Utilising Chromium-Based p-Type Transparent Conducting Oxides in Photovoltaic Devices

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A thesis submitted to the University of Dublin in partial fulfilment for the degree of Doctor of Philosophy

School of Physics
Trinity College Dublin

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Abstract
Declaration

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university. With the exception of the assistance noted in the acknowledgements and the text, this thesis is entirely my own work.
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Summary

This thesis deals with the growth of modern, highly performing p-type transparent conducting oxides, and their utilisation in two forms of photovoltaic devices. X-ray spectroscopic techniques are used to understand the electronic structure of these materials and the various interfaces they form when used in these photovoltaic devices.

Here, I examine the use of two of the current highest performing p-type transparent conducting oxides in two distinct photovoltaic devices: Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg as a hole transport layer in simple organic solar cells, and Cu$_x$CrO$_2$ and Cr$_2$O$_3$:Mg as a transparent p-type layer of a modern silicon heterojunction solar cell. A Cr$_2$O$_3$ anode buffer layer is found to improve the efficiency of organic solar cells by a factor of $\sim$3 compared to no buffer layer. The reason for the “S”-shaped characteristics exhibited by these cells is explored through band alignment measurements via in-situ high resolution photoelectron spectroscopy. An ultra-high vacuum transfer system necessary for the band alignment measurements was built to enable the spectroscopic analysis of samples after growth, prior to being exposed to ambient conditions. Simple n-Si/Cu$_x$CrO$_2$ solar cells are produced by spray pyrolysis while n-Si/Cr$_2$O$_3$:Mg solar cells are produced by molecular beam epitaxy. Band offset measurements performed by photoelectron spectroscopy determine that an oxide layer present on the surface of silicon is deteriorating their solar cell characteristics.
I would first like to thanks Professor Igor Shvets for allowing me to undertake research in the Applied Physics Research Group.

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List of Publications and Presentations

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**Presentations**

**Oral**

1. *Application of Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg as a Buffer Layer in Organic Solar Cells*
   Deutsche Physikalische Gesellschaft Spring Meeting, Regensburg, 2016

2. *Application of Cr$_2$O$_3$ and Mg$_x$Cr$(2-x)$O$_3$ as a Buffer Layer in Organic Solar Cells*
   Transparent Conducting Materials conference, Crete, 2016

**Poster**

1. *Application of Cr$_2$O$_3$ and Mg$_x$Cr$(2-x)$O$_3$ as a Buffer Layer in Organic Solar Cells*
   European Materials Society Spring Meeting, Lille, 2016
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<td>ABL</td>
<td>Anode Buffer Layer</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<td>AM</td>
<td>Air Mass</td>
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<tr>
<td>BHJ</td>
<td>Bulk HeteroJunction</td>
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<tr>
<td>CBO</td>
<td>Conduction Band Offset</td>
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<tr>
<td>CF</td>
<td>ConFlat</td>
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<tr>
<td>CIGS</td>
<td>Copper Indium Gallium Selenide</td>
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<tr>
<td>CMOS</td>
<td>Complementary Metal-Oxide-Semiconductor</td>
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<tr>
<td>CMVB</td>
<td>Chemical Modulation of the Valence Band</td>
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<td>CuPc</td>
<td>Copper Phthalocyanine</td>
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<td>DFT</td>
<td>Density Functional Theory</td>
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<td>FoM</td>
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<td>FTO</td>
<td>Fluorine-doped Tin Oxide (SnO$_2$:F)</td>
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<td>HOMO</td>
<td>Highest Occupied Molecular Orbital</td>
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<td>Inelastic Mean Free Path</td>
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<td>PID</td>
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<td>UHV</td>
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<td>Plasma Frequency</td>
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Chapter 1

Introduction

The study of materials, in particular, the problem of finding or discovering the best material for a given application has grown massively in the past few decades. In an ideal situation, there would exist a large database of materials, where one with the desired properties could be found instantly. Much work has been done on this recently with the materials design project [1], where the physical properties of nearly 70,000 inorganic materials have been calculated and catalogued, and the band structures of over 50,000 determined. The problem of “inverse-design” is also being explored, where a desired band structure is chosen, and a possible material with this band structure is then theoretically predicted [2].

