis grown samples, most noticeable at points A, B and C, which suggests slight differences in the chemical environment. The Zn:Sn ratio of the films is given in parentheses in the legend.

5.5 XANES at Sn K-edge

The XANES spectra measured at the Sn K-edge were collected using a transmission configuration between 29120 and 29300 eV. Similar to the Zn XANES data, multiple scans were recorded for each sample and then merged in order to reduce the signal to noise ratio. Spectra were also treated with a first order Victoreen function in the pre-edge region while a constant value was implemented in the post-edge region. Finally a Sn XANES data was treated with a FFT smoothing function with a box size of 5.

The XANES spectra at the Sn K-edge for magnetron grown ZTO is shown in Figure 5.6, this is dominated by transition from the Sn 1s orbital to the empty Sn 5p orbital in the conduction band. Similar to the Zn XANES spectra, the single broad peak at 29210 eV is typical of a-ZTO [75]. Within the magnetron grown samples, one notices the small increase in the white line intensity of MAG3, however the peak shape and absorption edge remain unchanged. Examining

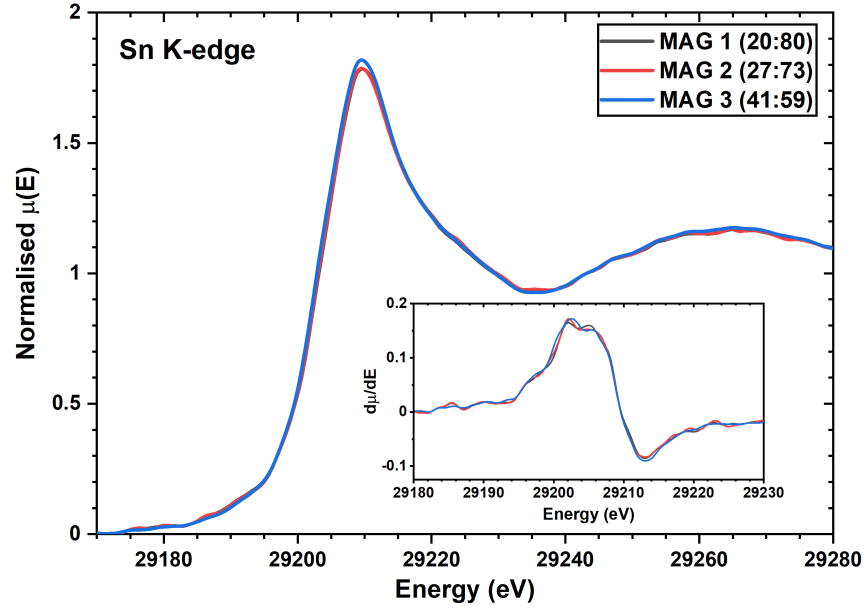


Figure 5.6: Normalised XANES spectra at the Sn K-edge for magnetron grown a-ZTO, and inset the $d\mu/dE$ of the XANES spectra. The Zn:Sn ratio of the films is given in parentheses in the legend.

the $d\mu/dE$ for magnetron grown ZTO in Figure 5.6, there are no discernible differences between the spectra of magnetron grown ZTO within the noise limit. All samples exhibit a relatively broad peak with a sharp maxima at 29202 eV.

There are several points of note when comparing the spray pyrolysis grown ZTO shown in Figure 5.7c. Firstly, SP4 is much akin to the magnetron grown

Sample name	Film Zn/Sn ratio (%)	Zn K-edge position (eV)	Sn K-edge position (eV)
MAG1	20:80	9663.3	29203.6
MAG2	27:73	9663.1	29203.4
MAG3	41:59	9663.0	29203.4
SP1	31:69	9663.1	29203.6
SP2	43:57	9662.5	29204.4
SP3	31:69	9662.3	29204.6
SP4	23:77	9662.4	29204.4

Table 5.3: Absorption edge positions for the Zn K-edge and the Sn K-edge for measured XANES spectra.

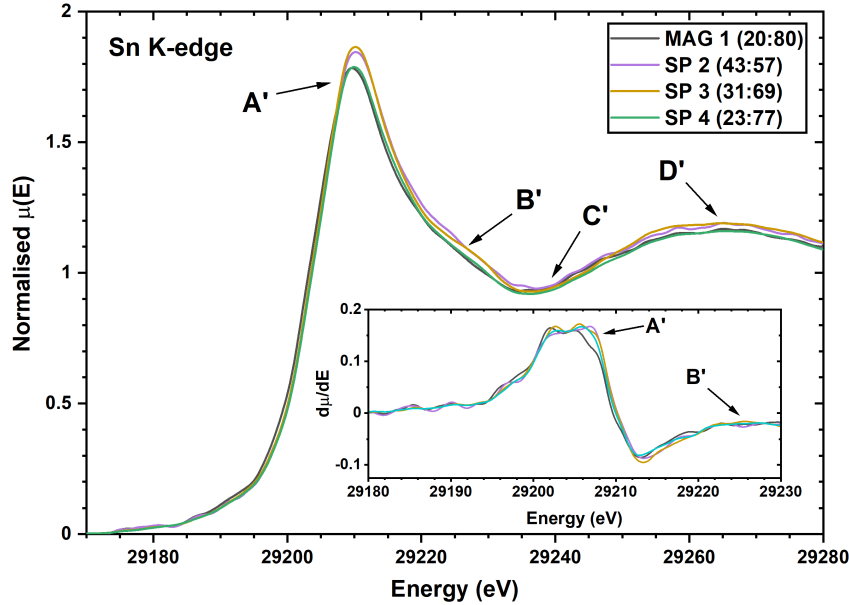


Figure 5.7: Normalised XANES spectra at the Sn K-edge for spray pyrolysis grown a-ZTO, and inset the $d\mu/dE$ of the XANES spectra. A blueshift in peak maxima in the $d\mu/dE$ is observed in samples SP2, SP3 and SP4 at point A'. The Zn:Sn ratio of the films is given in parentheses in the legend.

ZTO XANES spectra, suggesting extremely similar chemical environments. Secondly, samples SP2 and SP3 show a broader absorption peak and differences in the post-edge region most noticeable at the crossover points of points B', C' and D'. Finally, there is a slight blueshift in the absorption edge of spray grown samples, this is shown more clearly in Figure 5.7d. Examining the $d\mu/dE$ of spray-grown ZTO in Figure 5.7d, a feature at 29202 eV is still observed in all spectra however there is also a noticeable increase in intensity of the feature at 29206 eV in SP3 and SP4. This feature is continued to be blueshifted in SP2, with the maximum absorption seen at 29207 eV.

From XANES spectroscopy at the respective Zn and Sn K-edges it is evident that there is no change in the chemical environment or oxidation state in magnetron grown ZTO. This is shown in both $\mu(E)$ and $d\mu/dE$ of the Zn and Sn edge where there is no significant difference between spectra within the noise limit. In the case of spray grown a-ZTO, different growth precursors result in clear differences in the $\mu(E)$ and $d\mu/dE$, particularly in SP3 at the Zn edge. This is likely due to small amounts of unreacted precursor being present in the

sample which affect the local chemical environment of the cations.

5.6 EXAFS at Sn K-edge

In addition to the analysis of the near-edge regime shown above, EXAFS measurements of the extended post-edge range at the Sn K-edge were also recorded between 29080 and 30000 eV, to probe the local bonding environment in ZTO. A similar normalisation process as described above for the XANES data was carried out for the EXAFS spectra. Multiple scans were merged in order to reduce the noise present, and then spectra were normalised so $\mu(E)$ varied between 0 and 1. To achieve this a first order Victoreen function was applied to the pre-edge region while due to the extended signal range a quadratic function was applied to the post-edge region. EXAFS data was then treated with a 2nd order Savitzky-Golay smoothing function with a box size of 11.

Thereafter a smooth atomic signal (R_{bkg}) was subtracted from EXAFS data, $R_{bkg} = 0.8$, in order to subtract from the signal contribution of the absorbing atom. After data normalisation, EXAFS data was converted from energy space to k-space using the relationship described in Eq. 5.1, and the $\chi(k)$ was calculated for both magnetron grown and spray pyrolysis grown ZTO.

$$k^2 = 2m \frac{E - E_0}{\hbar^2} \quad (5.1)$$

where k is the electron wavenumber, m is the mass of an electron, E_0 is the K-edge absorption edge for the spectra and $\hbar$ is the reduced Planck constant.

Subsequently, $\chi(k)$ spectra were multiplied by k^2 in order to compensate for amplitude decay at higher k values. To achieve information on the shells surrounding the absorbing Sn atom, EXAFS spectra were multiplied by a Kaiser-Bessel window function with a range of 2-8 Å⁻¹ and a dk of = 4.0 Å⁻¹, and then Fourier transformed into R-space in the range of 1-8 Å. To extract quantitative information about the bond type, bond distance and Debye-Waller factors in a-ZTO the $\chi(R)$ spectra were fitted using the EXAFS equation (Eq. 5.2) and FEFF8 ab initio calculations in the Larix software package [228].

$$\chi(k) = S_0^2 \sum_j \frac{N_j f_j(k)}{k R_j^2} e^{-2k^2 \sigma_j^2} e^{-2R_j/\lambda(k)} \sin(2kR_j + \delta_j(k)) \quad (5.2)$$

where j indicates shells of like atoms, S_0^2 is the passive electron reduction factor,

N_j is the coordination number of an atom in the j th shell, k is the photoelectron wavenumber, R_j is the distance to the neighbouring atom, σ_j^2 is the Debye Waller factor and $\lambda(k)$ is the electron mean free path. There is also an induced scattering amplitude $f_j(k)$ and phase shift $\delta_j(k)$ which are dependent on the atomic number of the scattering atom. The FEFF8 calculations used to fit to the measured EXAFS data used a background function of $R_{bkg} = 0.8$, and a Kaiser Bessel window function with a range of $(2-8) \text{ \AA}^{-1}$ and a dk of $= 4.0 \text{ \AA}^{-1}$. Because the $\chi(R)$ spectra showed no extended range structure, fits in $\chi(R)$ space were limited between $(0.8-4.8) \text{ \AA}$.

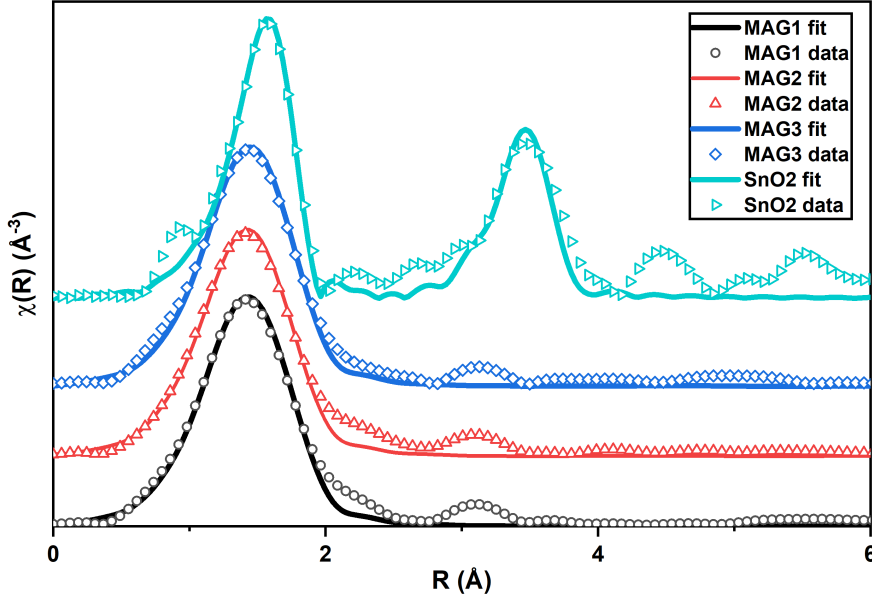


Figure 5.8: $\chi(R)$ spectra calculated from EXAFS measurements at the Sn K-edge and corresponding FEFF8 fits for magnetron grown a-ZTO and reference SnO_2 . Due to amorphous nature of the a-ZTO, a higher order signal is only observed for SnO_2 .

The first peak in the $\chi(R)$ spectra shown in Figures 5.8 and 5.9 comes from the first nearest neighbour (1NN) shell of atoms to the absorbing atom. It is possible for higher order shells to appear in $\chi(R)$ spectra, this where one would expect to see a signal from the ZnSn_2O_5 or ZnSn_3O_7 polymorphs, however due to the amorphous nature and lack of long-range order in the a-ZTO thin films, this higher order is quickly attenuated in all samples. This effect is observable in the $\chi(k)$ spectra shown in Figures 8.6a and 8.6b of the Appendix, whereby

EXAFS at Sn K-edge

Sample name	$N \cdot S_0^2$	R (Å)	σ^2
MAG1	6.1 ± 0.5	2.031 ± 0.009	0.008 ± 0.002
MAG2	6.1 ± 0.6	2.031 ± 0.009	0.008 ± 0.002
MAG3	6.0 ± 0.5	2.035 ± 0.009	0.007 ± 0.002
SP1	5.8 ± 0.6	2.042 ± 0.010	0.007 ± 0.002
SP2	6.1 ± 0.6	2.029 ± 0.010	0.008 ± 0.002
SP3	6.0 ± 0.7	2.041 ± 0.011	0.005 ± 0.002
SP4	5.7 ± 0.6	2.042 ± 0.011	0.006 ± 0.001
SnO ₂	5.6 ± 0.6	2.053 ± 0.007	0.003 ± 0.001

Table 5.4: FEFF8 fit parameters after fitting to the first shell, where; N is the Sn coordination number, R is the Sn-O bond distance, and σ^2 is the Debye Waller factor

the fine structure of the $k^2\chi(k)$ signal is quickly attenuated for all a-ZTO samples, while the SnO₂ reference sample shows features at 5 Å^{-1} , 6.5 Å^{-1} and beyond. This agrees with XRD characterisation shown in Figure 5.2. Due to this strong attenuation in the $\chi(R)$ signal, only the first shell of a-ZTO was fitted to in FEFF8 calculations, which in this case relates to Sn-O bonds. In addition, as only 1NN atoms are considered, only single scattering paths for the photoelectron are included in fitting. A small peak feature is visible at 3.2 Å , however it is too small to be able get a meaningful fit to due to the presence of multiple photoelectron scattering paths in this region. The starting inputs for the Sn-O path are based on rutile SnO₂, with space group (P42/mnm) [260]. The $\chi(R)$ spectra and fits are shown in Figures 5.8 and 5.9 and fit parameters shown in Table 5.4. A small shift of 0.02 Å is seen in the Sn-O bond length between sputtered a-ZTO samples and the SnO₂ reference sample. This SnO₂ reference thin film, also prepared via magnetron sputtering, shows good agreement with the Sn-O bond distance recorded in literature of 2.054 Å [260–262]. Additionally it is noted that the coordination number of the Sn atoms in the reference SnO₂ is slightly lower than the expected value of 6, this may suggest a slight O deficiency in the sample.

Analysis of the $\chi(R)$ spectra shows no long range order in any of the a-ZTO samples and hence discounts the formation of a-ZTO polymorphs at a local, next nearest neighbour scale as had previously been suggested [77, 256, 257]. Trejo et al. propose that the Sn atoms in a-ZTO form distorted SnO₂ polyhedra [263]. This is reflected in $\chi(R)$ data and Table 5.4 where the Sn atoms show a pronounced Sn-O shell and possess approximately octahedral coordination. I

attribute the large variation in Sn coordination number due to dangling bonds whose concentration increases as the amorphous nature of the films increases. I propose that as there is no long-range order in the films, these distorted SnO_2 octahedra, along with distorted ZnO tetrahedra[258] act as 'building blocks', which are randomly arranged throughout the entire material. As one changes the intercation ratio in the thin films, one is effectively changing the ratio of building blocks within the material. The conduction band minimum (CBM) of a-ZTO is known to be a mixture of Zn-4s and Sn 5s orbitals hybridised with O 2p orbitals [258]. Therefore by altering the intercation ratio one will affect the strength of hybridisation at the CBM and thus affect the properties that are dependent on the electronic structure at the CBM such as electron mobility, and bandgap [77, 263].

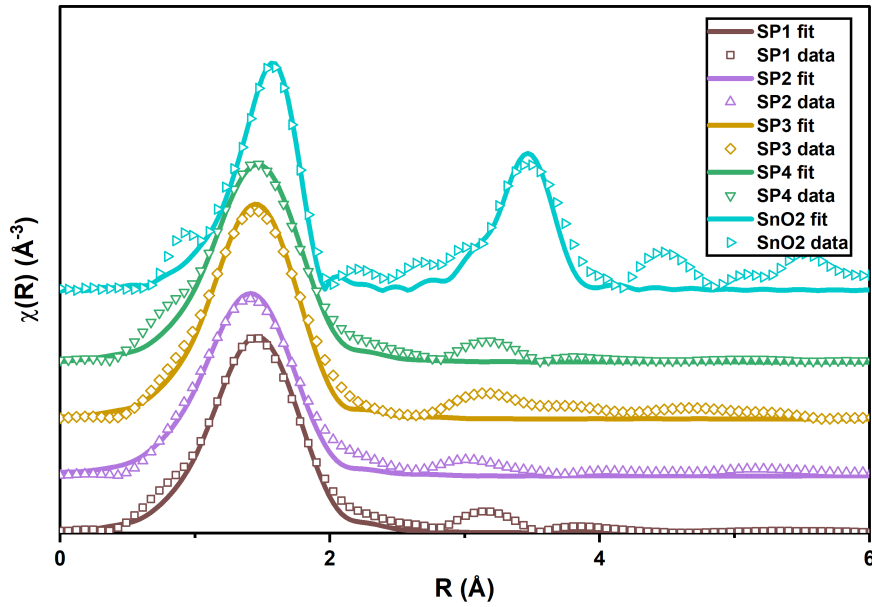


Figure 5.9: $\chi(R)$ spectra calculated from EXAFS measurements at the Sn K-edge and corresponding FEFF8 fits for spray-pyrolysis grown a-ZTO. As with the magnetron grown a-ZTO, only a first nearest neighbour scattering pathway is observed.

5.7 Conclusion

The results of this XAS study confirm the chemical bonding environment within a-ZTO does not vary greatly as the cation ratio is altered, showing no evidence for the presence of a-ZTO polymorphs. EXAFS at the Sn K-edge points towards approximately octahedral next-nearest-neighbour geometry in all measured a-ZTO samples, with no long range order present. In addition, it is observed that varying the deposition method has very little impact on the line shape of the XANES spectra. Furthermore, the spectra correlate well with previous XAS studies on ALD grown a-ZTO[75]. The next steps in this research are EXAFS at the Zn K-edge to confirm the tetrahedral bonding coordination hypothesised. Additionally, my results suggest that the mechanism responsible for the variation in conductivity values is smaller than the next nearest neighbour bond length that is visible from XAS, pointing towards the possible involvement of point defects. As point defects are extremely difficult to detect experimentally, computational methods may be necessary to confirm their contribution. This shall be discussed further in Chapter 7.

Chapter 6

Exploring V_2O_3 as a p-type TCO

In Chapter 5, I examined the local chemical and bonding environment of a-ZTO through a combination of XANES and EXAFS at the Zn and Sn K-edges so as to better understand the defect chemistry of the material and optimise its performance. In this chapter I shall move on from the well-explored field of n-type TCOs in favour of examining V_2O_3 as a promising p-type TCO. First, I focus on optimising the growth of the material, then I turn my attention towards attempting to improve its electronic performance by Mg doping. The results of this work are inconclusive, therefore following this I begin work creating V_2O_3 and Cu_2O nanolaminates. This nanolaminate approach goes beyond substitutional doping and large scale trial and error screening often used in the field, and instead offers a method to bypass the fundamental material limitations that interfere with current TCO performance.

6.1 Introduction

Research into p-type transparent conducting oxides has been an area of interest for several decades, despite this their performance has significantly lagged behind their n-type counterparts. The development of high performing p-type TCOs would allow significant efficiency increases in applications such as OLEDs and p-i-n photovoltaics. The challenge many p-type TCOs face is low optical

Introduction

transparency coupled with low hole mobility due to the O 2p nature of the VBM, and a difficulty finding suitable dopants that can act as shallow acceptors. High p-type mobility is observed in Cu₂O films, due to significant hybridisation between the O 2p⁶ and Cu 3d¹⁰ orbitals, which comprise the VBM. However, Cu₂O also exhibits extremely low charge carriers densities and an optical band gap of just 2.1 eV resulting in low overall optoelectronic performance. Several classes of materials such as delafossites, spinels and oxychalcogenides were developed building on the CMVB approach observed in Cu₂O but as discussed Section 2.3 in each case they exhibited limited success.

An alternative approach is the use of correlated metals as a TCOs. Some success has already been found with the use of the correlated metals SrVO₃ and CaVO₃ as n-type TCOs as they allow similar conductivities to ITO at much smaller thicknesses [165]. In a similar fashion both Cr₂O₃ and V₂O₃ have been highlighted as potential p-type TCO materials due to the high conductivity they exhibit. Due to strong electron correlation, stoichiometric Cr₂O₃ acts as a complete Mott insulator [168, 170]. This can also be expressed in terms of its renormalisation factor, $Z_k = 0$. For this reason Cr₂O₃ is often doped with Mg [171–174], Ni [171, 175] or Li [171, 176] to introduce extrinsic defects which may act as itinerant charge carriers. While Mg and N co-doped Cr₂O₃ has shown conductivities of 0.33 S/cm concurrent with 65 % transmittance for 150 nm film [177], the largest issue the material faces is its extremely low hole mobility. With $Z_k = 0$, no band conduction can occur, and as a result the hole conduction mechanism relies upon small polaron hopping leading to room temperature hole mobilities in the range of $9 \times 10^{-5} \text{ cm}^2/\text{V}\cdot\text{s}$ [178, 264].

A more promising option is V₂O₃ as a p-type correlated metal. V₂O₃ possesses a higher renormalisation factor ($Z_k = 0.12$), and thus exhibits higher conductivities than Cr₂O₃. Although the hole mobility still remains low, typically reported in the range of 0.15–0.21 cm²/V·s [265], an intrinsic charge carrier concentration in the range of $1 \times 10^{22} \text{ cm}^{-3}$ enables conductivities as high as 2122 S/cm for a 56 nm film [184]. Regarding its optical performance, V₂O₃ sees some absorption in the visible range due to d-d transitions however as there is no change in orbital angular momentum in this excitation, absorption remains low. A greater concern for a material with the charge carrier densities V₂O₃ typically exhibits is the encroachment of the reflection edge into the visible light region. The reflection edge occurs due to the fundamental excitation of charge

carriers and coincides with the screened plasma energy. This screened plasma energy, expressed in Eq. 2.6 can be tuned by controlling the n/m^* ratio in the films. In this regard, the low hole mobility resulting from electron correlation is of benefit to the material as it ensures $\hbar\omega_p$ remains below 1.75 eV, which is necessary for optical transparency. From ellipsometry measurements Hu et al. report a screened plasma energy of 0.97 eV for V_2O_3 , coupled with strong interband absorption that occurs at 3.6 eV from transitions between O 2p and V t_{2g} bands [184]. This value for the screened plasma energy is promising as it indicates there is some room to improve either or both of the charge carrier concentration or hole mobility in the system before the reflection edge enters the visible light region. In recent years, researchers have investigated substitutional doping as a means of further increasing the conductivity of V_2O_3 [266]. Using a high throughput study Mg, Sc and Y were suggested as potential dopants for the system. Further DFT calculations, concluded that Mg was the most promising dopant due to its good match in atomic radius ($\Delta R = 0.15$), and the low energy of formation of Mg_V defects [191]. Therefore as Mg-doping has repeatedly shown to be an effective dopant in Cr_2O_3 , I explore and evaluate its performance as a potential dopant for V_2O_3 .

In the final pages of this chapter I shall focus on the growth and characterisation of Cu_2O thin films with the intention of combining them with the previously optimised V_2O_3 films to form nanolaminates. Nanolaminates have been used previously in a wide variety of fields and applications to tune and control ferromagnetic properties [267], environmental stability [268, 269], and even in TCOs to tune the refractive index and band gap [196, 270]. By combining materials with complementary properties, the nanolaminate approach offers a means to overcome fundamental material limitations that hinder performance. Nanolaminates also offer a pathway to high performance p-type TCO performance using earth-abundant materials and low-cost methods instead of the increasingly complex strategies such as doping layered oxychalcogenides [135]. Here, I begin the work of combining parallel layers of Cu_2O , and high charge carrier density V_2O_3 with to objective of creating a composite material that can achieve high p-type conductivity.

6.2 Deposition

In this chapter I shall discuss the deposition and characterisation of V_2O_3 and Cu_2O films. As both V and Cu have multiple oxidation states available to them, I chose to use RF magnetron sputtering in a reactive gas atmosphere, instead of the non-reactive sputtering method used in previous chapters. While this adds an additional layer of complexity to film depositions, by limiting the O_2 partial pressure in the deposition chamber I could precisely control the oxidation state of the deposited material. This was particularly pertinent for the deposition of vanadium sesquioxide, as V has three stable oxidation states (V^{3+} , V^{4+} , V^{5+}) as well as the metastable Wadsley and Magnéli phases which possess mixed V valency.

Sputter depositions of V_2O_3 were performed using a V metal target of 99.9% atomic purity obtained from Kurt J. Lesker. V_2O_3 (0001) films were grown on single-side polished $1 \times 1 \text{ cm}^2$ (0001) Al_2O_3 substrates from MTI corporation. Prior to depositions substrates were chemically cleaned using isopropylalcohol and ultrasonicated for 10 minutes using acetone. A deposition temperature of 500° was used for sample growths as from previous work on spray pyrolysis grown V_2O_3 films, this temperature was found to optimise crystallinity. As before, upon the heater reaching the desired deposition temperature the system was left for one hour in order for the system to thermally equilibrate. A gas flow of 30 SCCM of Ar, and 1 SCCM of O_2 was added to deposition chamber in order to form a reactive sputtering atmosphere environment. The use of mass flow controllers for both the Ar and O_2 supply during growth allowed precise control over the oxygen partial pressure. The base pressure of the deposition chamber was 8×10^{-6} mbar, during growths this was raised to 6×10^{-4} mbar. A substrate temperature of 530°C was used during growth depositions crystalline films. A power density of 7.40 W/cm^2 was used for the V metal target which transferred to a deposition rate of approximately 5.4 nm/minute.

In the instances where the V_2O_3 films were doped with Mg this was achieved by simultaneously co-sputtering a MgO target during V_2O_3 depositions. The MgO sputtering target, of 99.95 % atomic purity, had a 2 inch diameter and was procured from Kurt J. Lesker. The Mg: V_2O_3 depositions utilised the same substrate, temperature, and gas flows as had previously been optimised for V_2O_3 growth. The power applied to the MgO target was varied from 0-50 W which

allowed for a variety of MgO doping concentrations to be obtained.

Cu_2O films were prepared via RF magnetron sputtering using a Cu metal target of 99.999 % atomic purity obtained from HMW Hauner. During the growth of Cu_2O films, the magnetron sputtering chamber retained a lower base pressure of 8×10^{-6} mbar. In order to match the previous work on V_2O_3 , films were deposited on single-side polished $1 \times 1 \text{ cm}^2$ (0001) Al_2O_3 substrates from MTI corporation. Deposition temperatures between (500-600) °C were investigated after consulting the relevant literature. Upon reaching the deposition temperature, the substrate was held at this temperature on order to thermally equilibrate. A power density of 3.45 W/cm was applied to the Cu target which led to a chamber pressure of 3×10^{-4} mbar during growths which corresponds to a deposition rate of approximately 5.2 nm/minute. A gas flow of 30 SCCM of Ar and 1.5 SCCM of O_2 was used for depositions as this O_2 partial pressure was found to produce the highest quality Cu_2O films.

6.3 Growth of V_2O_3 films

A study of the growth parameters that produced the optimal V_2O_3 films was performed. In this study, a number of growth parameters such as target power, substrate temperature and oxygen partial pressure were varied, then the elemental composition, oxidation state and crystallinity of the sputtered V_2O_3 films was examined via XRD and XPS. As V_2O_3 adopts the corundum structure, where O anions form the hexagonal close-packed structure around V cations, (0001) Al_2O_3 was chosen as a substrate. Al_2O_3 in the c-plane orientation also possesses a hexagonal crystal structure, with hexagonal lattice parameters $a = 4.759 \text{ Å}$, $c = 12.992 \text{ Å}$ [271]. This corresponds to a 4.0% in-plane lattice mismatch with the corundum V_2O_3 , which has the lattice parameters $a = 4.9492 \text{ Å}$, $c = 13.998 \text{ Å}$ [272].

The *ex-situ* XRD study was performed on a Bruker D8 Advance Plus XRD equipped with a Cu $K\alpha$ source and a Ge double bounce monochromator. Symmetric $\omega - 2\theta$ scans were performed around the (0001) reflex of Al_2O_3 which occurs at 41.676° , these are shown in Figure 6.1. At higher O_2 partial pressures, the growth of VO_2 is observed by the presence of the (020) crystalline phase at 39.9° and its higher order reflex at 86.0° [273]. As the O_2 flow is lowered, the oxygen partial pressure drops and there remains insufficient O concentra-

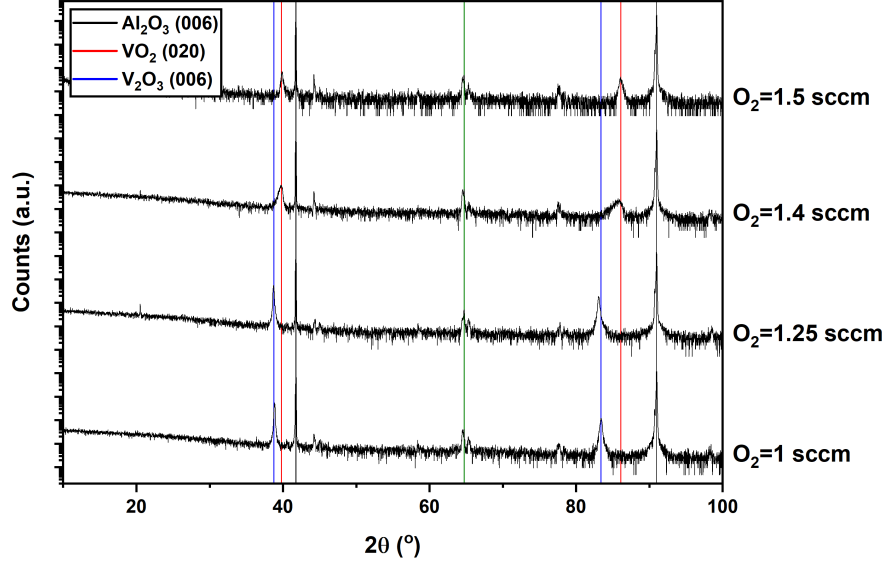


Figure 6.1: XRD spectra of vanadium oxides with varying O_2 pressure supplied during growths. As the O partial pressure is reduced, VO_2 growth is suppressed and growth of the V_2O_3 phase is promoted. A doublet peak centered at 64.5° is observed in all spectra which is attributed to the sample stage.

tion in the growth chamber for the formation of VO_2 , instead the growth of V_2O_3 is favoured. The (0001) orientation of the Al_2O_3 substrate promotes the crystalline growth of the corundum phase of V_2O_3 , which can be identified by the strong (006) V_2O_3 peak at 38.8° [272].

As the vanadium oxide film grown at 1 SCCM of O_2 flow showed the highest intensity (006) 2θ peak it was chosen for an XPS study to assess the oxidation state of the V atoms, and the elemental purity of the thin film. A 20 eV pass energy along with 4.5 mm slits were utilised to obtain an instrumental resolution of 0.6 eV. A survey spectrum, shown in the Appendix, as well as a core level spectrum of the V2p and O 1s region was recorded. The core level spectrum is shown in Figure 6.2a. It is noted that the V $2p_{3/2}$ core peak is not found at 515.5 eV as one would expected for a V_2O_3 , but rather a peak with two main components is observed, with the highest intensity showing at 517.2 eV, which is typical of V_2O_5 . The film then underwent a sputter and anneal cycle where an Ar^+ ion current was applied for a 10 minute period at 650 V. The film

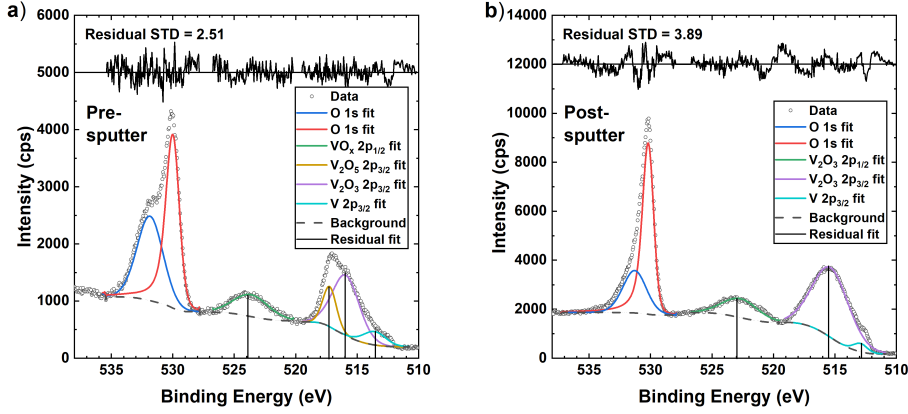


Figure 6.2: XPS was performed on the V 2p core levels to assess the oxidation state of the V_2O_3 films. In the pre-sputtered film surface oxidation is observed which corresponds to a V_2O_5 peak at 517.2 eV.

was then annealed at 530 °C for 2 hours to restore the surface reconstruction. The core level spectrum post sputter is shown in Figure 6.2b, it is noted that the V_2O_5 signal is removed and a single peak component at 515.3 eV is found. This V 2p_{3/2} peak position and 7.5 eV separation between the V 2p_{1/2} peak is characteristic of V_2O_3 [274, 275].

	Peak component	Peak position (eV)	Fitting line shape	FWHM (eV)	Area (%)
Pre-sputter	VO_x 2p _{1/2}	523.6	GL(30)	3.36	10.0
	V_2O_3 2p _{3/2}	515.9	GL(30)	3.33	11
	V_2O_5 2p _{3/2}	517.2	GL(30)	1.59	3.7
	V 2p _{3/2}	513.6	GL(20)	2.17	2.04
Post-sputter	VO_x 2p _{1/2}	522.7	GL(30)	3.45	11.8
	V_2O_3 2p _{3/2}	515.3	GL(30)	3.60	22.9
	V_2O_5 2p _{3/2}	-	-	-	-
	V 2p _{3/2}	512.9	GL(20)	1.35	1.0

Table 6.1: XPS fitting parameters of the V 2p peak region before and after the V_2O_3 film underwent a sputter and anneal cycle. Fitting parameters for the O 1s peak are available in Table 8.5 of the Appendix.

It is proposed therefore that upon exposure to ambient conditions the surface of the V_2O_3 film fully oxidises to V_2O_5 , while the bulk of the material remains

Growth of V_2O_3 films

as V_2O_3 . This is in agreement with the fitting of XRR spectra which indicates the existence of a very thin layer above the V_2O_3 film. From the XRR fitting the V_2O_5 layer is estimated to be 2.7 nm thick. In both spectra of Figure 6.2 a small shoulder is observed near 513 eV. A peak at 512.6 eV is characteristic of V metal [276], and thus this may suggest that the V_2O_3 film is slightly under stoichiometric. As the V_2O_3 films grown at 7.40 W/cm² power density and 30:1 Ar/O₂ SCCM gas flow, provided the highest crystalline quality films, the rest of the V_2O_3 films discussed in this chapter used these growth conditions.

Following the XRD and XPS characterisation, I performed SEM on the V_2O_3 film to investigate the surface morphology. Secondary electron imaging indicates that the morphology of the film is uniform and continuous. Due to the lack of topological features, the in-lens detector was utilised as this allowed higher resolution imaging and greater sensitivity to the surface signal from the film. Small bright features can be observed on the surface of the V_2O_3 films. These are small droplets of silver paint produced from the SEM sample preparation process. In the bottom left of Figure 6.3c, a series of gashes in the surface of the thin film can be observed. Upon closer inspection in Figure 6.3d, it appears that the V_2O_3 thin film has been damaged, in a series of parallel scores. I believe this is likely due to the handling of the thin film with tweezers, nonetheless it is useful information for the handling of the V_2O_3 films for future work.

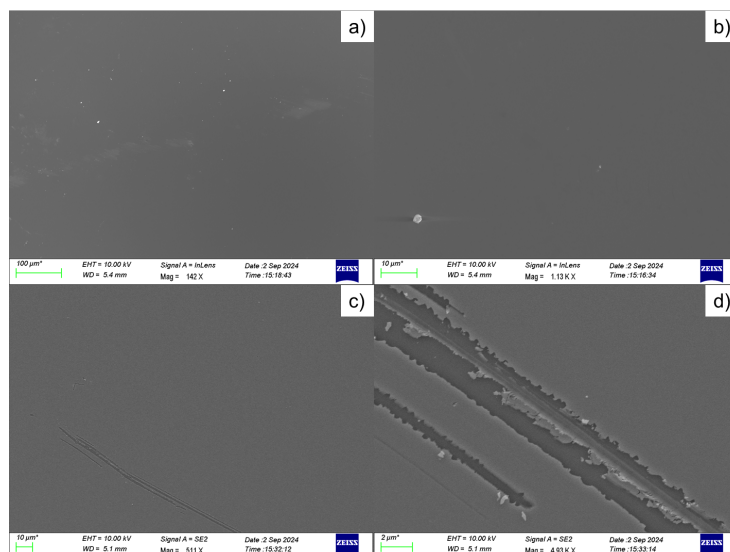


Figure 6.3: SEM imaging of a V_2O_3 film shows a smooth and continuous surface.

6.4 Mg doping of V_2O_3

Following the growth of high quality V_2O_3 thin films, I began the process of Mg doping. Vanadium cations in V_2O_3 take on a +3 oxidation state, therefore the inclusion of Mg^{2+} cations on the V site should introduce acceptor states and increase the conductivity of the material [191]. Doping was achieved by co-sputtering a MgO ceramic target during V_2O_3 growth depositions. All the Mg: V_2O_3 samples were grown to the same approximate thickness of 40 nm. The Mg concentration in the thin films was controlled by varying the power applied to the MgO sputtering target during growth. Four samples of Mg: V_2O_3 were grown in total; one pure V_2O_3 film, and three doped films with an applied MgO target power of 30 W, 40 W and 50 W. These samples shall be referred to as Mg: V_2O_3 -0W, Mg: V_2O_3 -30W, Mg: V_2O_3 -40W and Mg: V_2O_3 -50W respectively. To examine the effectiveness of Mg doping, the optical, electrical and structural properties of the Mg: V_2O_3 films were investigated.

To confirm the presence of Mg, and attempt to quantify its concentration XPS was performed on Mg: V_2O_3 -50W. A survey spectrum, shown in the Appendix, as well core level spectra of the V 2p/O 1s and the V 3s/Mg 2s regions were obtained. These core level spectra are presented in Figure 6.4. The observation of the Mg KLL Auger peak at 302.7 eV in the survey spectrum confirms the successful doping of the films with Mg. Due to experimental constraints at the time of measurement, an *in-vacuo* sample transfer was not possible, therefore the Mg: V_2O_3 -50W sample was loaded from atmospheric conditions resulting in the presence of a C 1s signal at 284.8 eV. Like the pre-sputtered spectrum shown in Figure 6.2a, an O 1s doublet is observed as well as the V 2p_{3/2} peak being shifted to 517.1 eV. This agrees with the previous observation that the V_2O_3 films will readily undergo surface oxidation to form a thin V_2O_5 layer at the film surface.

XPS typically allows quantification down to 0.1-1 atomic %, although some

Parameter	VO_x 2p _{1/2}	V_2O_3 2p _{3/2}	V_2O_5 2p _{3/2}
Peak position (eV)	523.6	515.7	517.1
Lineshape	GL(30)	GL(30)	GL(30)
FWHM (eV)	3.04	3.17	1.55

Table 6.2: Fitting parameters of the V 2p core level peaks from Mg: V_2O_3 -50W.

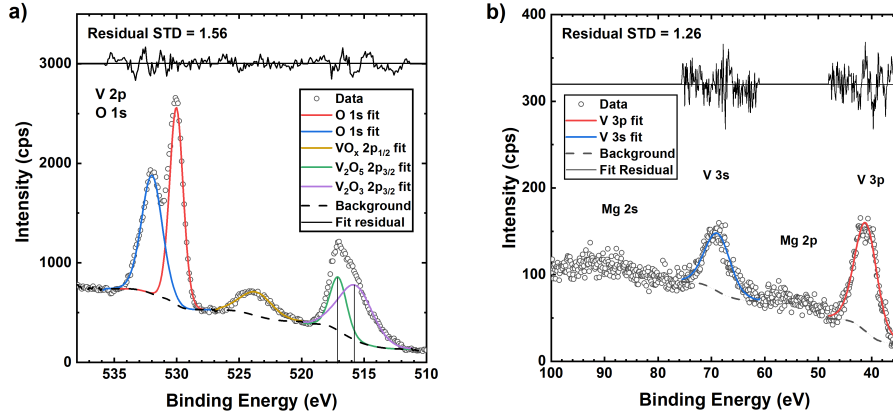


Figure 6.4: Core level XPS spectra from sample V_2O_3 -50W of a) the V 2p and O 1s core levels and b) the V 3s and 3p as well as Mg 2s and 2p core levels.

considerations must be given depending on the exact elemental combination [277]. An attempt was made to quantify the Mg concentration in the thin films by comparing the relative intensities of the Mg 2s and V 3s core peaks. This spectrum is shown in Figure 6.4b. Broad peak features centred at 90 eV and 54 eV coincide with the expected positions of the Mg 2s and 2p peaks respectively [278, 279], again pointing towards a Mg presence, however their intensities are too small to achieve a meaningful fit. As Mg: V_2O_3 -50W is the most highly doped V_2O_3 sample, the corresponding Mg 2s signal would be even less pronounced in Mg: V_2O_3 -30W and Mg: V_2O_3 -40W, and thus a quantifiable Mg signal would be difficult to obtain. High signal to noise can occur in XPS when using a smaller pass energy, and is typically resolved by scanning and integrating over a longer time period, however due to time constraints at the time of writing this was not possible.

Following XPS, XRD was performed on the Mg doped V_2O_3 samples. As before, a peak at 38.6° is observed indicating the presence of (006) oriented V_2O_3 . The presence of the higher order (0012) peak is also noted. Interestingly, sample Mg: V_2O_3 -30W exhibits the highest (006) peak intensity. As Mg was sputtered from a MgO target, this may indicate that a slightly higher O partial pressure is beneficial for increased crystallinity. Secondly, it indicates that exhibits good Mg incorporation into the films as the V_2O_3 films remain crystalline and no MgO peak is observed.

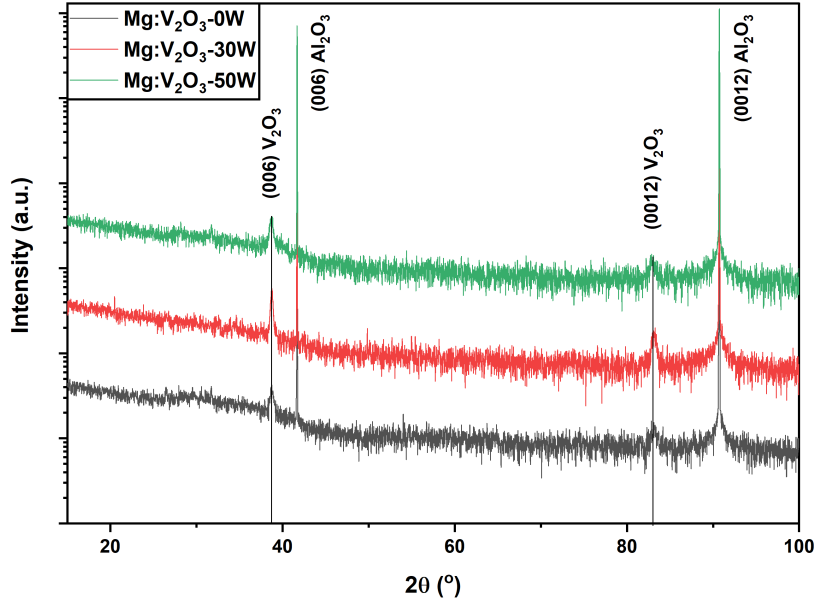


Figure 6.5: XRD of Mg doped samples shows a clear (006) V_2O_3 peak at 38.6°

The optical properties of the doped V_2O_3 films were measured using UV-vis spectrophotometry on a PerkinElmer Lambda 650S. Transmission and reflectance measurements were recorded and then combined to characterise the transmittance and absorption of the films as well as to calculate Tauc plots for each of the films. Tauc plots were modelled as directed allowed transitions ($\gamma = 1/2$). All of the V_2O_3 films exhibit a transmittance above 60 %, and less than 35 % absorbance in the visible range. While this is low compared to the high optical transparency typically observed in n-type materials, it is competitive with the transmittance observed for most p-type delafossites and spinels.

Although V_2O_3 does not have a band gap like many TCOs, it does exhibit a strong interband transition between O 2p and V 3d e_g orbitals. This interband transition is shown in Figure 6.6c, and is estimated to occur at 3.3 eV. It is noted that below this point the V_2O_3 films still see absorption which is attributed to transitions between split V 3d orbitals. These d-d transitions are forbidden as there is no change in orbital angular momentum, and thus absorption remains below 3.3 eV. These findings are in broad agreement with the optical characterisation of Hu et al. who report a interband transition energy of 3.6 eV [184].

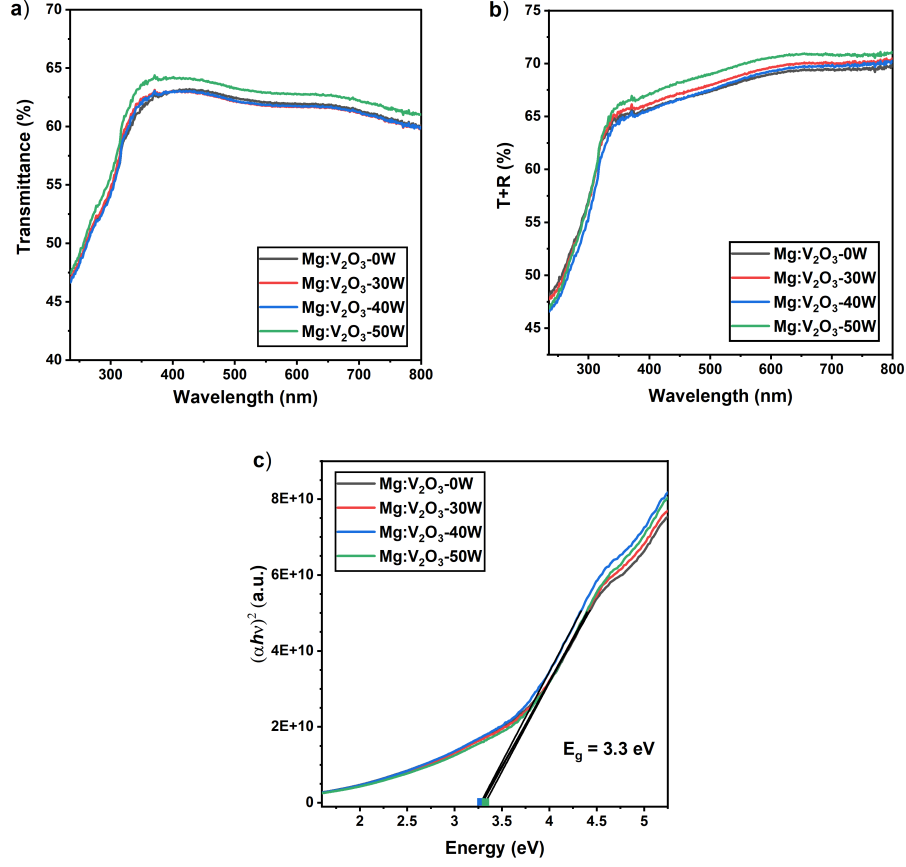


Figure 6.6: The a) transmittance and b) absorbance of the 40 nm doped V_2O_3 films shows viable performance as a p-type TCO. c) Tauc plots for various levels of doping, Mg inclusion has no noticeable impact on E_g .

Sample name	n (cm^{-3})	μ ($\text{cm}^2/\text{V.s}$)	σ (S/cm)	E_g (eV)	FoM^G (Ω^{-1})
Mg: V_2O_3 -0W	3.49×10^{22}	0.3 ± 0.1	1750 ± 175	3.3	0.050 ± 0.005
Mg: V_2O_3 -30W	1.03×10^{22}	0.9 ± 2.3	1483 ± 148	3.3	0.429 ± 0.04
Mg: V_2O_3 -40W	3.89×10^{22}	0.3 ± 0.1	1867 ± 187	3.3	0.535 ± 0.05
Mg: V_2O_3 -50W	2.01×10^{22}	0.4 ± 0.2	1286 ± 129	3.3	0.382 ± 0.04

Table 6.3: A slight increase in the hole mobility of Mg: V_2O_3 -30W is observed, however the large uncertainty makes drawing any conclusions difficult.

Notably it is seen that the inclusion of Mg in the V_2O_3 lattice has no significant effect on the transmission or interband absorption in V_2O_3 . It is worth stating that while Mg: V_2O_3 -50W shows a higher T and T+R, this is within the noise of the instrument, and no shift is seen in the subsequent Tauc plots.

The Hall mobility, charge carrier concentration and conductivity of the V_2O_3 films was measured via the Hall effect described in Section 3.3. Mg: V_2O_3 -0W exhibits the extremely high conductivity that is characteristic of V_2O_3 . It is observed from Table 6.3 that the film possesses metal like charge carrier concentrations with typically low hole mobilities observed in V_2O_3 thin films and single crystals [265]. Introducing Mg into the V_2O_3 matrix is found to initially increase the hole mobility, however at higher Mg concentrations in Mg: V_2O_3 -40W and Mg: V_2O_3 -50W the hole mobility falls to that of the pure V_2O_3 . The intention of Mg doping V_2O_3 was to introduce shallow acceptor states and increase the charge carrier concentration, thus these results suggest that Mg is not an effective dopant in V_2O_3 . The FoM^G was calculated by averaging α over the range of 1.5-3.1 eV, and then computed using Eq. 2.9. These compare favourably with the FoM^G reported for $CuCrO_2$ ($2.3 \times 10^{-4} \Omega^{-1}$) [280], $CuCr_{1-x}Mg_xO_2$ ($1.25 \times 10^{-4} \Omega^{-1}$) [121], and Mg: Cr_2O_3 (6.7×10^{-4}) [178]. It must be noted that due to the low mobility of the V_2O_3 films, I had difficulty measuring a congruent Hall mobility for some samples. To address this a number of Hall mobility scans were measured for each sample and the average value reported. This is also reflected in the high uncertainty in the Hall mobility. It can be seen from Eq. 3.5 that a stronger magnetic field allows greater sensitivity to a sample's Hall mobility. Therefore the sensitivity of the Hall effect instrument in this instance is limited by the field strength the electromagnet can apply. The Hall mobility of these samples is currently being remeasured using a stronger electromagnet, but due to time restraints results were not available upon the time of writing.

6.5 Electron Microscopy of V_2O_3

Following on from the electrical, optical and X-ray characterisation a microscopy study was performed on the Mg doped V_2O_3 films. This was undertaken as a 3-month placement as my Centre for Doctoral Training in the Advanced Characterisation of Materials (CDT ACM) research placement in the Ernst Ruska-

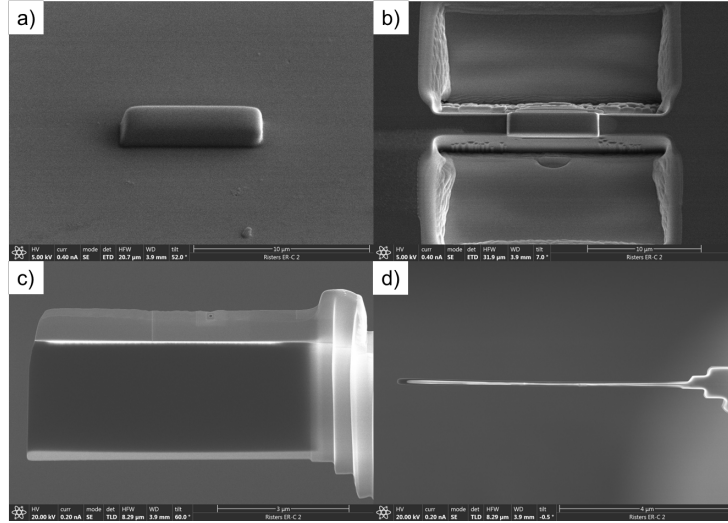


Figure 6.7: FIB SEM preparation of V_2O_3 STEM lamella. a) A protective C capping layer is deposited on the film surface to protect the region of interest. b) High angle trenches are milled into the surface of the sample which allow the lamella to be cut free from the rest of the sample. c) A side profile and d) top profile of the final lamella.

Centre for Microscopy, Jülich. While XPS spectra indicated a weak Mg presence in the V_2O_3 films, it remains unclear how the Mg^{2+} cations are incorporating into the V_2O_3 lattice. If MgO clustering is occurring in the film, or if Mg is located only along grain boundaries then this would affect its ability to generate acceptor defects in V_2O_3 . Through a combination of HAADF imaging, EDX and EELS mapping the objective of this study was to investigate the incorporation of the Mg dopants in the V_2O_3 crystal lattice.

Lamellae of V_2O_3 were prepared for STEM imaging by focused ion-beam scanning electron microscopy (FIB SEM). This is a common approach that is used to prepare bulk samples for TEM and STEM imaging. As the electron beam must transit through the sample in order to be detected, lamellae are prepared and thinned to a thickness of roughly 100-200 nm. This is achieved by sputtering the sample in controlled manner with Ga^+ ions. Images of the lamella preparation process are shown in Figure 6.7.

Firstly, an area of interest, roughly $8 \times 1 \mu m^2$, is identified on the film. Next, an electron protection layer is deposited on the surface of the film, followed by a C or Pt capping layer which acts to protect the film during the ion milling

process. Following this, using a focused Ga^+ ion beam high-angle trenches are milled into the film and substrate. By milling both sides of the protective capping layer a "J-cut" may be performed, cutting through the substrate and leaving the lamella attached to the rest of the film by a small bridge. Next, a lifting needle is brought into close contact with the capped region, and then bound to the lamella using a carbon gas injection system. Following this the lamella is cut completely free from the sample surface and using the carbon gas injection system again bound to a TEM grid. The final step is to iteratively mill both sides of the lamella to thin and polish it until it is approximately 150 nm thick. The final result of this lamella preparation process can be seen in Figures 6.7c and d. STEM lamella were prepared of Mg: V_2O_3 -0W, Mg: V_2O_3 -30W and Mg: V_2O_3 -50W respectively.

Initial STEM imaging was promising. The probe corrected ChemiSTEM Titan (80-200) used in this work allowed atomic resolution imaging of the substrate and V_2O_3 films. The first lamella investigated was Mg: V_2O_3 -0W, imaged in high angle annular dark field (HAADF) mode as this allowed greater sensitivity to higher Z-elements. Prior to imaging of the V_2O_3 film, the α and β tilt of the STEM sample holder were adjusted to align the beam to the crystallographic zone axis of the (0001) Al_2O_3 substrate. This image is shown in Figure 6.8a. It is interesting to observe the polycrystalline structure the V_2O_3 sample exhibits. Previous XRD scans presented in Figure 6.1 indicate a single phase V_2O_3 (006) film grown on (006) Al_2O_3 . In contrast to this, the HAADF images in Figure 6.8b and c, shows both cubic and hexagonal V_2O_3 phases. While the corundum phase of V_2O_3 is the most thermodynamically stable, in recent years there has been a number of reports of a bixbyite structure of V_2O_3 [183]. Recently, Rupp et al. have reported an in-depth study on the growth temperature dependence the V_2O_3 phases exhibit when grown on Pt [281]. Despite this, it remains surprising to observe the growth of the bixbyite phase directly on the corundum Al_2O_3 substrate, which can be clearly seen from a FFT performed on the first 10 nm of the film shown in Figure 6.8b.

In addition to HAADF imaging, core-level and low-loss electron energy loss spectroscopy (EELS) was performed on Mg: V_2O_3 -0W. The position and relative peak intensity of the L_2 and L_3 peaks from the V core level EELS spectra are typical of V_2O_3 , and are homogeneous across the film. The low-loss EELS region is populated by plasmon peaks that are indicative of the band structure

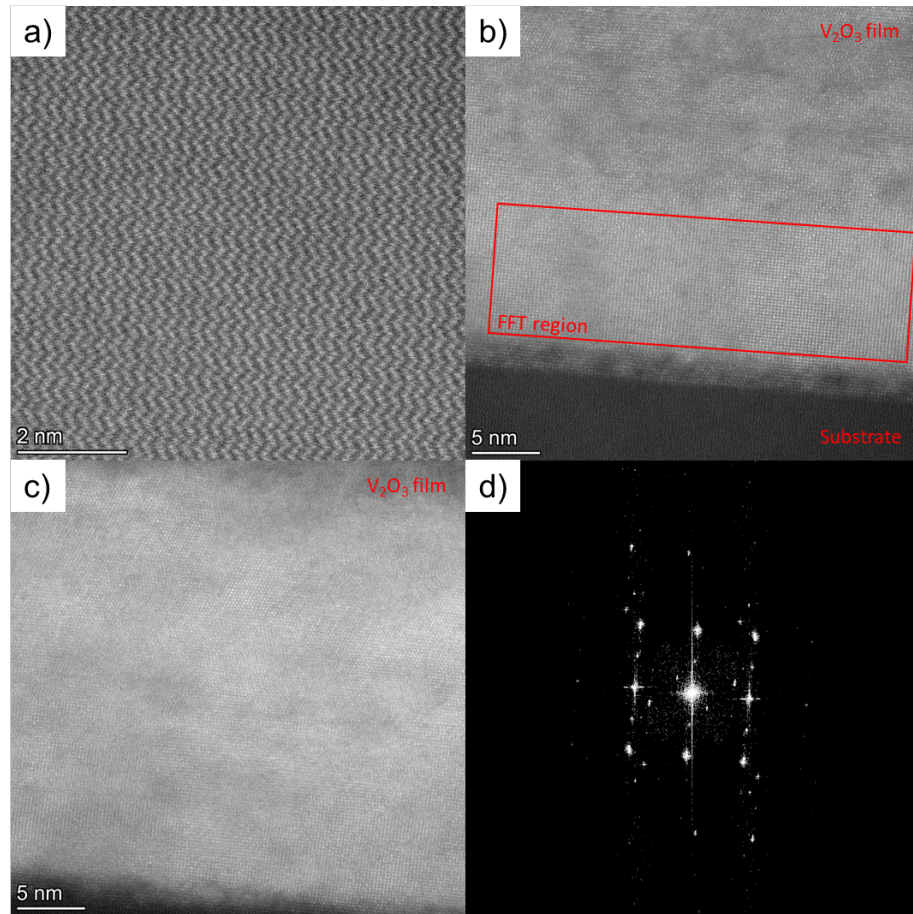


Figure 6.8: a) Imaging of the Al_2O_3 substrate to focus the microscope and align to the crystallographic zone axis. b) and c) High resolution imaging of pure V_2O_3 thin films, shows both a hexagonal and cubic V_2O_3 phase d) FFT of the first 10 nm of subfigure b) confirms the bixbyite phase grows comfortably on the corundum Al_2O_3 substrate.

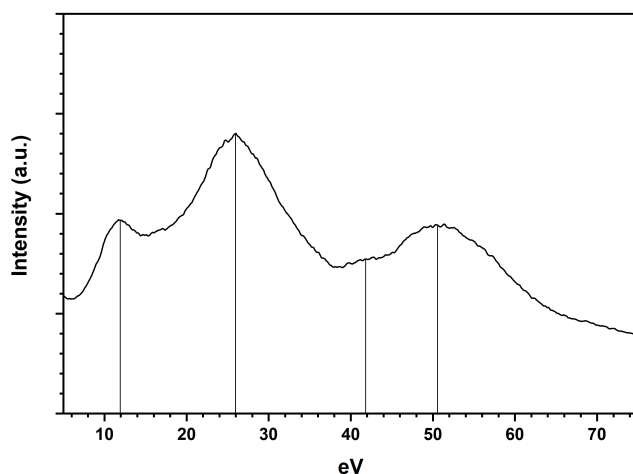


Figure 6.9: Core loss EELS spectrum obtained from Mg: V_2O_3 -0W. Characteristic plasmon peaks are observed at 12, 27, 41 and 52 eV.

of a material. The low-loss EELS spectrum of Mg: V_2O_3 -0W is presented in Figure 6.9, with a number of peaks visible. The most prominent of these occur at 12 and 27 eV, and are characteristic of the O 2p to V 3p transition, and the collective excitation of all valence electrons respectively [282].

A polycrystalline film, with both corundum and bixbyite phases present was observed in the Mg: V_2O_3 -50W lamella, shown in Figure 6.10. In this case the hexagonal phase is favoured for growth on the substrate while the cubic phase is seen in the bulk of the film, shown in the FFT of Figure 6.10d). In addition, it is noted that with increased Mg concentration the V_2O_3 film see a drop in crystallinity. Interestingly, it is observed that after approximately 5 nm there is the formation of dark regions in the lamella. As HAADF imaging relies upon the electron beam to be inelastically scattered these dark regions correspond to areas where there is a decrease in the atomic density, and so can be interpreted as voids in the film. It can be observed that some crystalline order still exists in these void regions however it is misaligned when compared to the surface normal of the Al_2O_3 substrate. In addition to the HAADF imaging and EELS previously discussed, EDX mapping was implemented during imaging to analyse the distribution of elements in the lamella. As mentioned above, one hypothesis for the low impact of Mg doping is Mg congregating into MgO clusters thus inhibiting the incorporation of Mg^{2+} cations onto the V site. However, EDX

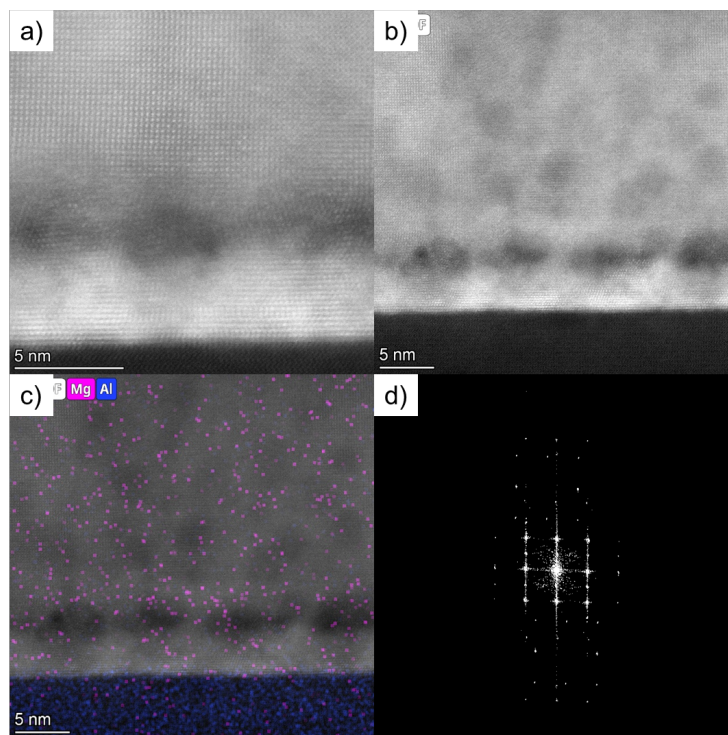


Figure 6.10: a) and b) Atomic resolution STEM imaging was obtained for $Mg:V_2O_3-50W$. Dark regions are observed within 5 nm of the substrate across the film. c) EDX mapping indicates a homogeneous Mg incorporation across the film. d) FFT of the bulk film indicates that despite a visible corundum structure at the substrate interface, the bixbyite phase readily forms in the bulk.

mapping indicates a homogenous Mg signal across the lamella. Following the microscopy of $Mg:V_2O_3-50W$, a lamella of $Mg:V_2O_3-30W$ was examined. In this lamella, the voiding that is observed in Figure 6.10 has deteriorated to such a point that the lamella is no longer intact. This is shown in Figures 6.11 a) and b). EDX mapping of these images indicates that the V atoms have shifted to bright regions of Figure 6.11 a). Upon reexamining the pristine V_2O_3 lamella, $Mg:V_2O_3-50W$ lamella, similar images were recorded. In electron microscopy it is not uncommon for the electron beam to damage the sample, especially in transmission electron microscopy, due to the high accelerating voltages typically used for the electron beam concentrated over a small area. In this instance, beam damage can be excluded as a contributing factor as $Mg:V_2O_3-30W$ had not been exposed to the electron beam and this damage was observed. As

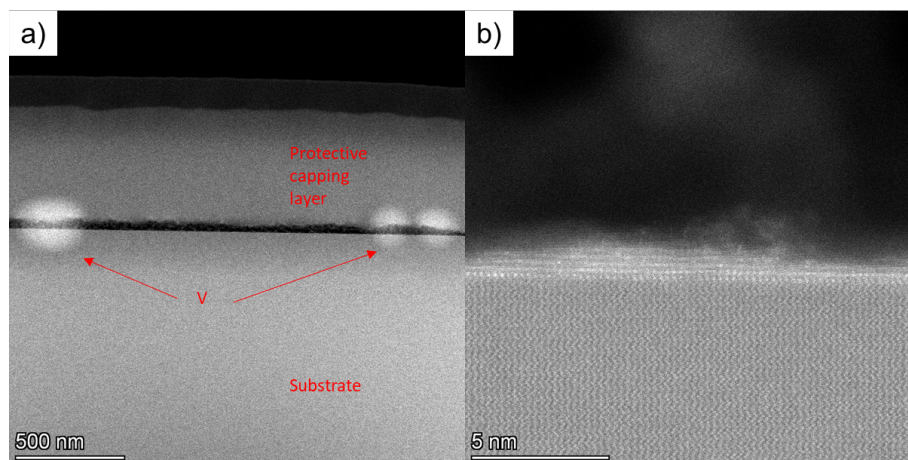


Figure 6.11: a) HAADF imaging indicates the V_2O_3 lamella has completely degraded. EDX indicates the V signal is localised to the bright circular regions. b) Atomic resolution imaging showed the beam was aligned to the substrate and film zone axis however the film had degraded.

discussed in Section 6.2, V can easily oxidise to higher oxidation states under ambient conditions however it is not expected this chemical reaction would result in such a drastic structural change.

A search of the available literature showed no reports of this behaviour report for V_2O_3 lamellae, however this degradation of lamellae did present as a significant challenge to further electron microscopy studies. For this reason a study was performed to investigate the sensitivity of the V_2O_3 lamellae to ambient conditions. For this study two lamellae were prepared via FIB SEM; one pure V_2O_3 films and one lamella from Mg: V_2O_3 -50W. To avoid oxidation due to ambient conditions these lamellae were kept in storage under vacuum conditions until the time of STEM imaging. Following this initial imaging the lamellae were exposed to ambient conditions for 10 months before being imaged again. The same crystal structure is observed in films before and after exposure to ambient conditions, indicating the V_2O_3 lamellae are not as sensitive to ambient conditions as was feared. The most logical explanation for the observed lamella degradation is that the V_2O_3 films became damaged due ion polishing processes prior to V_2O_3 STEM. While this is routine preparation work in order to eliminate molecules adsorbed to the surface of the lamella, it also may have damaged the structure of the film. Previous SEM microscopy work, shown in

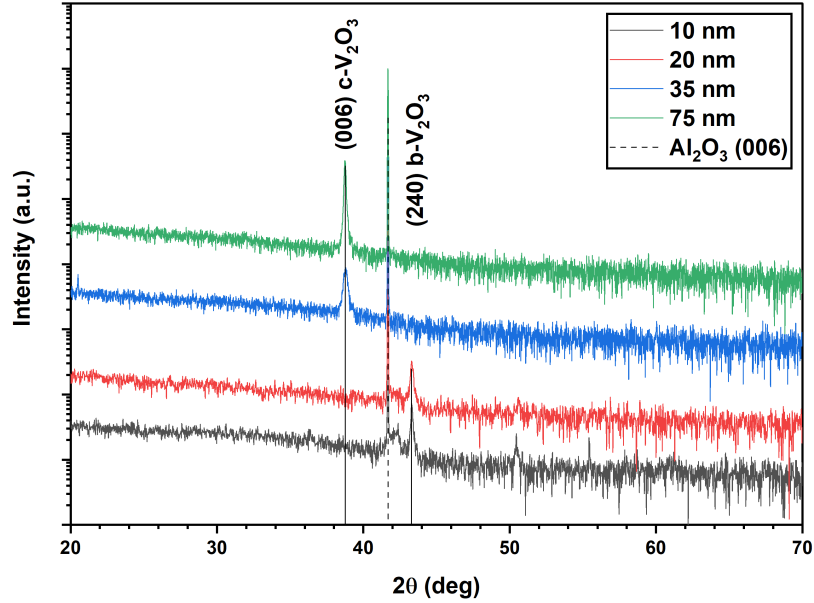


Figure 6.12: An XRD study on the crystalline phases of V_2O_3 . At low thicknesses the bixbyite phase ($b\text{-}V_2O_3$) appears prominent while above 35 nm the corundum phase ($c\text{-}V_2O_3$) begins to dominate the diffractogram. For visual clarity the spectra have been vertically offset.

Figure 6.3 has suggested that the V_2O_3 films are quite sensitive to physical damage. This information is extremely relevant to the bilayer work discussed in Section 6.6, as high resolution electron microscopy will be incredibly useful for characterising the growth of the bilayers or multilayers.

To follow up on the observation of both bixbyite and corundum phases of V_2O_3 during STEM imaging, an XRD study was performed. This is particularly relevant to the nanolaminate work as bilayers or multilayers of V_2O_3 will be grown, and having a clear picture of description of how the crystalline phase and structure of V_2O_3 changes with thickness will be crucial to their optimisation. Four V_2O_3 films were grown in accordance with the previously described method and growth parameters. These films varied in thickness from 10, 20, 35 and 75 nm respectively. XRD spectra, shown in 6.12 were measured in the form of $2\theta\text{-}\omega$ scans ranging from 20 to 70 °. At thicknesses lower than 35 nm, a clear [240] bixbyite V_2O_3 peak is seen, while above this thickness the corundum [006] peak begins to dominate. This agrees with STEM imaging which shows bixbyite

can grow directly on the corundum Al_2O_3 substrate. In the $[012]$ plane of the bixbyite phase, V_2O_3 possesses a pseudo-hexagonal structure where the V-V distances are 4.7 Å and 5.9 Å. It is hypothesised therefore that due to the close matching of the Al_2O_3 unit cell parameter (4.8 Å) to the 4.7 Å V-V distance, this $[024]$ orientation of the bixbyite phase may be preferred at lower thicknesses. To further investigate this hypothesis a phi scan of the low thickness V_2O_3 films is required.

6.6 Growth of Cu_2O

Successful Mg doping was theorised to increase the electrical performance of V_2O_3 by introducing shallow acceptor states near the VBM of the material. While Mg doping was not successful, I believe this approach fails to address the main limitations of conductivity in the material, namely its low hole mobility. To improve this mobility therefore, I began work creating $\text{V}_2\text{O}_3/\text{Cu}_2\text{O}$ bilayer and nanolaminate structures. The low charge carrier densities and high mobilities that Cu_2O typically exhibits nominally make it an well-suited material to pair with V_2O_3 . The remaining results in this chapter pertain to the growth and optimisation of Cu_2O layers.

The growth of Cu_2O films was performed via reactive RF magnetron sputtering of a Cu metal target. Cu has two oxidation states that it readily takes (Cu^+ and Cu^{2+}). Thus being able to control the oxygen partial pressure in the deposition chamber via the flow of O_2 during growths was essential. It is worth noting that CuO is also a p-type TCO. However, it possesses a band gap of only 1.3-2.1 eV [283], and in addition as it does not possess a full $3d^{10}$ electronic configuration, the band hybridising between Cu and O orbitals is reduced and therefore the hole mobility diminished [283]. Cu_2O is a heavily researched material, therefore the growth conditions for crystalline growth are well documented. Cu_2O has a cubic crystal structure [116], and as such is typically matched with a substrate that also possesses cubic structure however epitaxial Cu_2O has previously been grown on a glass substrate [100]. As the goal of this work was to pair these Cu_2O films with the previously optimised V_2O_3 films, I decided to continue using (0001) Al_2O_3 substrates. Initial work focused on optimising the growth temperature and O_2 flow during depositions. Following growth, the crystallinity of the films was analysed using XRD 2θ scans shown

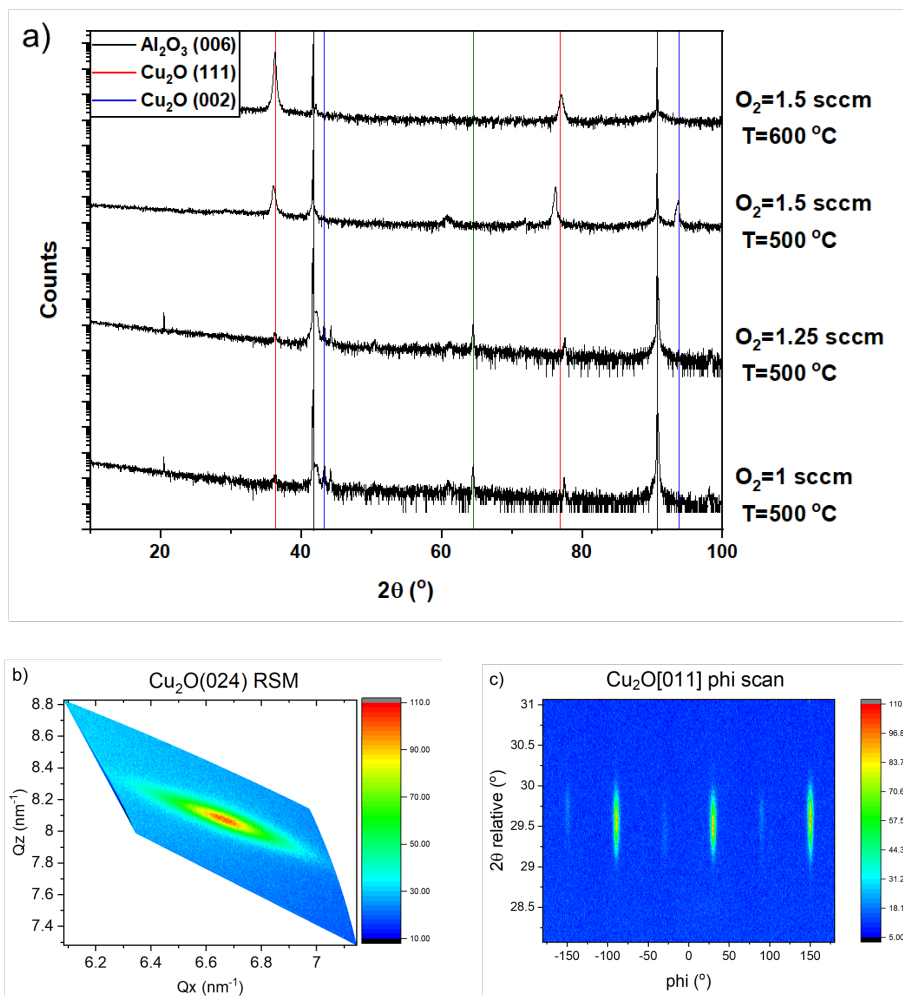


Figure 6.13: a) XRD 2θ scan showing that upon increasing the O_2 partial pressure and substrate temperature the (002) phase is suppressed and (111) Cu_2O is obtained. b) Reciprocal space map of the (024) Cu_2O reflex, and c) ϕ scan about the (011) Cu_2O reflex.

in Figure 6.13a. At low O₂ flow rates the films see poor crystallinity and the presence of both (111) and (002) phases. However, as the O₂ flow is increased to 1.5 SCCM, the crystallinity of the films improves resulting in a strong (111) peak at 36.1 °, and the suppression of the (002) Cu₂O phase. Increasing the O₂ flow beyond this point adds no benefit to the crystallinity, instead it promotes the growth of CuO phases.

After the 2θ scans, a ϕ scan of the (011) reflexes was recorded on the Cu₂O sample grown at 600 °C to investigate its epitaxial relationship between the substrate and film. This is presented in Figure 6.13c. As a cubic system, Cu₂O is two-fold symmetric. In contrast, the hexagonal structure (0001) plane Al₂O₃ possesses 3-fold symmetry. It is expected therefore that the resulting Cu₂O film would exhibit 6-fold symmetry as there is two equivalent orientations the Cu₂O unit cell may form on the substrate. In contrast to this, the ϕ scan shows threefold symmetry in the film, with each of the peaks separated by 120 °, indicating one dominant in-plane orientation of the (111) Cu₂O phase. This indicates the epitaxial growth of the Cu₂O layer on the Al₂O₃ substrate.

Subsequently, a reciprocal space map (RSM) was collected by performing a rocking curve about the Cu₂O (240) peak with the detector fully open and resolving along the 2θ direction. This is shown in Figure 6.13b. Using this RSM the in-plane and out-of-plane lattice vectors of the Cu₂O film, which correspond to the [01-1] and [111] directions respectively, were calculated. The in-plane parameter (1.501 Å), was found to match the expected value for bulk Cu₂O $d_{[02-2]} = 1.501$ Å, while the out of plane lattice parameter (1.239 Å) shows an approximately 1 % expansion compared to $d_{[222]}$. Overall, this indicates that extremely high quality epitaxial Cu₂O films were obtained.

Next XPS was performed on the CuO_x thin films to confirm their elemental and chemical state. A survey spectrum was performed and confirmed the Cu₂O films are elementally pure. To characterise the chemical and oxidation state of the copper oxide films a core level spectrum of the Cu 2p region was measured, and is presented in Figure 6.14. It is noted that the Cu 2p_{1/2} and 2p_{3/2} peaks both contain a shoulder at higher binding energy as well as the presence of two satellite peaks in the spectrum. The dominant Cu 2p_{1/2} and 2p_{3/2} peaks at 952.2 and 932.4 eV respectively align with the expected values for Cu₂O from literature [284]. In addition, I attribute the shoulders on both Cu 2p peaks to be due to surface oxidation of the film as this peak lines up extremely well

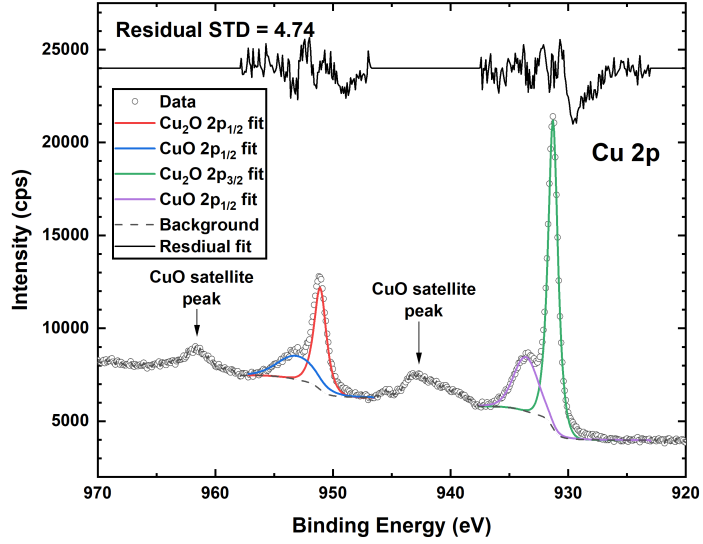


Figure 6.14: XPS spectrum of the Cu 2p core level. Peak shoulders on the Cu 2p peaks as well as CuO satellite peaks indicate surface oxidation of the Cu_2O film.

for those expected of CuO [284]. Furthermore, the satellite peaks at 944.3 and 962.9 eV are shake up peaks characteristic of the presence of CuO [285]. From XRR fitting, the CuO layer is estimated to be 0.5 nm thick.

Following the X-ray characterisation of the Cu_2O thin films, their optoelectronic properties were investigated. The films exhibit low transmittance, with a significant absorption onset observed at approximately 500 nm, this also reflected in Tauc plot presented in Figure 6.15b. The bandgap of the material was estimated as a direct allowed transition using the Tauc method discussed previously. The calculated value of 2.2 eV agrees strongly with values recorded in literature [84]. This band gap value is below the ideal threshold for a TCO material of 3.1 eV, and as a result the film sees significant absorption in the

Parameter	Cu_2O 2p _{1/2}	CuO 2p _{1/2}	Cu_2O 2p _{3/2}	CuO 2p _{3/2}
Peak position (eV)	951.10	952.52	931.29	933.57
Lineshape	GL(80)	LA(50)	GL(80)	LA(50)
FWHM (eV)	1.13	4.42	0.98	2.58

Table 6.4: XPS fitting parameters of the Cu 2p peak region

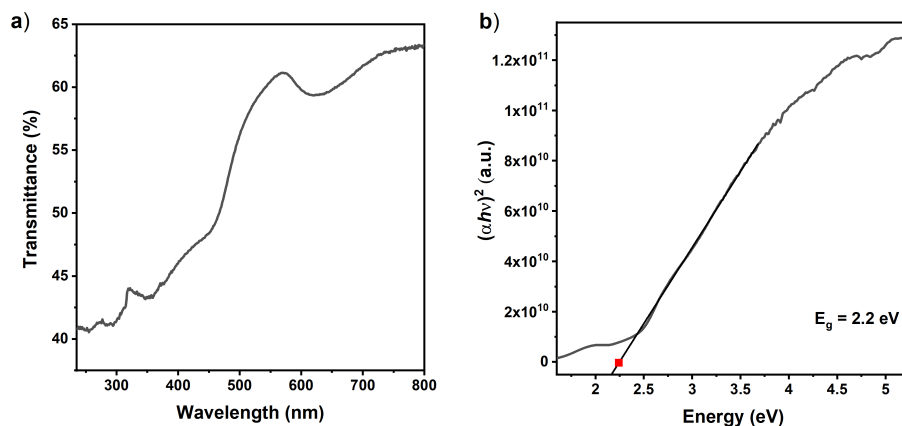


Figure 6.15: a) Transmittance spectrum and b) Tauc plot of Cu₂O. The observed band gap is in agreement with literature.

visible range, especially at thicknesses greater than 100 nm. This point is given further consideration in Chapter 7.

An attempt was made to characterise the electrical performance and hole mobility of the Cu₂O films using the Hall effect method described before. Due to the valence band hybridisation, the mobility of Cu₂O films strongly correlates to the grain size, hence growth temperature or post-growth annealing [100, 286]. The XRD characterisation was promising in this regard. Unfortunately, as each Cu₂O film exhibited resistances in the MOhm range, no mobility values could be extracted as the conductivity of the films was outside of the accepted tolerance of the Hall mobility instrument. While this high resistance behaviour is characteristic of Cu₂O which typically exhibits carrier concentrations as low as $1.7 \times 10^{14} \text{ cm}^{-3}$ [118], it also provides a challenge as currently it is difficult to obtain quantitative data on improvements in the electrical performance of either V₂O₃ or Cu₂O. Measuring the Hall mobility therefore presents as an obstacle of this current research, plans to address this issue shall be considered in Chapter 7.

6.7 Conclusion

In this chapter I have presented and discussed work on the growth and characterisation of V₂O₃ as a p-type TCO. Preliminary work focused on the growth of

Growth of Cu₂O films

high quality films, and indicated crystalline growth of the V₂O₃ films on (0001) orientated Al₂O₃ substrates. XPS spectra initially demonstrated a V₂O₅ signal which is attributed to surface oxidation of the top layer of the V₂O₃ film. Calculations from XRR spectra estimate this V₂O₅ layer to be 2.7 nm thick. Following this, a study was performed on the effectiveness of Mg as a dopant in V₂O₃. XPS spectra indicated a weak Mg presence, while XRD 2θ scans indicated the Mg had little affect on the crystallinity of the thin films. The V₂O₃ films showed excellent optoelectronic properties. Although some absorption is observed due to forbidden d-d transitions, the main interband transition is seen to occur at 3.3 eV, leading to an overall transparency above 60 % in the visible range. The films showed a characteristically low hole mobility, along with a metal like charge carrier density resulting in conductivities as high as 1867 ± 187 S/cm. These conductivities compare extremely well compared to other p-type TCOs such as Mg:Cr₂O₃ (0.17 S/cm) [178], CuCr_{0.95}Mg_{0.05}O₂ (220 S/cm) [121], and spray pyrolysis grown V₂O₃ (1079 S/cm) [287]. An increase in hole mobility is observed upon Mg incorporation however this result requires further verification. The observed conductivity values are below those of PLD grown V₂O₃ [184, 288], however the relatively high FoM^G is supportive of V₂O₃'s potential as a p-type TCO.

Subsequently, a microscopy study was performed on these doped and undoped V₂O₃ samples. Initial imaging indicated the presence of both corundum and bixbyite phases, with both phases observed to grow in the bulk and directly on the corundum substrate. Additionally, EDX mapping showed a homogeneous Mg incorporation which ruled out MgO clustering as explanation for the low impact of Mg doping on the films. Furthermore, the V₂O₃ lamellae showed serious degradation before and after STEM imaging. This presented a serious issue towards further microscopy imaging and characterisation due to the large time commitment to prepare a single lamella. A 10 month exposure study exhibited that the lamellae are not sensitive to ambient conditions therefore it hypothesised that pre-microscopy ion polishing is likely the cause of lamella degradation.

Finally, work on the growth and optimisation of Cu₂O layers was presented, laying the foundation for future studies on V₂O₃/Cu₂O bilayers and nanolaminates. These Cu₂O layers are shown to be grow epitaxially on Al₂O₃ substrates, and while no Hall mobility could be measured the high crystallinity of the films

is promising for future work. Lastly, the band gap of the material was measured and found to agree with bulk Cu_2O .

Chapter 7

Conclusions and Future Work

In this work there are three main studies that are presented. First, a thickness study that examines the optoelectronic performance of a-ZTO thin films as their thickness is reduced. The second study investigates the role that the inter-cation ratio in a-ZTO plays on the local chemical and bonding environment in the material. The objective of this work was to attempt to understand the correlation between changes in the inter-cation ratio and changes in the charge carrier concentration, electron mobility and band gap of the material. Finally, a study into V_2O_3 as a prospective p-type TCO was performed covering a wide number of circumstances including characterisation of the pristine material, Mg doping, microscopy study on the structures and finally a study on the growth of Cu_2O with the intention of combining it with V_2O_3 to form bilayer or multilayer structures.

In Chapter 4, the performance of a-ZTO in the low thickness regime is examined. A number of a-ZTO thin films were grown in the range of 3-56 nm and their optoelectronic properties were characterised. A drop in the conductivity below 12 nm is attributed to a decrease in the number of charge carrier generating defects as well as the more substantial break down in the 3D conduction network. Using the Tauc method a 0.33 eV shift is observed in the optical band gap of the a-ZTO films. X-ray characterisation was utilised to examine structure of the thin films. All of the films were observed to be X-ray amorphous, and an *in-vacuo* XPS study showed no chemical difference between a high and

Conclusions and future work

low thickness sample, however a 0.6 eV shift in the position of the VBM in the 6 nm film was observed. Following on from this, using a *in-vacuo* sample transfer a high and low thickness a-ZTO were examined using STM and STS. STM data agreed with previous SEM imaging that the a-ZTO present as smooth and continuous films, while STS was utilised to confirm the presence and scale of the bandgap shift. Interestingly, while the XPS spectra indicate that the shift is located in the VB, the STS spectra suggest the change is located in the CB as would be in line with the IQW model [251]. This result is significant for a-ZTO because changes in its band structure, either in the VB or CB, and electrical performance can have knock on implications for the efficiency of the optoelectronic and photovoltaic devices it has already seen some applications in [72, 289–291]. Whereas small energy barriers enable partial or full transport across an interface, significant separation (> 1 eV) between the energy bands of materials can act to inhibit charge carrier transport as energy barriers are generated that must be overcome. To further investigate and confirm the cause of this band gap shift would require detailed computational calculations on the effect of confining the dimensionality of a-ZTO or a focused examination of the VB and CB structure using techniques such as ultraviolet photoelectron spectroscopy (UPS), and inverse photoelectron spectroscopy (IPES). Both of these approaches are beyond the scope of this thesis but either could play a vital role in confirming the mechanism responsible for this bandgap shift in a-ZTO, and enabling further device integration. Further avenues for exploration of a-ZTO include temperature dependant measurements of conductance with respect to thickness to understand the scattering mechanisms at play within the material, and examining the role that film composition has upon the presence and scale of the band gap blueshift in a-ZTO.

In Chapter 5 through a combination of XANES and EXAFS at the Zn and Sn K-edges, the local bonding environment in a-ZTO was examined. While varying the intercation ratio in the thin films, no changes in the chemical environment were observed for magnetron grown films while subtle differences were observed in spray pyrolysis samples, likely caused by the chemical precursors used during sample growth affecting the reaction pathways of the SnO_2 and ZnO building blocks. EXAFS fitting at the Sn edge shows coordination numbers consistent with distorted SnO_2 octahedra, and a small decrease in Sn-O bond length for magnetron grown a-ZTO when compared to pure SnO_2 . I observe no evidence of ZnSn_2O_5 or ZnSn_3O_7 polymorphs in the form of discernable chemical environmental changes or next nearest neighbour scattering pathways. Rather,

this result supports the theory that a-ZTO is composed of "building blocks" of ZnO and SnO₂ polyhedra. I conclude that the observed changes in mobility and bandgap are likely derived from alterations in the level of orbital hybridisation that occurs at the conduction band minimum when the Zn/ Sn ratio is varied. The next step in this research is to perform EXAFS at the Zn K-edge to confirm the tetrahedral Zn coordination that is hypothesised. This was not possible in this study due to time constraints during beamline access, however it would confirm the ZnO and Sn₂O building block theory proposed. In addition, a DFT computational study on a-ZTO to uncover the defect mechanism responsible for the variation in conductivity and confirm the optimal electrical composition of a-ZTO for electrical performance would be beneficial. My XAS results indicate that this defect mechanism is smaller than the nearest neighbour or next nearest neighbour bond distance suggesting point defects may be responsible. Point defects are difficult to resolve experimentally and so computational methods may be necessary. To date, computational studies on a-ZTO have been lacking as DFT requires a repeating unit cell to model, however it is difficult to say with confidence what this should be for an amorphous material. In this regard my results may prove extremely pertinent as they elucidate the chemical and bonding environment present for Zn and Sn atoms in the a-ZTO.

In Chapter 6 a study is performed to determine the viability of V₂O₃ as a p-type TCO. Epitaxial (006) V₂O₃ films were grown on (0001) Al₂O₃ substrates and exhibited excellent TCO properties. Despite a characteristically low hole mobility, conductivities as high as 1750±175 S/cm were observed for a 40 nm film, along with a transmittance above 60 % in the visible range. This cumulated in Figure of Merit as high as 455.3±45.5 Ω⁻¹. This compares extremely well compared to current p-type TCO options such as CuCrO₂ [92]. The V₂O₃ films were subsequently doped with MgO, with the intention of introducing a shallow acceptor state and increasing the itinerant charge carrier density. The Mg presence was confirmed using a combination of XPS and EDX spectroscopies. The performance of the Mg:V₂O₃ films was then examined using UV-vis spectroscopy and Hall effect measurements. No clear improvement in either the transparency or the conductivity was observed. While this initial work is not promising there is a number of additional avenues to explore before it can be decisively stated whether Mg is an effective dopant. Firstly, the Mg:V₂O₃ samples were grown in conditions that produced the most crystalline V₂O₃ films. However the activation energy of various defects can be affected by the O partial pressure during depositions [100, 116], therefore this may be a

Conclusions and future work

route to explore in future studies. Furthermore it would be beneficial to remeasure the Hall mobility and conductivity of these Mg:V₂O₃ films. Although no improvement in the conductivity of these films was observed, the conductivity measurements recorded were on the limit of sensitivity of the Hall instrument, and thus have a high degree of uncertainty. To overcome this issue of sensitivity and corroborate the results, the samples are in the process of being remeasured with a Lake Shore Cryotronics 8404 Hall system which can reach higher magnetic fields and thus can measure μ values as low as $1 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$, however due to time constraints results were not available to include in this work.

The final results presented in Chapter 6 pertain to the optimisation and growth characteristics of V₂O₃ and Cu₂O films with the intention of using these materials to grow nanolaminates. Despite a strong (006) XRD peak being observed for pristine V₂O₃, a considerable presence of the bixbyite phase is observed in STEM imaging. Moreover, bixbyite V₂O₃ is also observed to grow directly on the corundum Al₂O₃ substrate. Although there is a low difference in the enthalpy of formation between the corundum and bixbyite V₂O₃ phases [183], this result was surprising given the matching crystal structure of corundum V₂O₃ and the (0001) Al₂O₃ substrate. A study of the crystalline phase of V₂O₃ indicated that the [024] bixbyite phase is preferred below thicknesses of 20 nm. It is then hypothesised that this may be due to the close matching of the Al₂O₃ unit cell parameter (4.8 Å) to the 4.7 Å V-V distance in this [024] orientation. An XRD ϕ scan is planned to clarify the structure of the low thickness V₂O₃ films. Next, the growth of crystalline Cu₂O is explored. XPS and UV-vis measurements were used to confirm the presence of Cu₂O films while XRD RSM and ϕ scans indicate the Cu₂O had grown epitaxially on the (0001) Al₂O₃ substrate. Although the Hall mobility of the films could not be measured as the mobility of Cu₂O strongly depends on the grain size and crystallinity of the material, the high crystallinity of the films is encouraging [100, 286]. The Lake Shore Cryotronics 8404 Hall system previously mentioned will also be used to measure the mobility of the Cu₂O films.

The next step in this research is to begin the growth of V₂O₃/Cu₂O bilayers. As the eventual goal of this work is to grow nanolaminates, both cases of Cu₂O and V₂O₃ acting as the seed layer will be explored. A large concern in this work is how the V₂O₃ and Cu₂O layers will grow on top of each other. While epitaxial growth has been observed on Al₂O₃ it is unclear how the films will behave when they are grown on another material, especially for Cu₂O where high crystallinity is essential [100, 286]. The growth and optimisation of the

individual layers is expected to reduce the workload in this study, however further optimisation may be required to stop individual layers contribute to the films bleeding into one another and the creation of mixed oxidation phases. This effectively introduces a temperature budget into the growth process which will have to be explored and optimised. As XPS on both materials indicates surface oxidation when exposed to ambient conditions, the ability to deposit from two sputtering cathodes will be pivotal to this work as it ensures that the oxides will remain phase pure. While the electrical properties of the bilayers are expected to surpass those of the individual layers the optical performance will be of interest. Both materials see some absorption in the visible light region therefore this could be a shortcoming of the bilayer, however quantum confinement of optical band gap has previously been reported for Cu_2O and therefore may be useful to increase the optical transparency of the bilayer system [292].

Chapter 8

Appendix

8.1 Section I - Thickness study on a-ZTO

In addition to the Zn 2p_{3/2} and Sn 3p_{3/2} core level spectra shown in Chapter 4, survey spectra and core level spectra of the O 1s region were also recorded from the 57 nm and 6 nm films. These are shown in Figures 8.1a, and 8.1b respectively. It is notable that in the survey spectrum of the 6 nm film there is the presence of a C 1s signal at 284.8 eV. This is caused by the 6 nm film being exposed to atmosphere before XPS measurements, while the 57 nm which was transferred *in-vacuo*. This exposure to ambient conditions can affect the surface states of the material due to adsorption from adventitious C and hydroxides, . This is shown in Figure 8.1b, where a significant shoulder is observed in the 6 nm film which is attributed to hydroxide molecules adsorbed to the film surface, and acts to broaden the FWHM of the core level peak.

While a 0.2 eV shift in the Zn 2p_{3/2} peak position is observed between the 57 nm and the 6 nm film, it is noted that the peak shape remains consistent suggesting that the chemical environment of the Sn and Zn atoms is quite stable under ambient conditions. This agrees with electrical measurements shown in Figure 8.2 and Table 8.2, which indicate that the a-ZTO samples retain high mobility and conductivity after 48 months of exposure to atmospheric conditions. While this exposure of the 6 nm sample to atmosphere allowed insight into the chemical stability of the cations in the a-ZTO film, if this study was to be repeated it would be desired to transfer both samples *in-vacuo* as this would allow a clearer comparison between the core level spectra of both samples.

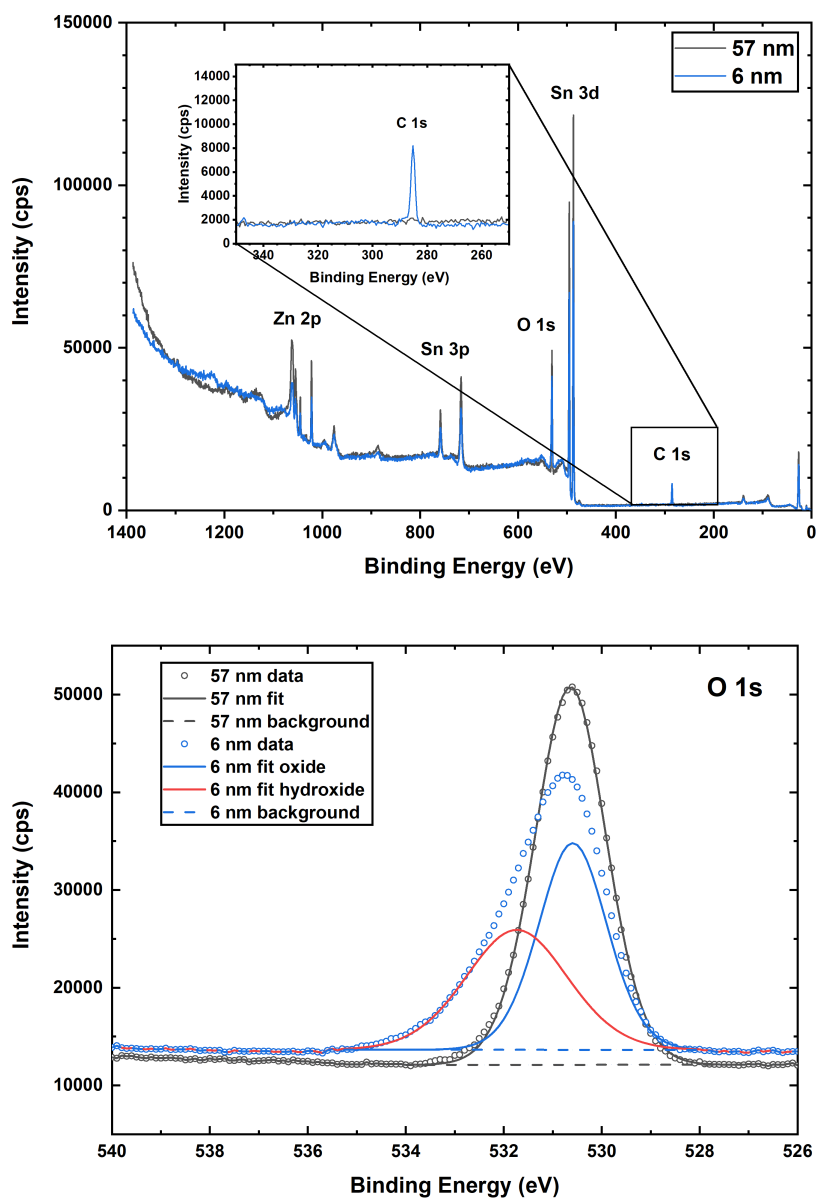


Figure 8.1: a) XPS survey spectrum of a 57 nm and 6 nm thick a-ZTO films, inset in the survey spectrum is a magnification of the C 1s core level area. Because the 6 nm film had been exposed to atmosphere a significant C signal is observed from adventitious C. b) XPS core level spectra of the O 1s peak of a 57 nm and 6 nm thick a-ZTO films. As the 6 nm sample was exposed to atmosphere a broadened O 1s peak is observed.

Sample	Peak component	Peak position (eV)	FWHM (eV)	Fitting line shape	Residual stan. dev.	Area (%)
57 nm	Zn 2p _{3/2}	1021.9	1.81	GL(57)	1.8	7.5
57 nm	Sn 3p _{3/2}	716.5	3.71	GL(75)	1.7	29.6
57 nm	O 1s	530.6	1.71	GL(30)	3.30	62.9
6 nm	Zn 2p _{3/2}	1022.1	1.87	GL(57)	2.1	5.3
6 nm	Sn 3p _{3/2}	716.6	3.66	GL(75)	2.0	24.9
6 nm	O 1s	530.6	1.64	GL(30)	2.47	32.4
6 nm	O 1s	531.7	2.45	GL(30)	-	37.4

Table 8.1: XPS fitting parameters of core level spectra for a 56 nm and 6 nm a-ZTO film.

As an intrinsic semiconductor a-ZTO relies on cation interstitials and O vacancies and is therefore quite sensitive to the concentration of O in the deposition chamber during growths. However, it is observed that once the a-ZTO are grown their electrical properties are quite stable. This is shown in Figure 8.2, and Table 8.2 which present the electrical properties of the a-ZTO films studied in Chapter 4, after 48 months of exposure to ambient conditions. These figures match up quite well to those presented in Table 4.2. Although there is drop in carrier concentration in most samples, resulting in a drop in the overall conductivity, the Hall mobility is seen to either be stable or increase. I postulate that this drop in charge carrier concentration is due to surface oxidation passifying oxygen vacancies and leading to the formation of a depletion region on the surface of the thin film. This theory would also explain why the charge carrier concentration of the 3.7 nm sample effectively does not change over this extended time period. As the thickness of the film is reduced the depletion layer will quickly form, however this layer cannot oxidise further and so the charge carrier density remains stable.

A total of 8 STS band gap heat-maps were measured. Histograms for two of these heat-maps are presented in Figures 4.10e and 4.10f, while the remaining are shown in Figure 8.3. A Gaussian line shape has been overlaid over the histograms as visual guide of the data distribution. Statistical values for the histograms are available in Table 8.3. The histograms from the 57 nm film, have a mean value of 2.56 ± 0.27 eV but plots F and G also show a large population at 2.625 eV. In comparison, the histograms from the 6 nm film have a mean value of 3.04 ± 0.25 eV, and show larger populations at higher band gap values.

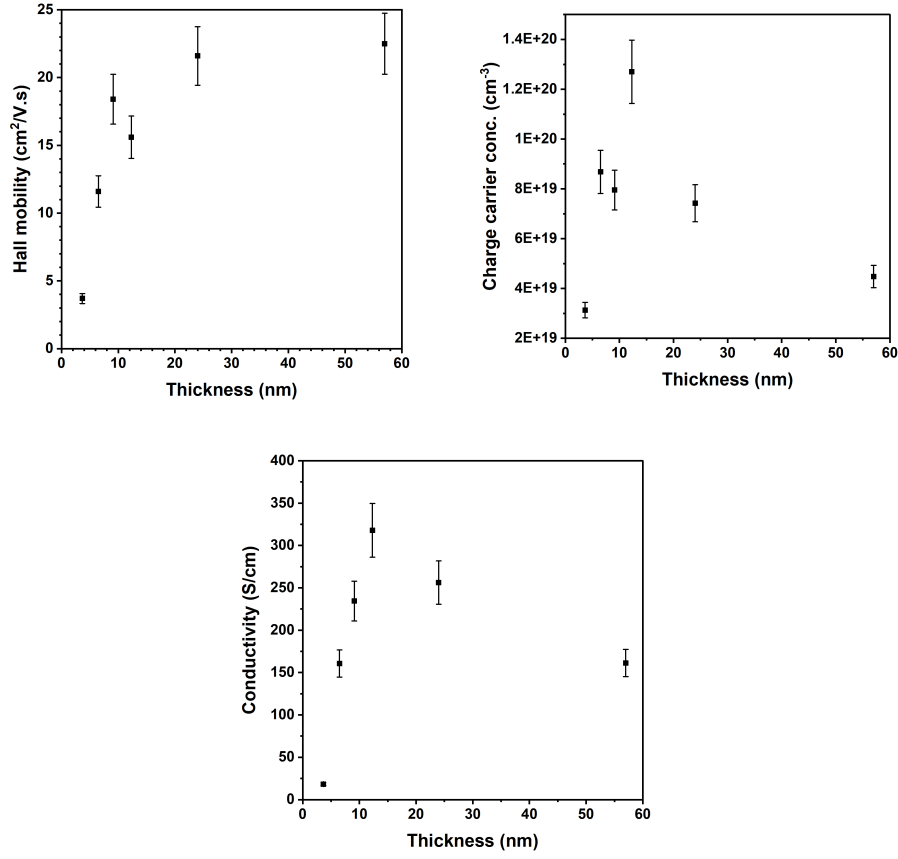


Figure 8.2: The variance of a) Hall mobility, b) charge carrier concentration and c) conductivity in a-ZTO as a function of thickness, after sample exposure to ambient conditions for 48 months. Similar trends in the mobility, and charge carrier density are observed when compared to Figure 4.6.

Sample (nm)	σ (S/cm)	μ_{Hall} ($\text{cm}^2/\text{V}\cdot\text{s}$)	n (cm^{-3})
56.7	161.3 ± 16.1	22.5 ± 2.3	$(7.4 \pm 0.7) \times 10^{19}$
24.1	256.3 ± 25.6	21.6 ± 2.2	$(4.5 \pm 0.5) \times 10^{19}$
12.3	317.9 ± 31.8	15.6 ± 1.6	$(1.3 \pm 0.1) \times 10^{20}$
9.1	234.4 ± 23.4	18.4 ± 1.8	$(8.0 \pm 0.8) \times 10^{19}$
6.4	160.6 ± 16.1	11.6 ± 1.2	$(8.7 \pm 0.9) \times 10^{19}$
3.7	18.3 ± 1.8	3.7 ± 0.4	$(3.1 \pm 0.3) \times 10^{19}$

Table 8.2: Electrical properties of a-ZTO thin films as thickness is varied after 48 months of exposure to atmospheric conditions.

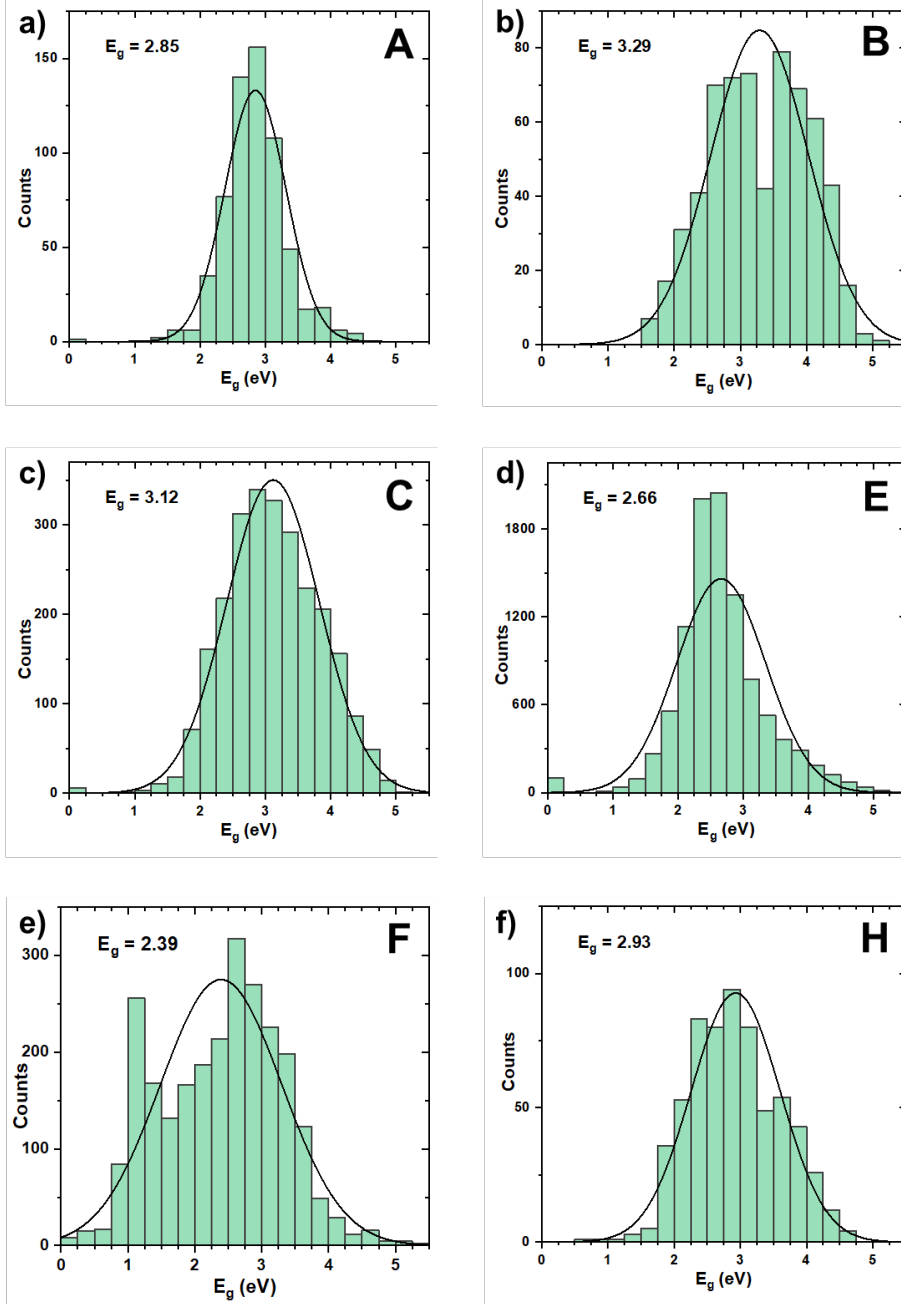


Figure 8.3: Histograms showing the range of band gap values during STS measurements of the band gap. Subfigures 8.3a, 8.3b, 8.3c and 8.3d show measurements from a 6 nm film. Subfigures 8.3e and 8.3f, represent band gap measurements taken on a 57 nm. Statistical values are available in Table 8.3.

Appendix

Plot	Mean	Median	Standard deviation	Kurtosis
A	2.85	2.84	0.47	2.85
B	3.29	3.26	0.74	-0.86
C	3.12	3.07	0.71	0.21
D	3.29	3.27	0.73	-0.06
E	2.66	2.60	0.68	2.45
avg.	3.04 ± 0.25	3.01 ± 0.29		
F	2.39	2.50	0.91	-0.45
G	2.34	2.36	0.53	1.42
H	2.93	2.91	0.67	-0.32
avg.	2.56 ± 0.27	2.59 ± 0.29		

Table 8.3: The mean, median, standard deviation and kurtosis of the band gap heat-maps measured by STS where plots A-E were measured on the 6 nm film, and plots F-H on the 56 nm film.

8.2 Section II - XPS and XAS study on a-ZTO

Shown in Figure 8.4a is an XPS survey spectra which correspond to the magnetron grown a-ZTO films studied in Chapter 5. All three of MAG1, MAG2, and MAG3 were transferred to the XPS instrument *in-vacuo* using a vacuum suitcase. From the inset plot, it is clear that there is extremely small C 1s signal in all three samples. For comparison, survey spectra from the spray pyrolysis grown a-ZTO films have also been shown. These samples were introduced to the XPS instrument from atmospheric pressure. They were later sputtered clean using Ar ion etching with a voltage of 750 V, and sputter current of 6 μ A for 10 minutes. Inset in the plots is a close-up of the C 1s region, the samples exhibit a small C 1s signal, however the survey spectra do also suggest a small amount of Ca and Ar contamination in the samples. The Ar signal is likely due to Ar ions that have embedded in the sample from the sputtering process, while the Ca presence may be due to residual spray pyrolysis precursors that have not completely evaporated during sample growth.

In addition to the survey spectrum, core level spectra of the Zn 2p_{3/2}, Sn 3p_{3/2} and O 1s region were recorded for each sample. This enabled the stoichiometries of each of the a-ZTO films studied to be calculated, these are presented in Table 8.4 in the form x , y , z , which corresponds to Zn _{x} Sn _{y} O _{z} . A spectrum of the O 1s core level region from the sample MAG1, is shown in Figure 8.5. The peak was fitted using a Shirley background, and a Gaussian/Lorentzian (GL35) line shape. The peak of the line shape is found at 530.6

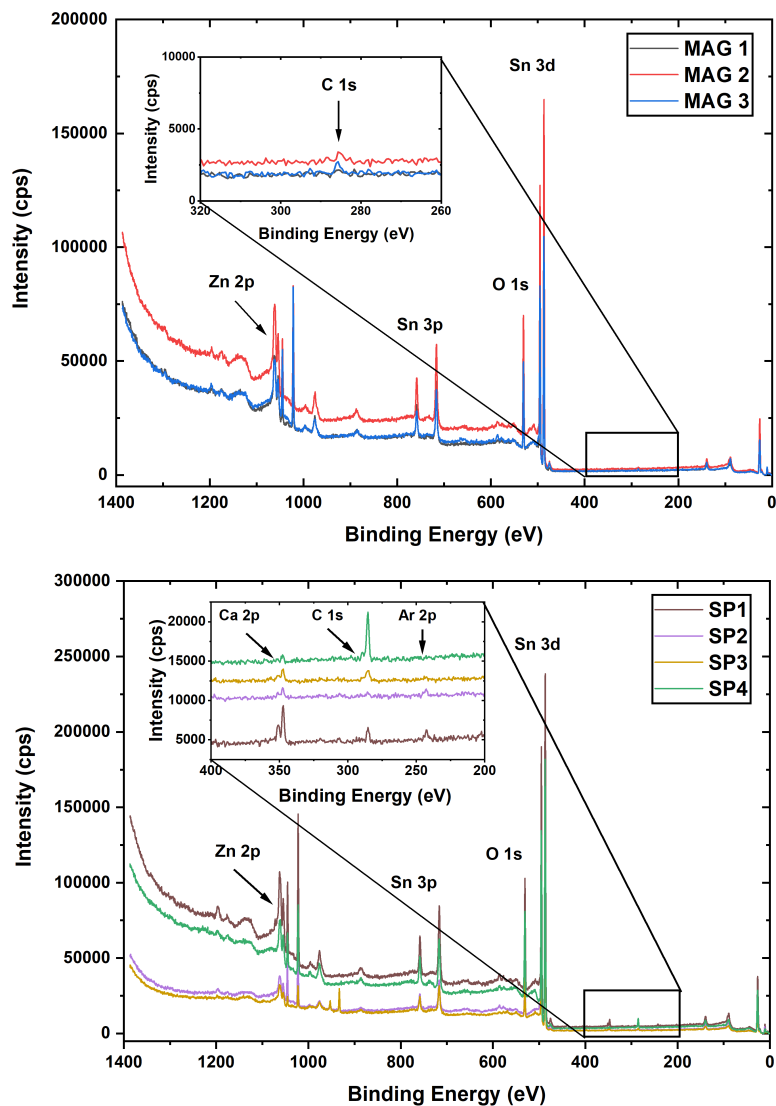


Figure 8.4: a) XPS survey spectrum for MAG1, MAG2 and MAG3. As the sample was transferred *in-vacuo* the C 1s signal remains small b) XPS survey spectrum for samples SP1, SP2, SP3 and SP4. As the samples were loaded from atmospheric pressure a C 1s signal is observed. Additionally, there is an Ar signal from sputter and annealing processes, and a small Ca 2p signal likely due to left over chemical precursor.

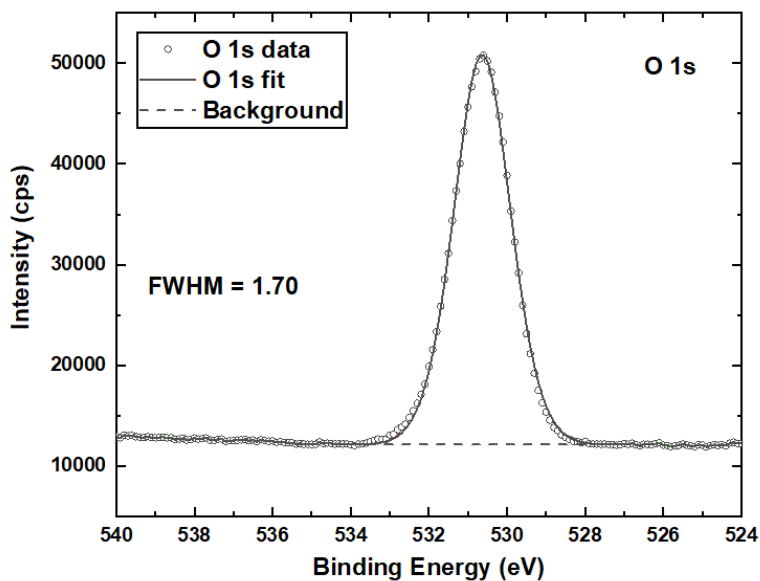


Figure 8.5: XPS core level spectrum of the O 1s region for sample MAG1.

eV and a FWHM of 1.70 eV. This is found to match the line shapes calculated in Table 8.1 for the magnetron grown a-ZTO of Chapter 4.

Following spectral normalisation and background subtraction, $k^2\chi(k)$ spectra were calculated from the EXAFS measurements. taken at the Sn K-edge of magnetron grown and spray pyrolysis grown a-ZTO thin films. $\chi(k)$ spectra show the scattering pathways that a photoelectron may take. Strongly scattering pathways have a large amplitude, while longer scattering pathways "turn-on"

Sample name	x (%)	y (%)	z (%)	Zn:Sn
MAG1	7.46	29.60	62.94	20:80
MAG2	10.47	28.37	61.16	27:73
MAG3	16.80	23.90	59.30	41:59
SP1	8.02	24.43	67.55	31:69
SP2	10.30	19.38	70.32	43:57
SP3	8.01	25.00	66.99	31:69
SP4	7.83	24.18	68.00	23:77

Table 8.4: Stoichiometries of the a-ZTO films studied by XAS, in the form of x , y , z , which corresponds to $Zn_xSn_yO_z$, where $x + y + z = 100\%$. For completeness the corresponding Zn:Sn ratios have also been included.

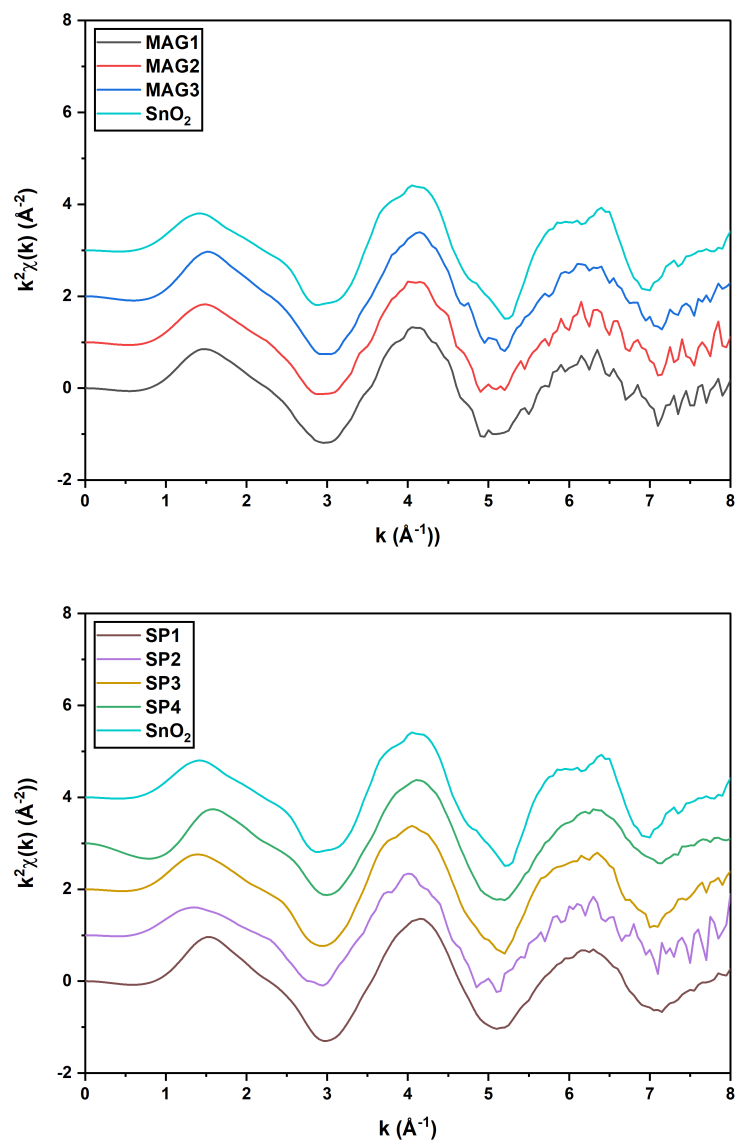


Figure 8.6: $k^2\chi(k)$ spectra calculated from EXAFS measurements taken at the Sn K-edge, for a) magnetron grown and b) spray pyrolysis grown a-ZTO thin films.

Appendix

at a higher k value. When one examines Figures 8.6a and 8.6b, one may notice there is some deviance in both figures below $1 \text{ \AA}^{-1}$ however these are artefacts that remain after background subtraction. All spectra demonstrate a regular amplitude and frequency between $(1.5-8) \text{ \AA}^{-1}$, this signal is that of the Sn-O scattering pathway. The uniformity of the amplitude of this signal suggests that all sample have similar O coordination and this is corroborated by FEFF8 fitting.

Beyond $5 \text{ \AA}^{-1}$, the SnO_2 sample continues to show fine structure features, specifically at the points $5 \text{ \AA}^{-1}$, and $6.5 \text{ \AA}^{-1}$. It is at this point that higher order features from Sn-Sn scattering pathways begin to overlap with the Sn-O signal and constructively and destructively interfere. In contrast to this, beyond $5 \text{ \AA}^{-1}$ the a-ZTO samples begin to show increased levels of noise. This is due to the lack of long-range order and regular scattering pathways for the photoelectron to travel back to the absorbing Sn atom. Spectra have been curtailed at $8 \text{ \AA}^{-1}$, as this is the limit of data collected for sample SP4 and also beyond this point the noise begins to dominate the a-ZTO spectra. The one exception to this behaviour is sample SP3, as it shows some similar spectral features to the SnO_2 reference sample. Moreover, this sample had previously indicated XANES features typical of ZnO, and had the lowest Debye-Waller factor of the a-ZTO films from FEFF8 fitting. It seems likely therefore that this sample is comprised of nanocrystalline grains of ZnO and SnO_2 that formed during spray pyrolysis growth.

8.3 Section III - Exploring V_2O_3 as a TCO

As described in Section 6.2, V_2O_3 films were grown by reactive sputtering of a V metal target in an Ar/O_2 environment. To analyse the elemental purity and verify the chemical composition of the thin films a survey spectrum was recorded along with a core level spectrum of the O 1s and V 2p region. The core level spectrum is discussed in Section 6.3 and the survey spectrum is shown below in Figure 8.7a. As expected the V 2p and O 1s peaks dominate the spectrum, however there is also the additional of a strong C 1s signal. This C incorporation is attributed to the SEM imaging that the V_2O_3 film underwent prior to XPS analysis. Due to the high energy of the electron beam in SEM and the low vacuum that the instrument typically operates at, it is not uncommon for SEM imaging to "burn" C onto the surface of a sample if the beam is left to dwell

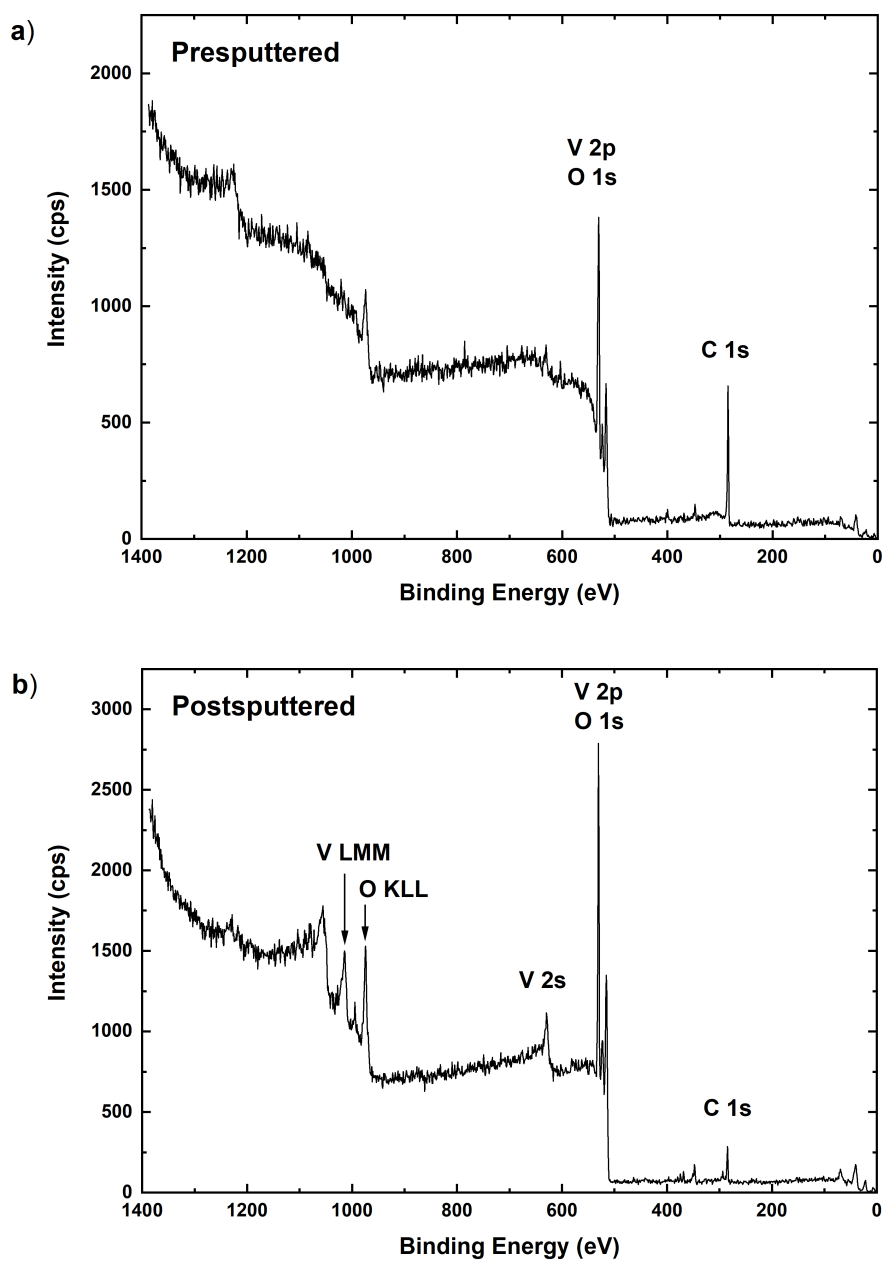


Figure 8.7: a) A XPS survey spectrum of pure V_2O_3 before the film underwent an Ar sputtering and anneal cycle. A significant C 1s signal is observed which is attributed to SEM imaging that was performed on the sample prior to XPS analysis. b) A XPS survey spectrum of pure V_2O_3 after an Ar sputter and anneal cycle.

Appendix

on a particular area for an extended period of time, as is typical when imaging. To combat this the V_2O_3 film underwent a sputter and anneal cycle where an Ar ion current was applied to the sample for a 10 minute period at 650 V, and then the film was annealed at 530 °C for 2 hours. After sputtering the C 1s signal is greatly diminished and the V 2s as well V and O Auger peaks become more prominent. In both spectra, a peak is observed at 347 eV, which may be indicative of a Ca contamination in the sample. Further analysis is required to confirm whether this is contamination is introduced during sample growth.

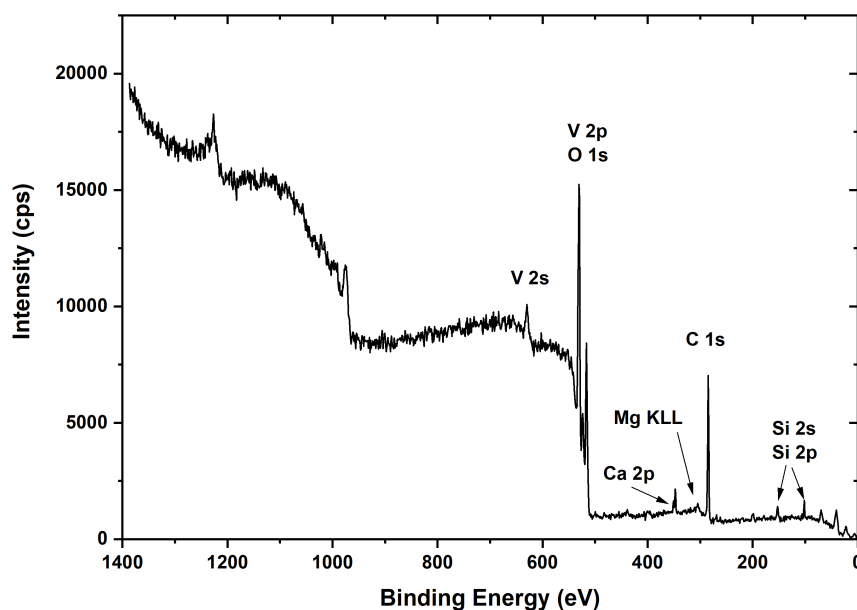


Figure 8.8: XPS survey spectrum of an unsputtered $\text{Mg}:\text{V}_2\text{O}_3$ film. The Mg KLL Auger peak confirms the doping of the sample with Mg, however core level peaks attributed to Ca and Si are also observed.

Following the successful growth of crystalline V_2O_3 , work began on doping the films with Mg with the intention of increasing the electrical performance of the thin films. To achieve this a MgO target was co-sputtered during V_2O_3 depositions. The desired doping level was approximately 1% Mg to V [191], so a low power density was applied to the MgO target in growths. In order to attempt to quantify the Mg concentration within the V_2O_3 films XPS was performed. In total, a survey spectrum at 50 eV pass energy as well as core level spectra of the V 2p/O 1s and V 3s/Mg 2s regions at 20 eV pass energy were recorded. The core level spectra are presented and discussed in Section 6.4, and

	Peak component	Peak position (eV)	Fitting line shape	FWHM (eV)	Area (%)
Pre-sputter	O 1s	529.9	TLA(1,12,230)	1.26	41.06
	O 1s	531.9	GL(30)	2.49	32.2
Post-sputter	O 1s	530.1	TLA(1,12,230)	1.04	44.7
	O 1s	531.3	GL(30)	2.25	19.6

Table 8.5: XPS fitting parameters of the O 1s peak in V_2O_3 . An asymmetric TLA line shape provides the best fit which suggests there may be screening of the core electrons.

the survey spectrum is presented below in Figure 8.8. As expected a Mg KLL Auger peak is observed at 303.8 eV, which serves to confirm the presence of Mg in the films.

A unexpected addition to the survey spectrum is an ostensive Ca 2p and Si signal from the Mg: V_2O_3 film. While a small Ca signal was seen in the growth of pure V_2O_3 , it is unclear where this Si contamination originates from. The MgO sputtering target, obtained from Kurt J. Lesker, is deemed to be of 99.95 % atomic purity. However, this sputtering target was reused from a previous study, so contamination may have occurred while the target was in storage. It is worth noting that during EDX measurements of Mg: V_2O_3 lamellae, no prominent Ca or Si signal was observed, thus the concentration of contaminants is expected to be low. As the Mg was not found to be an effective dopant in the concentration range examined, this matter was not explored further.

Following the exploration of Mg as a dopant in V_2O_3 to improve the electrical conductivity, Cu₂O was examined as a material to pair with V_2O_3 in order to form high conductivity multilayers. As part of this characterisation, XPS was performed in the form of a survey spectrum and core level spectra of the Cu 2p and O 1s regions. As discussed in Section 6.6, the Cu atoms are considered to be primarily in the +1 oxidation state as expected for Cu₂O, however some surface oxidation is observed which manifests in the form of a CuO shoulder on

Peak component	Peak position (eV)	Fitting line shape	FWHM (eV)	Area (%)
Cu ₂ O	531.6	GL(25)	1.60	32.2
CuO	530.4	GL(85)	0.84	17.8

Table 8.6: XPS fitting parameters of the O 1s peak in Cu₂O.

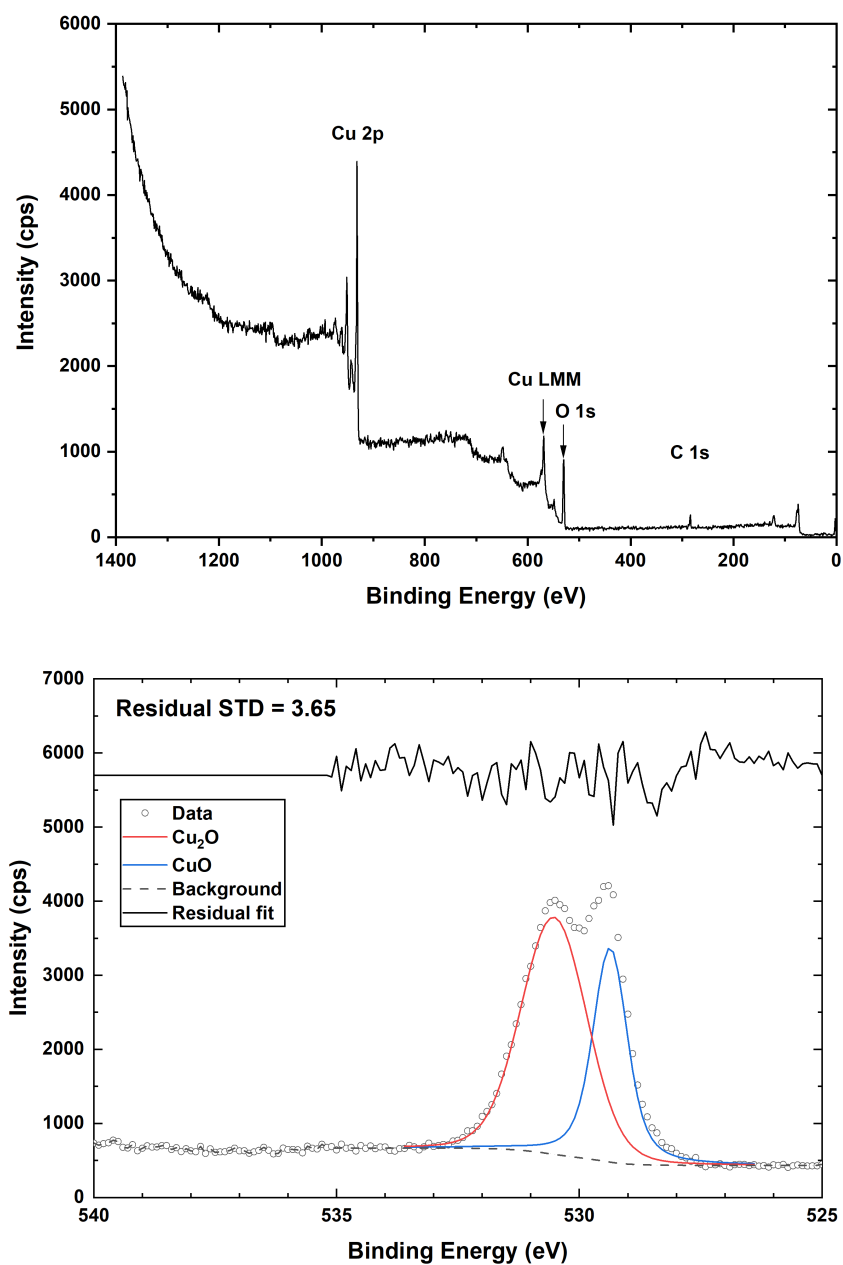


Figure 8.9: a) XPS survey spectrum of an unspattered Cu₂O film. A small C 1s signal is observed but no further contaminants are visible. b) O 1s core level spectrum from a Cu₂O sample. As the surface layer of the film has oxidised from exposure to ambient, a CuO peak component is observed.

the Cu_2O $2p_{1/2}$ and $2p_{3/2}$ peaks. The corresponding survey spectrum measured with 50 eV pass energy and shown in Figure 8.9a, indicates that excluding some adventitious C due to exposure of the film to ambient conditions, the Cu_2O thin film is elementally pure. For completeness the O 1s core level spectrum recorded with 20 eV pass energy and 4.5 mm slits, and corrected with reference to the C 1s peak at 284.8 eV, is shown in Figure 8.9b with the fit parameters given in Table 8.6. A strong peak signal is observed at 529.4 eV which is attributed to CuO [293], while a broad peak centered at 530.5 eV is characteristic of Cu_2O [294].

References

1. *OLED Market Size, Trends, Share & Insights Report, 2035* <https://www.rootsanalysis.com/oled-market>.
2. Rajachidambaram, J. S. *et al.* Characterization of amorphous zinc tin oxide semiconductors. *Journal of Materials Research* **27**, 2309–2317. ISSN: 2044-5326. <https://www.cambridge.org/core/journals/journal-of-materials-research/article/abs/characterization-of-amorphous-zinc-tin-oxide-semiconductors/9FE9CC0A8D1A2D174D0B883924E882B0> (Sept. 2012).
3. Dixon, S. C., Scanlon, D. O., Carmalt, C. J. & Parkin, I. P. N-Type doped transparent conducting binary oxides: An overview. *Journal of Materials Chemistry C* **4**, 6946–6961. ISSN: 20507526 (2016).
4. Barquinha, P., Martins, R., Pereira, L. & Fortunato, E. *Transparent Oxide Electronics: From Materials to Devices* 1st ed., 9–15. ISBN: 978-0-470-68373-6 (Wiley, 2012).
5. Major, S., Banerjee, A. & Chopra, K. L. Highly transparent and conducting indium-doped zinc oxide films by spray pyrolysis. *Thin Solid Films* **108**, 333–340. ISSN: 0040-6090 (Oct. 1983).
6. Moss, T. S. The Interpretation of the Properties of Indium Antimonide. *Proceedings of the Physical Society. Section B* **67**, 775. ISSN: 0370-1301. <https://iopscience.iop.org/article/10.1088/0370-1301/67/10/306> (Oct. 1954).
7. Burstein, E. Anomalous Optical Absorption Limit in InSb. *Phys. Rev.* **93**, 632–633. <https://link.aps.org/doi/10.1103/PhysRev.93.632> (Feb. 1954).

8. Hautier, G., Miglio, A., Waroquiers, D., Rignanese, G. M. & Gonze, X. How Does Chemistry Influence Electron Effective Mass in Oxides? A High-Throughput Computational Analysis. *Chemistry of Materials* **26**, 5447–5458. ISSN: 15205002. <https://pubs.acs.org/doi/full/10.1021/cm404079a> (Oct. 2014).
9. Fraser, D. B. & Cook, H. D. Highly Conductive, Transparent Films of Sputtered $\text{In}_{2-x}\text{Sn}_x\text{O}_3$. *Journal of The Electrochemical Society* **119**, 1368. ISSN: 1945-7111. <https://iopscience.iop.org/article/10.1149/1.2403999> (Oct. 1972).
10. Haacke, G. New figure of merit for transparent conductors. *Journal of Applied Physics* **47**, 4086–4089. ISSN: 0021-8979. <https://pubs.aip.org/aip/jap/article-abstract/47/9/4086/502461/New-figure-of-merit-for-transparent-conductors> (Sept. 1976).
11. Ellmer, K. Past achievements and future challenges in the development of optically transparent electrodes. *Nature Photonics* 2012 6:12 **6**, 809–817. ISSN: 1749-4893. <https://www.nature.com/articles/nphoton.2012.282> (Nov. 2012).
12. Gordon, R. G. Criteria for Choosing Transparent Conductors. *MRS Bulletin* **25**, 52–57. ISSN: 1938-1425. <https://www.cambridge.org/core/journals/mrs-bulletin/article/abs/criteria-for-choosing-transparent-conductors/A8FFCAA119DBA7A19D040E2B6B6ED964> (2000).
13. Bädeker, K. Über die elektrische Leitfähigkeit und die thermoelektrische Kraft einiger Schwermetallverbindungen. *Annalen der Physik* **327**, 749–766. ISSN: 15213889 (1907).
14. Baumbach, H. H. v. & Wagner, C. Die elektrische Leitfähigkeit von Zinkoxyd und Cadmiumoxyd. *Zeitschrift für Physikalische Chemie* **22B**, 199–211. ISSN: 2196-7156. <https://www.degruyter.com/document/doi/10.1515/zpch-1933-2215/html> (Mar. 1933).
15. Gudden, B. Elektrizitätsleitung in kristallisierten Stoffen unter Ausschluß der Metalle. *Ergebnisse der exakten naturwissenschaften*, 116–159. <https://link.springer.com/chapter/10.1007/BFb0111750> (Dec. 1924).

16. Liu, H., Avrutin, V., Izyumskaya, N., Özgr, Ü. & Morkoç, H. Transparent conducting oxides for electrode applications in light emitting and absorbing devices. *Superlattices and Microstructures* **48**, 458–484. ISSN: 0749-6036 (Nov. 2010).
17. McMaster, H. A. *Conductive coating for glass and method of application* Oct. 1942.
18. Minami, T. Present status of transparent conducting oxide thin-film development for Indium-Tin-Oxide (ITO) substitutes. *Thin Solid Films* **516**, 5822–5828. ISSN: 0040-6090 (July 2008).
19. Minami, T. Transparent conducting oxide semiconductors for transparent electrodes. *Semiconductor Science and Technology* **20**, S35. ISSN: 0268-1242. <https://iopscience.iop.org/article/10.1088/0268-1242/20/4/004> (Mar. 2005).
20. Fortunato, E., Ginley, D., Hosono, H. & Paine, D. C. Transparent conducting oxides for photovoltaics. *MRS Bulletin* **32**, 242–247. ISSN: 08837694. <https://link.springer.com/article/10.1557/mrs2007.29> (Jan. 2007).
21. Assunção, V. *et al.* Influence of the deposition pressure on the properties of transparent and conductive ZnO:Ga thin-film produced by r.f. sputtering at room temperature. *Thin Solid Films* **427**, 401–405. ISSN: 0040-6090 (Mar. 2003).
22. Canhola, P. *et al.* Role of annealing environment on the performances of large area ITO films produced by rf magnetron sputtering. *Thin Solid Films* **487**, 271–276. ISSN: 0040-6090 (Sept. 2005).
23. Rupprecht, G. Untersuchungen der elektrischen und lichtelektrischen Leitfähigkeit dünner Indiumoxydschichten. *Zeitschrift für Physik* 1954 139:5 **139**, 504–517. ISSN: 14346001. <https://link.springer.com/article/10.1007/BF01374559> (Oct. 1954).
24. Betz, U., Kharrazi Olsson, M., Marthy, J., Escolá, M. F. & Atamny, F. Thin films engineering of indium tin oxide: Large area flat panel displays application. *Surface and Coatings Technology* **200**, 5751–5759. ISSN: 0257-8972 (May 2006).

25. Nomura, K. *et al.* Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature* **432**, 488–492. ISSN: 00280836 (2004).
26. Hosono, H. Recent progress in transparent oxide semiconductors: Materials and device application. *Thin Solid Films* **515**, 6000–6014. ISSN: 00406090 (May 2007).
27. Sousa, M. G. & da Cunha, A. F. Optimization of low temperature RF-magnetron sputtering of indium tin oxide films for solar cell applications. *Applied Surface Science* **484**, 257–264. ISSN: 0169-4332 (Aug. 2019).
28. Hosono, H., Kikuchi, N., Ueda, N., Kawazoe, H. & Shimidzu, K. I. Amorphous transparent electroconductor 2CdO GeO₂: Conversion of amorphous insulating cadmium germanate by ion implantation. *Applied Physics Letters* **67**, 2663–2665. ISSN: 0003-6951. <https://pubs.aip.org/aip/apl/article-abstract/67/18/2663/522023/Amorphous-transparent-electroconductor-2CdO-GeO2> (Oct. 1995).
29. Hosono, H., Yamashita, Y., Ueda, N., Kawazoe, H. & Shimidzu, K. I. New amorphous semiconductor: 2CdO PbOx. *Applied Physics Letters* **68**, 661–663. ISSN: 0003-6951. <https://pubs.aip.org/aip/apl/article-abstract/68/5/661/66019/New-amorphous-semiconductor-2CdO-PbOx> (Jan. 1996).
30. Hosono, H., Yasukawa, M. & Kawazoe, H. Novel oxide amorphous semiconductors: transparent conducting amorphous oxides. *Journal of Non-Crystalline Solids* **203**, 334–344. ISSN: 0022-3093 (Aug. 1996).
31. Hosono, H., Kikuchi, N., Ueda, N. & Kawazoe, H. Working hypothesis to explore novel wide band gap electrically conducting amorphous oxides and examples. *Journal of Non-Crystalline Solids* **198-200**, 165–169. ISSN: 0022-3093 (May 1996).
32. Hosono, H. Ionic amorphous oxide semiconductors: Material design, carrier transport, and device application. *Journal of Non-Crystalline Solids* **352**, 851–858. ISSN: 0022-3093 (June 2006).
33. Fukutani, K. *et al.* Band gap tuning of a-Si:H from 1.55 eV to 2.10 eV by intentionally promoting structural relaxation. *Journal of Non-Crystalline Solids* **227-230**, 63–67. ISSN: 0022-3093 (May 1998).

34. Bernardo, G. *et al.* Polymer light-emitting diodes with amorphous indium-zinc oxide anodes deposited at room temperature. *Synthetic Metals* **159**, 1112–1115. ISSN: 0379-6779 (June 2009).
35. Troughton, J. & Atkinson, D. Amorphous InGaZnO and metal oxide semiconductor devices: An overview and current status. *Journal of Materials Chemistry C* **7**, 12388–12414 (2019).
36. Park, J. S., Maeng, W. J., Kim, H. S. & Park, J. S. Review of recent developments in amorphous oxide semiconductor thin-film transistor devices. *Thin Solid Films* **520**, 1679–1693. ISSN: 0040-6090 (Jan. 2012).
37. Kamiya, T., Nomura, K. & Hosono, H. Present status of amorphous In-Ga-Zn-O thin-film transistors. *Science and Technology of Advanced Materials* **11**. ISSN: 14686996 (Aug. 2010).
38. Minami, T., Nanto, H. & Takata, S. Highly Conductive and Transparent Aluminum Doped Zinc Oxide Thin Films Prepared by RF Magnetron Sputtering. *Japanese Journal of Applied Physics* **23**, L280–L282. ISSN: 13474065. <https://iopscience.iop.org/article/10.1143/JJAP.23.L280> (May 1984).
39. Chen, Z. *et al.* Fabrication of Highly Transparent and Conductive Indium Tin Oxide Thin Films with a High Figure of Merit via Solution Processing. *Langmuir* **13836**, 8. <https://pubs.acs.org/sharingguidelines> (2013).
40. Royal Society of Chemistry. *Indium - Element information, properties and uses* <https://www.rsc.org/periodic-table/element/49/indium>.
41. Ellmer, K. Resistivity of polycrystalline zinc oxide films: current status and physical limit. *Journal of Physics D: Applied Physics* **34**, 3097. ISSN: 0022-3727. <https://iopscience.iop.org/article/10.1088/0022-3727/34/21/301> (Oct. 2001).
42. European Commission. *Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability* tech. rep. (2020). <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:52020DC0474>.

43. European Commission. *Study on the critical raw materials for the EU 2023* tech. rep. (Publications Office of the EU, 2023). <https://op.europa.eu/en/publication-detail/-/publication/57318397-fdd4-11ed-a05c-01aa75ed71a1>.
44. Kim, J. *et al.* High-temperature optical properties of indium tin oxide thin-films. *Scientific Reports* 2020 10:1 **10**, 1–8. ISSN: 2045-2322. <https://www.nature.com/articles/s41598-020-69463-4> (July 2020).
45. Lan, Y. F., Peng, W. C., Lo, Y. H. & He, J. L. Durability under mechanical bending of the indium tin oxide films deposited on polymer substrate by thermionically enhanced sputtering. *Organic Electronics* **11**, 670–676. ISSN: 1566-1199 (Apr. 2010).
46. Gomez De Arco, L. *et al.* Continuous, highly flexible, and transparent graphene films by chemical vapor deposition for organic photovoltaics. *ACS Nano* **4**, 2865–2873. ISSN: 19360851. <https://pubs.acs.org/doi/full/10.1021/nn901587x> (May 2010).
47. Hines, C. J., Roberts, J. L., Andrews, R. N., Jackson, M. V. & Deddens, J. A. Use of and occupational exposure to indium in the United States. *Journal of Occupational and Environmental Hygiene* **10**, 723–733. ISSN: 15459624. <https://pubmed.ncbi.nlm.nih.gov/24195539/> (2013).
48. Ministry of Health, L. & Welfare. Technical guideline for preventing health impairment of workers engaged in the indium tin oxide handling processes [in Japanese]. *Tokyo, Japan : Government of Japan* (2010).
49. Cummings, K. J. *et al.* Respirable indium exposures, plasma indium, and respiratory health among indium-tin oxide (ITO) workers. *American journal of industrial medicine* **59**, 522–531. ISSN: 1097-0274. <https://pubmed.ncbi.nlm.nih.gov/27219296/> (July 2016).
50. Homma, T., Ueno, T., Sekizawa, K., Tanaka, A. & Hirata, M. Interstitial pneumonia developed in a worker dealing with particles containing indium-tin oxide. *Journal of occupational health* **45**, 137–139. ISSN: 1341-9145. <https://pubmed.ncbi.nlm.nih.gov/14646287/> (May 2003).
51. Chonan, T., Taguchi, O. & Omae, K. Interstitial pulmonary disorders in indium-processing workers. *European Respiratory Journal* **29**, 317–324. ISSN: 0903-1936. <https://erj.ersjournals.com/content/29/2/317> (Feb. 2007).

52. Nakano, M. *et al.* Causal Relationship between Indium Compound Inhalation and Effects on the Lungs. *Journal of Occupational Health* **51**, 513–521. ISSN: 1341-9145 (Nov. 2009).
53. Knobelspies, S. *et al.* Photo-Induced Room-Temperature Gas Sensing with a-IGZO Based Thin-Film Transistors Fabricated on Flexible Plastic Foil. *Sensors* **18**, 358. ISSN: 14248220. <https://www.mdpi.com/1424-8220/18/2/358/htm> (Jan. 2018).
54. Peng, R. Y. & Liu, W. C. Study of a High-Performance Chemoresistive Ethanol Gas Sensor Synthesized with Au Nanoparticles and an Amorphous IGZO Thin Film. *IEEE Transactions on Electron Devices* **68**, 753–760. ISSN: 15579646 (Feb. 2021).
55. Tang, H. *et al.* Ultra-High Sensitive NO₂ Gas Sensor Based on Tunable Polarity Transport in CVD-WS₂/IGZO p-N Heterojunction. *ACS Applied Materials and Interfaces* **11**, 40850–40859. ISSN: 19448252. <https://pubs.acs.org/doi/abs/10.1021/acsami.9b13773> (Oct. 2019).
56. White, S. J. O. & Shine, J. P. Exposure Potential and Health Impacts of Indium and Gallium, Metals Critical to Emerging Electronics and Energy Technologies. *Current environmental health reports* **3**, 459–467. ISSN: 21965412. <https://link.springer.com/article/10.1007/s40572-016-0118-8> (Dec. 2016).
57. Minami, T. New n-Type Transparent Conducting Oxides. *MRS Bulletin* **25**, 38–44. ISSN: 1938-1425. <https://www.cambridge.org/core/journals/mrs-bulletin/article/abs/new-ntype-transparent-conducting-oxides/FFA121D1B28B388914BA7D5F801A4A18> (2000).
58. Raimondi, D. L. & Kay, E. High Resistivity Transparent ZnO Thin Films. *Journal of Vacuum Science and Technology* **7**, 96. ISSN: 0022-5355. <https://avs.scitation.org/doi/abs/10.1116/1.1315841> (Dec. 2000).
59. Ji, Y.-C., Zhang, H.-X., Zhang, X.-H. & Li, Z.-Q. Structures, optical properties, and electrical transport processes of SnO₂ films with oxygen deficiencies. *physica status solidi (b)* **250** (Oct. 2013).
60. Yu-Sheng, S. & Tian-Shu, Z. Preparation, structure and gas-sensing properties of ultramicro ZnSnO₃ powder. *Sensors and Actuators B: Chemical* **12**, 5–9. ISSN: 0925-4005 (Mar. 1993).

61. Fu, X. *et al.* Hydrothermal synthesis, characterization, and photocatalytic properties of Zn₂SnO₄. *Journal of Solid State Chemistry* **182**, 517–524. ISSN: 0022-4596 (Mar. 2009).
62. Sato, Y. *et al.* Study on inverse spinel zinc stannate, Zn₂SnO₄, as transparent conductive films deposited by rf magnetron sputtering. *Thin Solid Films* **518**, 1304–1308. ISSN: 0040-6090 (Dec. 2009).
63. Kurz, A. & Aegerter, M. A. Transparent conducting films in the Zn-Sn-O tie line. *Journal of Sol-Gel Science and Technology* **31**, 267–271. ISSN: 09280707 (Aug. 2004).
64. Young, D. L., Moutinho, H., Yan, Y. & Coutts, T. J. Growth and characterization of radio frequency magnetron sputter-deposited zinc stannate, Zn₂SnO₄, thin films. *Journal of Applied Physics* **92**, 310–319 (July 2002).
65. Rucavado, E. *et al.* Enhancing the optoelectronic properties of amorphous zinc tin oxide by subgap defect passivation: A theoretical and experimental demonstration. *Physical Review B* **95**, 245204. ISSN: 24699969. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.95.245204> (June 2017).
66. Kim, Y. H., Han, J. I. & Park, S. K. Effect of Zinc/Tin composition ratio on the operational stability of solution-processed Zinc-Tin-Oxide Thin-Film transistors. *IEEE Electron Device Letters* **33**, 50–52. ISSN: 07413106 (Jan. 2012).
67. Callaghan, P. J. *et al.* Variation in the Bandgap of Amorphous Zinc Tin Oxide: Investigating the Thickness Dependence via In Situ STS. *ACS Omega*, 7262–7268. ISSN: 24701343. <https://pubs.acs.org/doi/full/10.1021/acsomega.3c09958> (Feb. 2024).
68. Morales-Masis, M. *et al.* An Indium-Free Anode for Large-Area Flexible OLEDs: Defect-Free Transparent Conductive Zinc Tin Oxide. *Advanced functional materials* **26**, 384–392. ISSN: 1616-301X. <https://research.utwente.nl/en/publications/an-indium-free-anode-for-large-area-flexible-oleds-defect-free-tr> (Jan. 2016).

69. Chiang, H. Q., Wager, J. F., Hoffman, R. L., Jeong, J. & Keszler, D. A. High mobility transparent thin-film transistors with amorphous zinc tin oxide channel layer. *Applied Physics Letters* **86**, 2003–2006. ISSN: 00036951 (2005).
70. Zhussupbekova, A. *et al.* Low-Cost, High-Performance Spray Pyrolysis-Grown Amorphous Zinc Tin Oxide: The Challenge of a Complex Growth Process. *ACS applied materials & interfaces* **12**, 46892–46899. ISSN: 19448252. <https://dx.doi.org/10.1021/acsami.0c12148> (2020).
71. Park, J. *et al.* High-Performance Zinc Tin Oxide Semiconductor Grown by Atmospheric-Pressure Mist-CVD and the Associated Thin-Film Transistor Properties. *ACS Applied Materials and Interfaces* **9**, 20656–20663. ISSN: 19448252. <https://pubs.acs.org/doi/full/10.1021/acsami.7b04235> (June 2017).
72. Seo, S. J., Choi, C. G., Hwang, Y. H. & Bae, B. S. High performance solution-processed amorphous zinc tin oxide thin film transistor. *Journal of Physics D: Applied Physics* **42**, 035106. ISSN: 00223727 (Jan. 2009).
73. Jayaraj, M. K., Saji, K. J., Nomura, K., Kamiya, T. & Hosono, H. Optical and electrical properties of amorphous zinc tin oxide thin films examined for thin film transistor application. *Journal of Vacuum Science and Technology B: Microelectronics and Nanometer Structures* **26**, 495–501. ISSN: 1071-1023 (Jan. 2008).
74. Park, S. K., Kim, Y. H., Kim, H. S. & Han, J. I. High performance solution-processed and lithographically patterned zinc-tin oxide thin-film transistors with good operational stability. *Electrochemical and Solid-State Letters* **12**, H256–H258. ISSN: 10990062 (Jan. 2009).
75. Siah, S. C. *et al.* X-ray absorption spectroscopy elucidates the impact of structural disorder on electron mobility in amorphous zinc-tin-oxide thin films. *Applied Physics Letters* **104**, 242113. ISSN: 00036951. <https://pubs.aip.org/aip/apl/article-abstract/104/24/242113/385086/X-ray-absorption-spectroscopy-elucidates-the> (June 2014).
76. Mullings, M. N. *et al.* Thin film characterization of zinc tin oxide deposited by thermal atomic layer deposition. *Thin Solid Films* **556**, 186–194. ISSN: 00406090 (Apr. 2014).

77. Zhussupbekova, A. *et al.* Importance of Local Bond Order to Conduction in Amorphous, Transparent, Conducting Oxides: The Case of Amorphous ZnSnOy. *ACS Applied Materials and Interfaces* **11**, 44399–44405. ISSN: 19448252 (Nov. 2019).
78. Hong, D., Chiang, H. Q. & Wager, J. F. Zinc tin oxide thin-film transistors via reactive sputtering using a metal target. *Journal of Vacuum Science and Technology B: Microelectronics and Nanometer Structures* **24**, L23–L25. ISSN: 1071-1023 (Jan. 2006).
79. Sanctis, S. *et al.* Toward an Understanding of Thin-Film Transistor Performance in Solution-Processed Amorphous Zinc Tin Oxide (ZTO) Thin Films. *ACS Applied Materials and Interfaces* **9**, 21328–21337. ISSN: 19448252. <https://pubs.acs.org/doi/full/10.1021/acsami.7b06203> (June 2017).
80. Pandey, R. *et al.* Fluorine doped zinc tin oxide multilayer transparent conducting Oxides for organic photovoltaic's Cells. *Solar Energy Materials and Solar Cells* **134**, 5–14. ISSN: 0927-0248. <https://pure.ewha.ac.kr/en/publications/fluorine-doped-zinc-tin-oxide-multilayer-transparent-conducting-o> (2015).
81. Dutta, S. & Dodabalapur, A. Zinc tin oxide thin film transistor sensor. *Sensors and Actuators, B: Chemical* **143**, 50–55. ISSN: 09254005. <https://publications.iitm.ac.in/publication/zinc-tin-oxide-thin-film-transistor-sensor> (Dec. 2009).
82. Fernandes, C. *et al.* A Sustainable Approach to Flexible Electronics with Zinc-Tin Oxide Thin-Film Transistors. *Advanced Electronic Materials* **4**, 1800032. ISSN: 2199160X. <https://onlinelibrary.wiley.com/doi/full/10.1002/aelm.201800032> (July 2018).
83. Fakhri, M., Theisen, M., Behrendt, A., Gorrn, P. & Riedl, T. Top-gate zinc tin oxide thin-film transistors with high bias and environmental stress stability. *Applied Physics Letters* **104**, 251603–251603. ISSN: ISSN 0003-6951. http://inis.iaea.org/Search/search.aspx?orig_q=RN:46010015 (June 2014).
84. Wang, Z., Nayak, P. K., Caraveo-Frescas, J. A. & Alshareef, H. N. Recent Developments in p-Type Oxide Semiconductor Materials and Devices. *Advanced Materials* **28**, 3831–3892. ISSN: 1521-4095. <https://>

- onlinelibrary.wiley.com/doi/full/10.1002/adma.201503080 (May 2016).
85. Martins, R. *et al.* Complementary metal oxide semiconductor technology with and on paper. *Advanced Materials* **23**, 4491–4496. ISSN: 09359648 (Oct. 2011).
 86. Sze, S. & Ng, K. K. *Physics of Semiconductor Devices* 3rd. ISBN: 9780471143239. <https://onlinelibrary.wiley.com/doi/book/10.1002/0470068329> (John Wiley & Sons, Oct. 2006).
 87. Dunlap-Shohl, W. A. *et al.* Room-temperature fabrication of a delafossite CuCrO₂ hole transport layer for perovskite solar cells. *Journal of Materials Chemistry A* **6**, 469–477. ISSN: 2050-7496. <https://pubs.rsc.org/en/content/articlehtml/2018/ta/c7ta09494a> (Jan. 2018).
 88. Wang, J., Lee, Y. J. & Hsu, J. W. Sub-10 nm copper chromium oxide nanocrystals as a solution processed p-type hole transport layer for organic photovoltaics. *Journal of Materials Chemistry C* **4**, 3607–3613. ISSN: 2050-7534. <https://pubs.rsc.org/en/content/articlehtml/2016/tc/c6tc00541a> (Apr. 2016).
 89. Gil, B. *et al.* CuCrO₂ Nanoparticles Incorporated into PTAA as a Hole Transport Layer for 85 °C and Light Stabilities in Perovskite Solar Cells. *Nanomaterials* *2020*, Vol. 10, Page 1669 **10**, 1669. ISSN: 2079-4991. <https://www.mdpi.com/2079-4991/10/9/1669/htm> (Aug. 2020).
 90. United Nations Framework Convention on Climate Change. Paris Agreement.
 91. Qin, P. L. *et al.* Copper-Doped Chromium Oxide Hole-Transporting Layer for Perovskite Solar Cells: Interface Engineering and Performance Improvement. *Advanced Materials Interfaces* **3**, 1500799. ISSN: 2196-7350. <https://onlinelibrary.wiley.com/doi/full/10.1002/admi.201500799> (July 2016).
 92. Fleischer, K., Norton, E., Mullarkey, D., Caffrey, D. & Shvets, I. V. Quantifying the Performance of P-Type Transparent Conducting Oxides by Experimental Methods. *Materials* *2017*, Vol. 10, Page 1019 **10**, 1019. ISSN: 1996-1944. <https://www.mdpi.com/1996-1944/10/9/1019/htm> (Sept. 2017).

93. Zhang, H. & Park, N.-G. Progress and issues in p-i-n type perovskite solar cells. *DeCarbon* **3**, 100025. ISSN: 2949-8813 (Mar. 2024).
94. Hoffman, R. L. *Development, fabrication, and characterization of transparent electronic devices* PhD thesis (June 2002). https://ir.library.oregonstate.edu/concern/graduate_thesis_or_dissertations/5425kf220?locale=en.
95. Zunger, A. Practical doping principles. *Applied Physics Letters* **83**, 57–59. ISSN: 0003-6951. <https://pubs.aip.org/aip/apl/article-abstract/83/1/57/116073/Practical-doping-principles> (July 2003).
96. Swallow, J. E. *et al.* Resonant doping for high mobility transparent conductors: the case of Mo-doped In₂O₃. *Materials Horizons* **7**, 236–243. ISSN: 2051-6355. <https://pubs.rsc.org/en/content/articlehtml/2020/mh/c9mh01014a> (Jan. 2020).
97. Williamson, B. A. *et al.* Resonant Ta Doping for Enhanced Mobility in Transparent Conducting SnO₂. *Chemistry of Materials* **32**, 1964–1973. ISSN: 15205002. <https://pubs.acs.org/doi/full/10.1021/acs.chemmater.9b04845> (Mar. 2020).
98. Dixon, S. C. *et al.* Transparent conducting n-type ZnO:Sc – synthesis, optoelectronic properties and theoretical insight. *Journal of Materials Chemistry C* **5**, 7585–7597. ISSN: 20507526. <https://pubs.rsc.org/en/content/articlehtml/2017/tc/c7tc02389h> (Aug. 2017).
99. Hautier, G., Miglio, A., Ceder, G., Rignanese, G. M. & Gonze, X. Identification and design principles of low hole effective mass p-type transparent conducting oxides. *Nature Communications* **4**, 1–7. ISSN: 2041-1723. <https://www.nature.com/articles/ncomms3292> (Aug. 2013).
100. Li, B. S., Akimoto, K. & Shen, A. Growth of Cu₂O thin films with high hole mobility by introducing a low-temperature buffer layer. *Journal of Crystal Growth* **311**, 1102–1105. ISSN: 0022-0248 (Feb. 2009).
101. Kikuchi, N. & Tonooka, K. Electrical and structural properties of Ni-doped Cu₂O films prepared by pulsed laser deposition. *Thin Solid Films* **486**, 33–37. ISSN: 0040-6090 (Aug. 2005).

102. Tanaka, H., Shimakawa, T., Miyata, T., Sato, H. & Minami, T. Electrical and optical properties of TCO–Cu₂O heterojunction devices. *Thin Solid Films* **469–470**, 80–85. ISSN: 0040-6090 (Dec. 2004).
103. Chen, A. *et al.* Controlled growth and characteristics of single-phase Cu₂O and CuO films by pulsed laser deposition. *Vacuum* **83**, 927–930. ISSN: 0042-207X (Feb. 2009).
104. Kwon, J. D. *et al.* Controlled growth and properties of p-type cuprous oxide films by plasma-enhanced atomic layer deposition at low temperature. *Applied Surface Science* **285**, 373–379. ISSN: 0169-4332 (Nov. 2013).
105. Lee, S. W. *et al.* Improved Cu₂O-Based Solar Cells Using Atomic Layer Deposition to Control the Cu Oxidation State at the p-n Junction. *Advanced Energy Materials* **4**, 1301916. ISSN: 1614-6840. <https://onlinelibrary.wiley.com/doi/full/10.1002/aenm.201301916> (Aug. 2014).
106. Dhakal, D. *et al.* Surface chemistry of a Cu(I) beta-diketonate precursor and the atomic layer deposition of Cu₂O on SiO₂ studied by x-ray photoelectron spectroscopy. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **32**, 41505. ISSN: 0734-2101. <https://pubs.aip.org/avs/jva/article-abstract/32/4/041505/244962/Surface-chemistry-of-a-Cu-I-beta-diketonate> (July 2014).
107. Saji, K. J., Populoh, S., Tiwari, A. N. & Romanyuk, Y. E. Design of p-CuO/n-ZnO heterojunctions by rf magnetron sputtering. *physica status solidi (a)* **210**, 1386–1391. ISSN: 1862-6319. <https://onlinelibrary.wiley.com/doi/full/10.1002/pssa.201228293> (July 2013).
108. Fortunato, E. *et al.* Thin-film transistors based on p-type Cu₂O thin films produced at room temperature. *Applied Physics Letters* **96**. ISSN: 00036951. <https://pubs.aip.org/aip/apl/article-abstract/96/19/192102/120048/Thin-film-transistors-based-on-p-type-Cu2O-thin> (May 2010).
109. Hu, J. P. *et al.* On-site interband excitations in resonant inelastic x-ray scattering from Cu₂O. *Physical Review B - Condensed Matter and Materials Physics* **77**, 155115. ISSN: 1550235X. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.77.155115> (Apr. 2008).

110. Ruiz, E., Alvarez, S., Alemany, P. & Evarestov, R. A. Electronic structure and properties of Cu₂O. *Physical Review B* **56**, 7189. ISSN: 1550235X. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.56.7189> (Sept. 1997).
111. Nie, X., Wei, S. H. & Zhang, S. B. First-principles study of transparent p-type conductive SrCu₂O₂ and related compounds. *Physical Review B* **65**, 075111. ISSN: 1550235X. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.65.075111> (Jan. 2002).
112. Hodby, J. W., Jenkins, T. E., Schwab, C., Tamura, H. & Trivich, D. Cyclotron resonance of electrons and of holes in cuprous oxide, Cu₂O. *Journal of Physics C: Solid State Physics* **9**, 1429. ISSN: 0022-3719. <https://iopscience.iop.org/article/10.1088/0022-3719/9/8/014> (Apr. 1976).
113. Raebiger, H., Lany, S. & Zunger, A. Origins of the p-type nature and cation deficiency in Cu₂O and related materials. *Physical Review B - Condensed Matter and Materials Physics* **76**, 045209. ISSN: 10980121. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.76.045209> (July 2007).
114. Scanlon, D. O., Morgan, B. J., Watson, G. W. & Walsh, A. Acceptor levels in p-type Cu₂O: Rationalizing theory and Experiment. *Physical Review Letters* **103**, 096405. ISSN: 00319007. <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.103.096405> (Aug. 2009).
115. Paul, G. K., Nawa, Y., Sato, H., Sakurai, T. & Akimoto, K. Defects in Cu₂O studied by deep level transient spectroscopy. *Applied Physics Letters* **88**, 141901. ISSN: 00036951. <https://pubs.aip.org/aip/apl/article-abstract/88/14/141901/327435/Defects-in-Cu2O-studied-by-deep-level-transient> (Apr. 2006).
116. Svensson, B. G., Pearton, S. J. & Jagadish, C. *Oxide semiconductors* English, 2-330. ISBN: 9780123965455 (Academic Press, 2013).
117. Scanlon, D. O., Morgan, B. J. & Watson, G. W. Modeling the polaronic nature of p-type defects in Cu₂O: The failure of GGA and GGA+U. *Journal of Chemical Physics* **131**. ISSN: 00219606. <https://pubs.aip.org/aip/jcp/article-abstract/131/12/124703/895582/Modeling-the-polaronic-nature-of-p-type-defects-in> (Sept. 2009).

118. Matsuzaki, K. *et al.* Epitaxial growth of high mobility Cu₂O thin films and application to p-channel thin film transistor. *Applied Physics Letters* **93**, 202107. ISSN: 00036951. <https://pubs.aip.org/aip/apl/article-abstract/93/20/202107/336078/Epitaxial-growth-of-high-mobility-Cu2O-thin-films> (Nov. 2008).
119. Kawazoe, H. *et al.* P-type electrical conduction in transparent thin films of CuAlO₂. *Nature* 1997 389:6654 **389**, 939–942. ISSN: 1476-4687. <https://www.nature.com/articles/40087> (1997).
120. Yanagi, H. *et al.* Electronic structure and optoelectronic properties of transparent p-type conducting CuAlO₂. *Journal of Applied Physics* **88**, 4159–4163. ISSN: 0021-8979. <https://pubs.aip.org/aip/jap/article-abstract/88/7/4159/290503/Electronic-structure-and-optoelectronic-properties> (Oct. 2000).
121. Nagarajan, R., Draeseke, A. D., Sleight, A. W. & Tate, J. p-type conductivity in CuCr_{1-x}MgxO₂ films and powders. *Journal of Applied Physics* **89**, 8022–8025. ISSN: 00218979 (June 2001).
122. Zhang, N., Sun, J. & Gong, H. Transparent p-Type Semiconductors: Copper-Based Oxides and Oxychalcogenides. *Coatings* **9**, 137 (Feb. 2019).
123. Scanlon, D. O. & Watson, G. W. Understanding the p-type defect chemistry of CuCrO₂. *Journal of Materials Chemistry* **21**, 3655–3663. ISSN: 1364-5501. <https://pubs.rsc.org/en/content/articlehtml/2011/jm/c0jm03852k> (Mar. 2011).
124. Ingram, B. J., Mason, T. O., Asahi, R., Park, K. T. & Freeman, A. J. Electronic structure and small polaron hole transport of copper aluminate. *Physical Review B* **64**, 155114. ISSN: 01631829. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.64.155114> (Sept. 2001).
125. Ingram, B. J. *et al.* Transport and defect mechanisms in cuprous delafosites. 1. Comparison of hydrothermal and standard solid-state synthesis in CuAlO₂. *Chemistry of Materials* **16**, 5616–5622. ISSN: 08974756 (Dec. 2004).
126. Dekkers, M., Rijnders, G. & Blank, D. H. ZnIr₂O₄, a p-type transparent oxide semiconductor in the class of spinel zinc-d6-transition metal oxide. *Applied Physics Letters* **90**, 021903. ISSN: 00036951. <https://pubs.aip.org/aip/apl/article-abstract/90/2/021903/1006623/ZnIr2O4-a-p-type-transparent-oxide-semiconductor> (Jan. 2007).

- org/aip/apl/article-abstract/90/2/021903/333019/ZnIr2O4-a-p-type-transparent-oxide-semiconductor (Jan. 2007).
127. Amini, M. N., Dixit, H., Saniz, R., Lamoen, D. & Partoens, B. The origin of p-type conductivity in ZnM_2O_4 ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) spinels. *Physical Chemistry Chemical Physics* **16**, 2588–2596. ISSN: 14639076 (Feb. 2014).
 128. Mansourian-Hadavi, N. *et al.* Transport and band structure studies of crystalline ZnRh_2O_4 . *Physical Review B - Condensed Matter and Materials Physics* **81**, 075112. ISSN: 10980121. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.81.075112> (Feb. 2010).
 129. Singh, D. J. Electronic and thermoelectric properties of CuCoO_2 : Density functional calculations. *Physical Review B - Condensed Matter and Materials Physics* **76**, 085110. ISSN: 10980121. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.76.085110> (Aug. 2007).
 130. Kim, S. H. *et al.* Room temperature deposited oxide p-n junction using p-type zinc-cobalt-oxide. *Journal of Applied Physics* **107**, 103538. ISSN: 00218979. <https://pubs.aip.org/aip/jap/article-abstract/107/10/103538/147221/Room-temperature-deposited-oxide-p-n-junction> (May 2010).
 131. Perkins, J. D. *et al.* Inverse design approach to hole doping in ternary oxides: Enhancing p-type conductivity in cobalt oxide spinels. *Physical Review B - Condensed Matter and Materials Physics* **84**, 205207. ISSN: 10980121. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.84.205207> (Nov. 2011).
 132. Zhang, K. H., Xi, K., Blamire, M. G. & Egdell, R. G. P-type transparent conducting oxides. *Journal of Physics: Condensed Matter* **28**, 383002. ISSN: 0953-8984 (July 2016).
 133. Ueda, K., Inoue, S., Hirose, S., Kawazoe, H. & Hosono, H. Transparent p-type semiconductor: LaCuOS layered oxysulfide. *Applied Physics Letters* **77**, 2701–2703. ISSN: 0003-6951. <https://pubs.aip.org/aip/apl/article-abstract/77/17/2701/112609/Transparent-p-type-semiconductor-LaCuOS-layered> (Oct. 2000).
 134. Hiramatsu, H. *et al.* Preparation of transparent p-type $(\text{La}_{1-x}\text{Sr}_x\text{O})\text{CuS}$ thin films by r.f. sputtering technique. *Thin Solid Films* **411**, 125–128. ISSN: 0040-6090 (May 2002).

135. Hiramatsu, H. *et al.* Heavy hole doping of epitaxial thin films of a wide gap p-type semiconductor, LaCuOSe, and analysis of the effective mass. *Applied Physics Letters* **91**, 012104. ISSN: 00036951. <https://pubs.aip.org/aip/apl/article-abstract/91/1/012104/844674/Heavy-hole-doping-of-epitaxial-thin-films-of-a> (July 2007).
136. Hosono, H. Built-in Nanostructures in Transparent Oxides for Novel Photonic and Electronic Functions Materials. *International Journal of Applied Ceramic Technology* **1**, 106–118. ISSN: 1744-7402. <https://onlinelibrary.wiley.com/doi/full/10.1111/j.1744-7402.2004.tb00160.x> (Apr. 2004).
137. Hiramatsu, H., Orita, M., Hirano, M., Ueda, K. & Hosono, H. Electrical conductivity control in transparent p-type (LaO)CuS thin films prepared by rf sputtering. *Journal of Applied Physics* **91**, 9177–9181. ISSN: 0021-8979. <https://pubs.aip.org/aip/jap/article-abstract/91/11/9177/180430/Electrical-conductivity-control-in-transparent-p> (June 2002).
138. Hiramatsu, H. *et al.* Heteroepitaxial growth of a wide-gap p-type semiconductor, LaCuOS. *Applied Physics Letters* **81**, 598–600. ISSN: 0003-6951. <https://pubs.aip.org/aip/apl/article-abstract/81/4/598/513829/Heteroepitaxial-growth-of-a-wide-gap-p-type> (July 2002).
139. Willis, J. & Scanlon, D. O. Latest directions in p-type transparent conductor design. *Journal of Materials Chemistry C* **9**, 11995–12009. ISSN: 20507526 (Sept. 2021).
140. Popper, P. & Ingles, T. A. Boron Phosphide, a III–V Compound of Zinc-Blende Structure. *Nature* **179**, 1075. ISSN: 1476-4687. <https://www.nature.com/articles/1791075a0> (1957).
141. Dai, X., Lei, H., Chen, C., Guo, Y. & Fang, G. A simple synthesis of transparent and highly conducting p-type Cu_xAl_{1-x}S_y nanocomposite thin films as the hole transporting layer for organic solar cells. *RSC Advances* **8**, 16887–16896. ISSN: 20462069. <https://pubs.rsc.org/en/content/articlehtml/2018/ra/c8ra01299g> (May 2018).

142. Huang, F. Q., Liu, M. L. & Yang, C. Highly enhanced p-type electrical conduction in wide band gap $\text{Cu}_{1+x}\text{Al}_{1-x}\text{S}_2$ polycrystals. *Solar Energy Materials and Solar Cells* **95**, 2924–2927. ISSN: 0927-0248 (Oct. 2011).
143. Maurya, S. K. *et al.* High figure-of-merit p-type transparent conductor, Cu alloyed ZnS via radio frequency magnetron sputtering. *Journal of Physics D: Applied Physics* **50**, 505107. ISSN: 0022-3727. <https://iopscience.iop.org/article/10.1088/1361-6463/aa95b3> (Nov. 2017).
144. Diamond, A. M. *et al.* Copper-alloyed ZnS as a p-type transparent conducting material. *physica status solidi (a)* **209**, 2101–2107. ISSN: 1862-6319. <https://onlinelibrary.wiley.com/doi/full/10.1002/pssa.201228181> (Nov. 2012).
145. Yude, Y., Boysen, H. & Schulz, H. Neutron powder investigation of CuI. *Zeitschrift fur Kristallographie - New Crystal Structures* **191**, 79–91. ISSN: 00442968. <https://www.degruyter.com/document/doi/10.1524/zkri.1990.191.1-2.79/html> (Jan. 1990).
146. Matsubara, T. Note on the Phase Transition in CuI. *Journal of the Physical Society of Japan* **38**, 1076–1079. ISSN: 13474073 (1975).
147. Adamo, C. & Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *The Journal of Chemical Physics* **110**, 6158–6170. ISSN: 0021-9606. <https://pubs.aip.org/aip/jcp/article-abstract/110/13/6158/476177/Toward-reliable-density-functional-methods-without> (Apr. 1999).
148. Wang, J., Li, J. & Li, S. S. Native p-type transparent conductive CuI via intrinsic defects. *Journal of Applied Physics* **110**. ISSN: 00218979. <https://pubs.aip.org/aip/jap/article-abstract/110/5/054907/991770/Native-p-type-transparent-conductive-CuI-via> (Sept. 2011).
149. Huang, D. *et al.* First-principles study of γ -CuI for p-type transparent conducting materials. *Journal of Physics D: Applied Physics* **45**, 145102. ISSN: 0022-3727. <https://iopscience.iop.org/article/10.1088/0022-3727/45/14/145102> (Mar. 2012).
150. Chen, H., Wang, C. Y., Wang, J. T., Wu, Y. & Zhou, S. X. First-principles study of point defects in solar cell semiconductor CuI. *Physica B: Condensed Matter* **413**, 116–119. ISSN: 0921-4526 (Mar. 2013).

151. Grundmann, M. *et al.* Cuprous iodide - A p-type transparent semiconductor: History and novel applications. *Physica Status Solidi (A) Applications and Materials Science* **210**, 1671–1703. ISSN: 18626300 (Sept. 2013).
152. Herrick, C. S. & Tevebaugh, A. D. Oxygen-Controlled Conduction in Thin Films of Cuprous Iodide: A Mixed Valency Anion Semiconductor. *Journal of The Electrochemical Society* **110**, 119. ISSN: 00134651. <https://iopscience.iop.org/article/10.1149/1.2425687> (Feb. 1963).
153. Shohn, K., Takigawa, M. & Nakada, T. Epitaxial growth of BP compounds on Si substrates using the B₂H₆-PH₃-H₂ system. *Journal of Crystal Growth* **24-25**, 193–196. ISSN: 0022-0248 (Oct. 1974).
154. Varley, J. B. *et al.* High-Throughput Design of Non-oxide p-Type Transparent Conducting Materials: Data Mining, Search Strategy, and Identification of Boron Phosphide. *Chemistry of Materials* **29**, 2568–2573. ISSN: 15205002. <https://pubs.acs.org/doi/full/10.1021/acs.chemmater.6b04663> (Mar. 2017).
155. Ha, V. A. *et al.* Boron phosphide as a p-type transparent conductor: Optical absorption and transport through electron-phonon coupling. *Physical Review Materials* **4**, 065401. ISSN: 24759953. <https://journals.aps.org/prmaterials/abstract/10.1103/PhysRevMaterials.4.065401> (June 2020).
156. Woo, K., Lee, K. & Kovnir, K. BP: synthesis and properties of boron phosphide. *Materials Research Express* **3**, 074003. ISSN: 2053-1591. <https://iopscience.iop.org/article/10.1088/2053-1591/3/7/074003> (July 2016).
157. Nikolaev, Y. A., Rud, V. Y., Rud, Y. V. & Terukov, E. I. Photosensitive Structures Based on Boron Phosphide Single Crystals. *Semiconductors* **37**, 923–926. ISSN: 10637826. <https://link.springer.com/article/10.1134/1.1601659> (Aug. 2003).
158. Stone, B. & Hill, D. Semiconducting Properties of Cubic Boron Phosphide. *Physical Review Letters* **4**, 282. ISSN: 00319007. <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.4.282> (Mar. 1960).
159. Liu, W. *et al.* Structural, mechanical properties and composition analysis of boron phosphide coatings. *Journal of Alloys and Compounds* **538**, 169–172. ISSN: 0925-8388 (Oct. 2012).

160. Hu, L. *et al.* Design strategy for p-type transparent conducting oxides. *Journal of Applied Physics* **128**, 140902. ISSN: 10897550. <https://pubs.aip.org/aip/jap/article/128/14/140902/287426/Design-strategy-for-p-type-transparent-conducting> (Oct. 2020).
161. Zheng, H. Electronic structure of CoO. *Physica B: Condensed Matter* **212**, 125–138. ISSN: 0921-4526 (July 1995).
162. Imada, M., Fujimori, A. & Tokura, Y. Metal-insulator transitions. *Reviews of Modern Physics* **70**, 1039. ISSN: 00346861. <https://journals.aps.org/rmp/abstract/10.1103/RevModPhys.70.1039> (Oct. 1998).
163. Georges, A., Kotliar, G., Krauth, W. & Rozenberg, M. J. Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions. *Reviews of Modern Physics* **68**, 13. ISSN: 00346861. <https://journals.aps.org/rmp/abstract/10.1103/RevModPhys.68.13> (Jan. 1996).
164. Brinkman, W. F. & Rice, T. M. Application of Gutzwiller's Variational Method to the Metal-Insulator Transition. *Physical Review B* **2**, 4302. ISSN: 01631829. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.2.4302> (Nov. 1970).
165. Zhang, L. *et al.* Correlated metals as transparent conductors. *Nature Materials* **15**, 204–210. ISSN: 1476-4660. <https://www.nature.com/articles/nmat4493> (Dec. 2015).
166. Boileau, A. *et al.* Highly Transparent and Conductive Indium-Free Vanadates Crystallized at Reduced Temperature on Glass Using a 2D Transparent Nanosheet Seed Layer. *Advanced Functional Materials* **32**, 2108047. ISSN: 1616-3028. <https://onlinelibrary.wiley.com/doi/full/10.1002/adfm.202108047> (Jan. 2022).
167. Newnham, E. & Haan, M. Refinement of the α -Al₂O₃, Ti₂O₃, V₂O₃ and Cr₂O₃ structures. *Zeitschrift für Kristallographie - Crystalline Materials* **117**, 235–237. ISSN: 2196-7105. https://www.degruyter.com/document/doi/10.1524/zkri.1962.117.16.235/html?lang=en&srsltid=AfmB0oryBLjrnaV5BPHmJCypBMhF7CuSQzG_Ln6uSdBT7qIjHU3HhJFZ (Dec. 1962).

168. Keller, G., Held, K., Eyert, V., Vollhardt, D. & Anisimov, V. I. Electronic structure of paramagnetic V₂O₃: Strongly correlated metallic and Mott insulating phase. *Physical Review B - Condensed Matter and Materials Physics* **70**, 205116. ISSN: 01631829. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.70.205116> (Nov. 2004).
169. Uozumi, T. *et al.* Theoretical and experimental studies on the electronic structure of M₂O₃ (M = Ti, V, Cr, Mn, Fe) compounds by systematic analysis of high-energy spectroscopy. *Journal of Electron Spectroscopy and Related Phenomena* **83**, 9–20. ISSN: 0368-2048 (Jan. 1997).
170. Held, K., Keller, G., Eyert, V., Vollhardt, D. & Anisimov, V. Mott-Hubbard Metal-Insulator Transition in Paramagnetic : An Study. *Physical review letters* **86**, 5345–5348. <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.86.5345> (June 2001).
171. Crosbie, G. M., Tennenhouse, G. J., Tischer, R. P. & Wroblowa, H. S. Electronically Conducting Doped Chromium Oxides. *Journal of the American Ceramic Society* **67**, 498–503. ISSN: 1551-2916. <https://onlinelibrary.wiley.com/doi/full/10.1111/j.1151-2916.1984.tb19642.x> (July 1984).
172. Park, J. S. & Kim, H. G. Electrical Conductivity and Defect Models of MgO-Doped Cr₂O₃. *Journal of the American Ceramic Society* **71**, 173–176. ISSN: 1551-2916. <https://onlinelibrary.wiley.com/doi/full/10.1111/j.1151-2916.1988.tb05024.x> (Mar. 1988).
173. Holt, A. & Kofstad, P. Electrical conductivity and defect structure of Mg-doped Cr₂O₃. *Solid State Ionics* **100**, 201–209. ISSN: 0167-2738 (Oct. 1997).
174. Ku, R. C. & Winterbottom, W. L. Electrical conductivity in sputter-deposited chromium oxide coatings. *Thin Solid Films* **127**, 241–256. ISSN: 0040-6090 (May 1985).
175. Uekawa, N. & Kaneko, K. Dopant reduction in p-type oxide films upon oxygen absorption. *Journal of Physical Chemistry* **100**, 4193–4198. ISSN: 00223654. <https://pubs.acs.org/doi/full/10.1021/jp952784m> (Mar. 1996).

176. Hagel, W. C. & Appl Phys, J. Electrical Conductivity of Li-Substituted Cr₂O₃. *Journal of Applied Physics* **36**, 2586–2587. ISSN: 0021-8979. <https://pubs.aip.org/aip/jap/article-abstract/36/8/2586/508990/Electrical-Conductivity-of-Li-Substituted-Cr2O3> (Aug. 1965).
177. Arca, E., Fleischer, K. & Shvets, I. V. Magnesium, nitrogen codoped Cr₂O₃: A p-type transparent conducting oxide. *Applied Physics Letters* **99**, 111910. ISSN: 00036951. <https://pubs.aip.org/aip/apl/article-abstract/99/11/111910/923091/Magnesium-nitrogen-codoped-Cr2O3-A-p-type> (Sept. 2011).
178. Farrell, L. *et al.* Conducting mechanism in the epitaxial p-type transparent conducting oxide Cr₂O₃:Mg. *Physical Review B - Condensed Matter and Materials Physics* **91**, 125202. ISSN: 1550235X (Mar. 2015).
179. Dabaghmanesh, S., Saniz, R., Neyts, E. & Partoens, B. Sulfur-alloyed Cr₂O₃: a new p-type transparent conducting oxide host. *RSC Advances* **7**, 4453–4459. ISSN: 2046-2069. <https://pubs.rsc.org/en/content/articlehtml/2017/ra/c6ra27852c> (Jan. 2017).
180. Mott, N. F. & Friedman, L. Metal-insulator transitions in VO₂, Ti₂O₃ and Ti_{2-x}V_xO₃. *Philosophical Magazine* **30**, 389–402. ISSN: 00318086. <https://www.tandfonline.com/doi/abs/10.1080/14786439808206565> (1974).
181. Wessel, C. *et al.* Electronic Structure and Thermodynamics of V₂O₃ Polymorphs. <https://onlinelibrary.wiley.com/doi/10.1002/jcc.23046>.
182. Weber, D. A., Schwickert, C., Senyshyn, A., Lerch, M. & Pöttgen, R. Physical properties and lattice dynamics of bixbyite-type V₂O₃. *Journal of Materials Research* **32**, 2397–2404. ISSN: 0884-2914. <https://www.cambridge.org/core/journals/journal-of-materials-research/article/physical-properties-and-lattice-dynamics-of-bixbyitetype-v2o3/BB8C009AB07A32DCFD4E6D0D4AF350CE> (June 2017).
183. Weber, D. *et al.* Bixbyite-type V₂O₃ - A metastable polymorph of vanadium sesquioxide. *Inorganic Chemistry* **50**, 6762–6766. ISSN: 00201669 (2011).

184. Hu, L. *et al.* Exploring High-Performance p-Type Transparent Conducting Oxides Based on Electron Correlation in V₂O₃ Thin Films. *Physical Review Applied* **12**, 044035. ISSN: 23317019. <https://journals.aps.org/prapplied/abstract/10.1103/PhysRevApplied.12.044035> (Oct. 2019).
185. Barker, A. S. & Remeika, J. P. Optical properties of V₂O₃ doped with chromium. *Solid State Communications* **8**, 1521–1524. ISSN: 0038-1098 (Oct. 1970).
186. Caffrey, D. *et al.* Decoupling the refractive index from the electrical properties of transparent conducting oxides via periodic superlattices. *Scientific Reports* **6**, 1–9. ISSN: 20452322 (2016).
187. McWhan, D. B., Rice, T. M. & Remeika, J. P. Mott Transition in Cr-Doped V₂O₃. *Physical Review Letters* **23**, 1384. ISSN: 00319007. <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.23.1384> (Dec. 1969).
188. McWhan, D. B. *et al.* Electronic Specific Heat of Metallic Ti-Doped V₂O₃. *Physical Review Letters* **27**, 941. ISSN: 00319007. <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.27.941> (Oct. 1971).
189. Kuwamoto, H., Honig, J. M. & Appel, J. Electrical properties of the (V_{1-x}Cr_x)₂O₃ system. *Physical Review B* **22**, 2626. ISSN: 01631829. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.22.2626> (Sept. 1980).
190. Metcalf, P. A. *et al.* Electrical, structural, and optical properties of Cr-doped and non-stoichiometric V₂O₃ thin films. *Thin Solid Films* **515**, 3421–3425. ISSN: 0040-6090 (Feb. 2007).
191. Sarmadian, N., Saniz, R., Partoens, B. & Lamoen, D. Ab initio study of shallow acceptors in bixbyite V₂O₃. *Journal of Applied Physics* **117**. ISSN: 10897550 (Jan. 2015).
192. Abe, K., Nomura, K., Kamiya, T. & Hosono, H. Optical evidence for quantization in transparent amorphous oxide semiconductor superlattice. *Physical Review B - Condensed Matter and Materials Physics* **86**, 081202. ISSN: 10980121. <https://journals.aps.org/prb/abstract/10.1103/PhysRevB.86.081202> (Aug. 2012).

193. Matsumoto, K. *et al.* Selective reduction of layers at low temperature in artificial superlattice thin films. *Scientific Reports* 2011 1:1 **1**, 1–4. ISSN: 2045-2322. <https://www.nature.com/articles/srep00027> (June 2011).
194. Ohta, H. Two-dimensional thermoelectric Seebeck coefficient of SrTiO₃-based superlattices. *physica status solidi (b)* **245**, 2363–2368. ISSN: 1521-3951. <https://onlinelibrary.wiley.com/doi/full/10.1002/pssb.200844248>
<https://onlinelibrary.wiley.com/doi/abs/10.1002/pssb.200844248>
<https://onlinelibrary.wiley.com/doi/10.1002/pssb.200844248> (Nov. 2008).
195. Venkatasubramanian, R., Siivola, E., Colpitts, T. & O’Quinn, B. Thin-film thermoelectric devices with high room-temperature figures of merit. *Nature* 2001 413:6856 **413**, 597–602. ISSN: 1476-4687. <https://www.nature.com/articles/35098012> (Oct. 2001).
196. Caffrey, D. *et al.* Increasing the refractive index of materials via nanolamination: A-IGZO/TiO₂ nanolaminates. *Physical Review Materials* **2**, 1–8. ISSN: 24759953 (2018).
197. Niang, K. M., Cho, J., Heffernan, S., Milne, W. I. & Flewitt, A. J. Optimisation of amorphous zinc tin oxide thin film transistors by remote-plasma reactive sputtering. *Journal of Applied Physics* **120**, 85312. ISSN: 10897550. <https://pubs.aip.org/aip/jap/article/120/8/085312/381990/Optimisation-of-amorphous-zinc-tin-oxide-thin-film> (Aug. 2016).
198. Sun, G., Cao, X., Long, S., Li, R. & Jin, P. Optical and electrical performance of thermochromic V₂O₃ thin film fabricated by magnetron sputtering. *Applied Physics Letters* **111**, 53901. ISSN: 00036951. <https://pubs.aip.org/aip/apl/article-abstract/111/5/053901/150001/Optical-and-electrical-performance-of> (July 2017).
199. Kelly, P. J. & Arnell, R. D. Magnetron sputtering: a review of recent developments and applications. *Vacuum* **56**, 159–172. ISSN: 0042-207X (Mar. 2000).
200. Chapman, B. N. *Glow discharge processes : sputtering and plasma etching* 406. ISBN: 978-0-471-07828-9. <https://www.wiley.com/en-us/>

- Glow+Discharge+Processes%3A+Sputtering+and+Plasma+Etching-p-9780471078289 (Wiley, Sept. 1980).
201. Gudmundsson, J. T., Lundin, D. & Minea, T. *High Power Impulse Magnetron Sputtering: Fundamentals, Technologies, Challenges, and Applications* 1–48. ISBN: 9780128124543 (Elsevier, Jan. 2019).
 202. De Bosscher, W. & Lievens, H. Advances in magnetron sputter sources. *Thin Solid Films* **351**, 15–20. ISSN: 0040-6090 (Aug. 1999).
 203. Bräuer, G., Szyszka, B., Vergöhl, M. & Bandorf, R. Magnetron sputtering – Milestones of 30 years. *Vacuum* **84**, 1354–1359. ISSN: 0042-207X (June 2010).
 204. Ellmer, K. Magnetron sputtering of transparent conductive zinc oxide: relation between the sputtering parameters and the electronic properties. *Journal of Physics D: Applied Physics* **33**, R17. ISSN: 0022-3727. <https://iopscience.iop.org/article/10.1088/0022-3727/33/4/201> (Feb. 2000).
 205. Mattox, D. M. *Handbook of Physical Vapor Deposition (PVD) Processing* 2, revised (William Andrew, 2010).
 206. Musil, J., Baroch, P., Vlček, J., Nam, K. H. & Han, J. G. Reactive magnetron sputtering of thin films: present status and trends. *Thin Solid Films* **475**, 208–218. ISSN: 0040-6090 (Mar. 2005).
 207. Roger, C. *et al.* Principles of molecular precursor selection for aerosol synthesis of materials. *Nanostructured Materials* **4**, 529–535. ISSN: 09659773 (1994).
 208. Arca, E., Fleischer, K. & Shvets, I. V. Influence of the precursors and chemical composition of the solution on the properties of zno thin films grown by spray pyrolysis. *Journal of Physical Chemistry C* **113**, 21074–21081. ISSN: 19327455. <https://pubs.acs.org/doi/full/10.1021/jp907990z> (2009).
 209. Tauc, J. Optical properties and electronic structure of amorphous Ge and Si. *Materials Research Bulletin* **3**, 37–46. ISSN: 0025-5408 (Jan. 1968).

210. Tauc, J., Grigorovici, R. & Vancu, A. Optical Properties and Electronic Structure of Amorphous Germanium. *physica status solidi (b)* **15**, 627–637. ISSN: 1521-3951. <https://onlinelibrary.wiley.com/doi/full/10.1002/pssb.19660150224> (Jan. 1966).
211. Mott, N. F. (F. & Davis, E. A. (A. *Electronic processes in non-crystalline materials* 2d ed. ISBN: 9780198512882 (Oxford University Press, Oxford, 1979).
212. Klein, J. *et al.* Limitations of the Tauc Plot Method. *Advanced Functional Materials* **33**, 2304523. ISSN: 16163028 (Nov. 2023).
213. Spieß, L., Teichert, G., Schwarzer, R., Behnken, H. & Genzel, C. *Moderne Röntgenbeugung: Röntgendiffraktometrie für Materialwissenschaftler, Physiker und Chemiker* 2nd ed., 564 (Vieweg+Teubner Verlag Wiesbaden, 2009).
214. Widjonarko, N. E. Introduction to Advanced X-ray Diffraction Techniques for Polymeric Thin Films. *Coatings* **6**, 54. ISSN: 2079-6412. <https://www.mdpi.com/2079-6412/6/4/54/htm> (Nov. 2016).
215. De Boer, D. K., Leenaers, A. J. & van den Hoogenhof, W. W. Glancing-incidence x-ray analysis of thin-layered materials: A review. *X-Ray Spectrometry* **24**, 91–102. ISSN: 10974539 (1995).
216. Kiessig, H. Interferenz von Röntgenstrahlen an dünnen Schichten. *Annalen der Physik* **402**, 769–788. ISSN: 1521-3889. <https://onlinelibrary.wiley.com/doi/full/10.1002/andp.19314020702> (Jan. 1931).
217. Stoev, K. N. & Sakurai, K. Review on grazing incidence X-ray spectrometry and reflectometry. *Spectrochimica Acta Part B: Atomic Spectroscopy* **54**, 41–82. ISSN: 0584-8547 (Jan. 1999).
218. Johnston, R. L. Metal Nanoparticles and Nanoalloys. *Frontiers of Nanoscience* **3**, 1–42. ISSN: 1876-2778 (Jan. 2012).
219. Greczynski, G. & Hultman, L. A step-by-step guide to perform x-ray photoelectron spectroscopy. *Journal of Applied Physics* **132**, 11101. ISSN: 10897550. <https://pubs.aip.org/aip/jap/article/132/1/011101/2837063/A-step-by-step-guide-to-perform-x-ray> (July 2022).
220. Heide, P. V. d. *X-ray photoelectron spectroscopy: an introduction to principles and practices* (John Wiley & Sons, 2011).

221. Powell, C. J., Jablonski, A., Tilinin, I. S., Tanuma, S. & Penn, D. R. Surface sensitivity of Auger-electron spectroscopy and X-ray photoelectron spectroscopy. *Journal of Electron Spectroscopy and Related Phenomena* **98-99**, 1–15. ISSN: 0368-2048 (Jan. 1999).
222. Fadley, C. S. X-ray photoelectron spectroscopy: Progress and perspectives. *Journal of Electron Spectroscopy and Related Phenomena* **178-179**, 2–32. ISSN: 0368-2048 (May 2010).
223. Newville, M. Larch: An Analysis Package for XAFS and Related Spectroscopies. *Journal of Physics: Conference Series* **430**, 012007. ISSN: 1742-6596. <https://iopscience.iop.org/article/10.1088/1742-6596/430/1/012007> (Apr. 2013).
224. Victoreen, J. A. The calculation of x-ray mass absorption coefficients. *Journal of Applied Physics* **20**, 1141–1147. ISSN: 00218979 (1949).
225. Weng, T. C., Waldo, G. S. & Penner-Hahn, J. E. A method for normalization of X-ray absorption spectra. *Journal of Synchrotron Radiation* **12**, 506–510. ISSN: 09090495 (2005).
226. Rehr, J. J. & Albers, R. C. Theoretical approaches to x-ray absorption fine structure. *Reviews of Modern Physics* **72**, 621. ISSN: 00346861. <https://journals.aps.org/rmp/abstract/10.1103/RevModPhys.72.621> (July 2000).
227. Rehr, J. J. *et al.* Ab initio theory and calculations of X-ray spectra. *Comptes Rendus Physique* **10**, 548–559. ISSN: 1631-0705 (July 2009).
228. Rehr, J. J., Kas, J. J., Vila, F. D., Prange, M. P. & Jorissen, K. Parameter-free calculations of X-ray spectra with FEFF9. *Physical Chemistry Chemical Physics* **12**, 5503–5513. ISSN: 1463-9084. <https://pubs.rsc.org/en/content/articlehtml/2010/cp/b926434e> (May 2010).
229. Ericson, T. *et al.* Zinc-Tin-Oxide Buffer Layer and Low Temperature Post Annealing Resulting in a 9.0% Efficient Cd-Free Cu₂ZnSnS₄ Solar Cell. *Solar RRL* **1**, 1700001. ISSN: 2367198X (May 2017).
230. Hegazy, A. R., Salameh, B. & Alsmadi, A. M. Optical transitions and photoluminescence of fluorine-doped zinc tin oxide thin films prepared by ultrasonic spray pyrolysis. *Ceramics International* **45**, 19473–19480. ISSN: 02728842 (Oct. 2019).

231. Zhao, Y. *et al.* Impacts of Sn precursors on solution-processed amorphous zinc-tin oxide films and their transistors. *RSC Advances* **2**, 5307–5313. ISSN: 20462069 (June 2012).
232. Rucavado, E. *et al.* New Route for "Cold-Passivation" of Defects in Tin-Based Oxides. *Journal of Physical Chemistry C* **122**, 17612–17620. <https://pubs.acs.org/sharingguidelines> (Aug. 2018).
233. Islam, M. A. *et al.* Tailoring of the Structural and Optoelectronic Properties of Zinc-Tin-Oxide Thin Films via Oxygenation Process for Solar Cell Application. *IEEE Access* **8**, 193560–193568. ISSN: 21693536 (Jan. 2020).
234. Zhussupbekov, K. *et al.* Surface modification and subsequent fermi density enhancement of Bi(111). *Journal of Physical Chemistry C* **125**, 5549–5558. ISSN: 19327455. <https://pubs.acs.org/doi/full/10.1021/acs.jpcc.0c07345> (Mar. 2021).
235. Zhao, Y. *et al.* Band Gap Tunable Zn₂SnO₄ Nanocubes through Thermal Effect and Their Outstanding Ultraviolet Light Photoresponse. *Scientific Reports 2014 4:1* **4**, 1–7. ISSN: 2045-2322. <https://www.nature.com/articles/srep06847> (Oct. 2014).
236. Zhu, H. *et al.* High-quality and single-crystal ZnSnO₃ thin films: Fabrication and properties. *Vacuum* **197**, 110811. ISSN: 0042-207X (Mar. 2022).
237. Zhussupbekova, A. *X-ray Photoelectron Spectroscopy of Novel Ternary Materials* PhD thesis (Trinity College Dublin, 2021).
238. Morgan, W. E. & Van Wazer, J. R. Binding energy shifts in the X-ray photoelectron spectra of a series of related group IV-a compounds. *Journal of Physical Chemistry* **77**, 964–969. ISSN: 00223654 (1973).
239. Dake, L. S., Baer, D. R. & Zachara, J. M. Auger parameter measurements of zinc compounds relevant to zinc transport in the environment. *Surface and Interface Analysis* **14**, 71–75. ISSN: 10969918 (1989).
240. Biesinger, M. C., Lau, L. W., Gerson, A. R. & Smart, R. S. C. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn. *Applied Surface Science* **257**, 887–898. ISSN: 01694332. https://drive.google.com/file/d/1YYw701JVW4Ni_3GJv72uTE9KVE4Cg1S9/view?usp=drive_web&usp=embed_facebook (Nov. 2010).

241. Ramalingam, G. *et al.* in *Quantum Dots - Fundamental and Applications* 7–16 (IntechOpen, Jan. 2020). ISBN: 978-1-83880-919-5. <https://www.intechopen.com/chapters/70534%20undefined/chapters/70534>.
242. Zhou, F. *et al.* Quantum confined two-dimensional electron/hole gas switching by facet orientation of perovskite oxides. *RSC Advances* **8**, 20477–20482. ISSN: 2046-2069. <https://pubs.rsc.org/en/content/articlehtml/2018/ra/c8ra03928c> (June 2018).
243. Santander-Syro, A. F. *et al.* Quantum interference effects of out-of-plane confinement on two-dimensional electron systems in oxides. *Physical Review B* **102**, 75101 (2020).
244. Nazir, S., Behtash, M. & Yang, K. Towards enhancing two-dimensional electron gas quantum confinement effects in perovskite oxide heterostructures. *J. Appl. Phys* **117**, 115305. <http://dx.doi.org/10.1063/1.4915950%5D> (2015).
245. Ansari, L. *et al.* Quantum confinement-induced semimetal-to-semiconductor evolution in large-area ultra-thin PtSe₂ films grown at 400 °C. *npj 2D Materials and Applications* **3**. ISSN: 23977132. <http://dx.doi.org/10.1038/s41699-019-0116-4> (2019).
246. Zou, H. *et al.* Electronic property modulation in two-dimensional lateral superlattices of monolayer transition metal dichalcogenides. *Nanoscale* **14**, 10439–10448. ISSN: 2040-3372. <https://pubs.rsc.org/en/content/articlehtml/2022/nr/d2nr02189g> (July 2022).
247. Gan, Z. X., Liu, L. Z. & Wu, H. Y. Quantum confinement effects across two-dimensional planes in MoS₂ quantum dots. *Appl. Phys. Lett* **106**, 233113. <https://doi.org/10.1063/1.4922551> (2015).
248. Kim, B. H. *et al.* Metallic phase transition metal dichalcogenide quantum dots showing different optical charge excitation and decay pathways. *NPG Asia Materials* **13**, 1–9. ISSN: 18844057 (Dec. 2021).
249. Isakov, I. *et al.* Quantum Confinement and Thickness-Dependent Electron Transport in Solution-Processed In₂O₃ Transistors. *Advanced Electronic Materials* **6**, 2000682. ISSN: 2199160X (Nov. 2020).

250. Barnasas, A. *et al.* Quantum confinement effects of thin ZnO films by experiment and theory. *Physica E: Low-dimensional Systems and Nanostructures* **120**, 114072. ISSN: 1386-9477 (June 2020).
251. Labram, J. G. *et al.* Signatures of Quantized Energy States in Solution-Processed Ultrathin Layers of Metal-Oxide Semiconductors and Their Devices. *Advanced Functional Materials* **25**, 1727–1736. ISSN: 1616-3028. <https://onlinelibrary.wiley.com/doi/full/10.1002/adfm.201403862> (Mar. 2015).
252. Feenstra, R. M. Tunneling spectroscopy of the (110) surface of direct-gap III-V semiconductors. *Physical Review B* **50**, 4561. ISSN: 01631829 (1994).
253. Medvedeva, J. E., Buchholz, D. B. & Chang, R. P. Recent Advances in Understanding the Structure and Properties of Amorphous Oxide Semiconductors. *Advanced Electronic Materials* **3**, 1700082. ISSN: 2199160X (Sept. 2017).
254. Han, W. H. & Chang, K. J. Subgap States near the Conduction-Band Edge Due to Undercoordinated Cations in Amorphous In-Ga-Zn-O and Zn-Sn-O Semiconductors. *Physical Review Applied* **6**, 044011. ISSN: 23317019. <https://journals.aps.org/prapplied/abstract/10.1103/PhysRevApplied.6.044011> (Oct. 2016).
255. Wahila, M. J. *et al.* Accelerated optimization of transparent, amorphous zinc-tin-oxide thin films for optoelectronic applications. *APL Materials* **7**, 022509. ISSN: 2166532X. <https://pubs.aip.org/aip/apm/article/7/2/022509/1064086/Accelerated-optimization-of-transparent-amorphous> (Feb. 2019).
256. The Materials Project. Materials Data on ZnSn2O5 (SG:63) by Materials Project (Sept. 2014).
257. The Materials Project. Materials Data on ZnSn3O7 by Materials Project (May 2020).
258. Lee, I.-J., Park, J., Sung, N. E. & Kim, J. X-ray absorption fine structure investigation of the local structure of SnO 2-doped ZnO films. *Materials Chemistry and Physics* **206**, 103–109. <https://doi.org/10.1016/j.matchemphys.2017.12.004> (Feb. 2018).

259. Haug, J. *et al.* Characterization of lattice defects by x-ray absorption spectroscopy at the Zn K-edge in ferromagnetic, pure ZnO films. *Journal of Applied Physics* **110**. ISSN: 00218979. /aip/jap/article/110/6/063507/151132/Characterization-of-lattice-defects-by-x-ray (Sept. 2011).
260. Baur, W. H. & Khan, A. A. Rutile-type compounds. IV. SiO₂, GeO₂ and a comparison with other rutile-type structures. *Acta Crystallographica Section B* **27**, 2133–2139. ISSN: 1600-5740. <https://onlinelibrary.wiley.com/doi/full/10.1107/S0567740871005466> (Nov. 1971).
261. Bolzan, A. A., Fong, C., Kennedy, B. J. & Howard, C. J. Structural Studies of Rutile-Type Metal Dioxides. *Acta Crystallographica, Section B* **53**, 373–380. ISSN: 0108-7681. //scripts.iucr.org/cgi-bin/paper?br0044 (June 1997).
262. Wyckoff, R. W. G. *Crystal Structures* 2nd edition, 239–444 (Interscience Publishers, New York, 1963).
263. Trejo, O., Cho, T. H., Sainio, S. & Dasgupta, N. P. XANES Studies of Zinc Tin Oxide Films Deposited by Atomic Layer Deposition: Revealing Process-Structure Relationships for Amorphous Oxide Semiconductors. *Journal of Physical Chemistry C* **127**, 31. <https://doi.org/10.1021/acs.jpcc.2c05656> (2023).
264. Iordanova, N., Dupuis, M. & Rosso, K. M. Theoretical characterization of charge transport in chromia (α -Cr₂O₃). *Journal of Chemical Physics* **123**, 74710. ISSN: 00219606. <https://pubs.aip.org/aip/jcp/article-abstract/123/7/074710/931506/Theoretical-characterization-of-charge-transport> (Aug. 2005).
265. Grygiel, C. *et al.* Thickness dependence of the electronic properties in V₂O₃ thin films. *Applied Physics Letters* **91**, 262103. ISSN: 00036951 (2007).
266. Sarmadian, N. *et al.* High throughput first-principles calculations of bixbyite oxides for TCO applications. *Physical Chemistry Chemical Physics* **16**, 17724–17733. ISSN: 1463-9084. <https://pubs.rsc.org/en/content/articlehtml/2014/cp/c4cp02788d> (July 2014).

267. Nanda, B. R., Satpathy, S. & Springborg, M. S. Electron leakage and double-exchange ferromagnetism at the interface between a metal and an antiferromagnetic insulator: CaRuO₃/CaMnO₃. *Physical Review Letters* **98**, 216804. ISSN: 00319007. <https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.98.216804> (May 2007).
268. Wang, C. Y. *et al.* Organic Field-Effect Transistors with a Bilayer Gate Dielectric Comprising an Oxide Nanolaminate Grown by Atomic Layer Deposition. *ACS Applied Materials and Interfaces* **8**, 29872–29876. ISSN: 19448252. <https://pubs.acs.org/doi/abs/10.1021/acsami.6b10603> (Nov. 2016).
269. Kim, L. H. *et al.* Al₂O₃/TiO₂ nanolaminate thin film encapsulation for organic thin film transistors via plasma-enhanced atomic layer deposition. *ACS Applied Materials and Interfaces* **6**, 6731–6738. ISSN: 19448252. <https://pubs.acs.org/doi/abs/10.1021/am500458d> (May 2014).
270. Iatsunskyi, I. *et al.* Study on Structural, Mechanical, and Optical Properties of Al₂O₃-TiO₂ Nanolaminates Prepared by Atomic Layer Deposition. *Journal of Physical Chemistry C* **119**, 20591–20599. ISSN: 19327455. <https://pubs.acs.org/doi/abs/10.1021/acs.jpcc.5b06745> (Aug. 2015).
271. Suzuki, T., Hishita, S., Oyoshi, K. & Souda, R. Structure of α -Al₂O₃(0001) surface and Ti deposited on α -Al₂O₃(0001) substrate: CAICISS and RHEED study. *Surface Science* **437**, 289–298. ISSN: 0039-6028 (Sept. 1999).
272. Robinson, W. R. High-temperature crystal chemistry of V₂O₃ and 1% chromium-doped V₂O₃. *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry* **31**, 1153–1160. ISSN: 0567-7408 (1975).
273. Okimura, K., Sakai, J. & Ramanathan, S. In situ x-ray diffraction studies on epitaxial VO₂ films grown on c-Al₂O₃ during thermally induced insulator-metal transition. *Journal of Applied Physics* **107**. ISSN: 00218979. <https://pubs.aip.org/aip/jap/article-abstract/107/6/063503/370512/In-situ-x-ray-diffraction-studies-on-epitaxial-VO2?redirectedFrom=fulltext> (Mar. 2010).

274. Mendialdua, J., Casanova, R. & Barbaux, Y. XPS studies of V₂O₅, V₆O₁₃, VO₂ and V₂O₃. *Journal of Electron Spectroscopy and Related Phenomena* **71**, 249–261. ISSN: 03682048 (1995).
275. Biener, J. *et al.* Growth and electronic structure of vanadium on α -Al₂O₃(0001). *Surface Science* **449**, 50–60. ISSN: 0039-6028 (Mar. 2000).
276. Powell, C. J. Recommended Auger parameters for 42 elemental solids. *Journal of Electron Spectroscopy and Related Phenomena* **185**, 1–3. ISSN: 03682048 (Mar. 2012).
277. Shard, A. G. Detection limits in XPS for more than 6000 binary systems using Al and Mg K α X-rays. *Surface and Interface Analysis* **46**, 175–185. ISSN: 01422421 (Mar. 2014).
278. Vasquez, R. P. MgO(100) by XPS. *Surface Science Spectra* **2**, 13–19. ISSN: 1055-5269 (Jan. 1993).
279. Peng, X. D. & Barteau, M. A. Spectroscopic characterization of surface species derived from HCOOH, CH₃COOH, CH₃OH, C₂H₅OH, HCOOCH₃, and C₂H₂ on MgO thin film surfaces. *Surface Science* **224**, 327–347. ISSN: 00396028 (Dec. 1989).
280. Cr  pell  re, J. *et al.* Transparent conductive CuCrO₂ thin films deposited by pulsed injection metal organic chemical vapor deposition: Up-scalable process technology for an improved transparency/conductivity trade-off. *Journal of Materials Chemistry C* **4**, 4278–4287. ISSN: 20507526 (2016).
281. Rupp, J. A. J. *et al.* Competition between V₂O₃ phases deposited by one-step reactive sputtering process on polycrystalline conducting electrode. <https://doi.org/10.1016/j.tsf.2020.138063> (2020).
282. Abe, H., Terauchi, M., Tanaka, M. & Shin, S. Electron energy-loss spectroscopy study of the metal-insulator transition in V₂O₃. *Japanese Journal of Applied Physics* **37**, 584–588. ISSN: 00214922 (1998).
283. Murali, D. S. *et al.* Synthesis of Cu₂O from CuO thin films: Optical and electrical properties. *AIP Advances* **5**, 047143. ISSN: 21583226. <https://pubs.aip.org/aip/adv/article/5/4/047143/595806/Synthesis-of-Cu2O-from-CuO-thin-films-Optical-and> (Apr. 2015).

284. Capece, F. M. *et al.* "Copper chromite" Catalysts: XPS structure elucidation and correlation with catalytic activity. *Journal of Electron Spectroscopy and Related Phenomena* **27**, 119–128. ISSN: 03682048 (1982).
285. Poulston, S., Parlett, P. M., Stone, P. & Bowker, M. Surface Oxidation and Reduction of CuO and Cu₂O Studied Using XPS and XAES. *Surface and Interface Analysis* **24**, 811–820 (1996).
286. Han, S. & Flewitt, A. J. Analysis of the Conduction Mechanism and Copper Vacancy Density in p-type Cu₂O Thin Films. *Scientific Reports 2017 7:1* **7**, 1–8. ISSN: 2045-2322. <https://www.nature.com/articles/s41598-017-05893-x> (July 2017).
287. Ainabayeve, A. *et al.* High-performance p-type V₂O₃ films by spray pyrolysis for transparent conducting oxide applications. *Scientific Reports 2024 14:1* **14**, 1–10. ISSN: 2045-2322. <https://www.nature.com/articles/s41598-024-52024-4> (Jan. 2024).
288. Zhu, M. *et al.* Enhancing the performances of V₂O₃ thin films as p-Type transparent conducting oxides via compressive strain. *Applied Physics Letters* **121**. ISSN: 00036951. /aip / apl / article / 121 / 6 / 061903 / 2834053/Enhancing-the-performances-of-V2O3-thin-films-as-p (Aug. 2022).
289. Thambidurai, M., Shini, F., Harikesh, P. C., Mathews, N. & Dang, C. Highly stable and efficient planar perovskite solar cells using ternary metal oxide electron transport layers. *Journal of Power Sources* **448**, 227362. ISSN: 03787753 (Feb. 2020).
290. Wei, J., Yin, Z., Chen, S. C. & Zheng, Q. Low-Temperature Solution-Processed Zinc Tin Oxide Film as a Cathode Interlayer for Organic Solar Cells. *ACS Applied Materials and Interfaces* **9**, 6186–6193. ISSN: 19448252 (Feb. 2017).
291. Görrn, P., Lehnhardt, M., Riedl, T. & Kowalsky, W. The influence of visible light on transparent zinc tin oxide thin film transistors. *Applied Physics Letters* **91**, 193504. ISSN: 00036951 (Jan. 2007).
292. Pouloupoulos, P. *et al.* Intense quantum confinement effects in Cu₂O thin films. *Journal of Physical Chemistry C* **115**, 14839–14843. ISSN: 19327447. <https://pubs.acs.org/doi/full/10.1021/jp203145n> (Aug. 2011).

293. Piñon-Espitia, M., Lardizabal-Gutiérrez, D., Camacho-Ríos, M. L., Herrera-Pérez, G. & Ochoa-Lara, M. T. Electronic structure comparison of Cu 2p and O 1s X-Ray photoelectron spectra for Cu_xO nanofibers ($x = 1, 2, i$). *Materials Chemistry and Physics* **272**, 124981. ISSN: 0254-0584 (Nov. 2021).
294. Wagner, C. *Handbook of x-ray photoelectron spectroscopy : a reference book of standard data for use in x-ray photoelectron spectroscopy* <https://cir.nii.ac.jp/crid/1130000794672797312> (Perkin-Elmer Co., 1979).