In reality, a large amount of new materials are first discovered through experiment and their potential for applications is decided later. Transparent Conducting Materials (TCMs) simultaneously possess the contrasting properties of electrical conductivity and high transparency to visible light. This combination of properties is very useful and so is prevalent in industry and many modern consumer devices which require optoelectronic devices such as touchscreens, solar cells, light emitting diodes, liquid-crystal displays and smart windows [3]. The main classes of these TCMs include Transparent Conducting Oxides (TCOs), metal nanowire networks and two dimensional materials, such as graphene. Unlike nanowires, which are made of gold or silver and require a highly controllable deposition density to achieve optical transparency, or graphene, which requires large-area synthesis of highly pure and defect free material, TCOs typically require facile synthesis methods, are environmentally stable, resistant to wear and only require common materials. These reasons have led to TCOs being the most common class of transparent conducting materials, and are the only class currently used in mass-manufactured devices.

All of the previously mentioned applications make use of high performance n-type TCOs. A TCO which shows p-type character and comparable performance has yet to be discovered. While n-type TCOs can fulfil the majority of applications
Chapter 1. Introduction

which require a transparent conductor, there remain two areas where a p-type material is needed. The first, the realisation of fully transparent electronics through development of a Complementary Metal-Oxide-Semiconductor (CMOS) device is currently unfeasible, as the performance of p-type TCOs is currently too low [4]. The second application is as a buffer layer or hole transport layer in solar cells and light emitting diodes. In this thesis, the use of p-type TCOs as a buffer layer in solar cells will be explored. Furthermore, a novel n-silicon/p-TCO heterojunction device will be fabricated, and its feasibility as a modern, low cost solar cell architecture analysed.

1.1 Thesis Outline

Chapter 2 describes the history of TCOs, both n-type and p-type. The theoretical ideas which have led to the discovery of p-type TCOs, the state of the art, and methods for quantification of their performance are discussed. Particular attention is paid to the chromium-based p-type TCOs used in this work: \( \text{Cr}_2\text{O}_3 \), \( \text{Cr}_2\text{O}_3: \text{Mg} \), and \( \text{Cu}_x\text{CrO}_2 \). The history and state of the art of both organic solar cells and silicon heterojunction solar cells are discussed.

In Chapter 3 the techniques used to grow and characterise the optical and electrical properties of the above p-type TCOs are discussed. While a wide range of characterisation techniques are employed in this thesis, particular emphasis is placed on the photoelectron spectroscopy techniques which are used to obtain information about the electronic structure of the materials, in particular, the band alignment between the two materials which comprise a heterojunction. The ultra high vacuum transfer system which was constructed is also discussed in this chapter. Keeping samples in ultra high vacuum is of the utmost importance if accurate measurements on the surfaces of materials, such as band alignment measurements are to be performed.

In Chapter 4 the results obtained when using \( \text{Cr}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3: \text{Mg} \) as a hole transport layer/anode buffer layer in an organic solar cell are presented. The modification of the growth procedure of \( \text{Cr}_2\text{O}_3: \text{Mg} \) necessary to grow on common solar cell anode materials as opposed to epitaxial substrates of \( \text{Al}_2\text{O}_3 \) is discussed. The fundamental electronic properties of the anode/anode buffer layer interface are measured with photoelectron spectroscopy, while the solar cells containing these layers are characterised. While the detailed band alignment measurements performed here are typically too time consuming to be used to screen potential materials for buffer layer applications, it is one of the few methods that provides insight into the electronic structure of an interface at the nanometre level, and is used here to observe the presence of any barriers to hole transport that exist within the solar cell.

In Chapter 5 another solar cell architecture employing p-type TCOs is explored. This is a simple n-silicon/p-TCO heterojunction solar cell. Here, the material
Cu$_x$CrO$_2$ is grown on as-obtained n-silicon via spray pyrolysis to construct a low temperature, facile cell fabrication. Cr$_2$O$_3$;Mg is grown via molecular beam epitaxy on n-silicon which has been thermally treated to have its native oxide layer removed, to obtain a clean interface. The band alignment between these two materials is measured in much the same way as in Chapter 4, to determine the fundamental electronic limitations of such a device.

In Chapter 6, the results obtained are summarised and placed into the context of the current state of the art in the field of p-type TCOs. Future work and ideas arising from this work is discussed.
Bibliography


Chapter 2

Transparent Conducting Oxides

Transparent Conducting Oxides (TCOs) are an interesting class of materials which combine the often mutually exclusive properties of transparency to visible light along with the ability to conduct electricity. The transparency is due to the large band gap of these materials, which must be greater than \( \sim 3.1 \text{ eV} \) if there is to be no absorption in the visible spectrum. An example of a material with a band gap of 3.8 eV is shown in Figure 2.1; here, no photon in the visible spectrum has enough energy to excite an electron from the valence band to the conduction band, and thus will pass through the material without being absorbed.

While materials with a band gap of this magnitude would be considered transparent, they would also be expected to be highly insulating; for example, the most common conductive materials are metals, which possess no band gap and are highly reflective, while common insulators such as glass and plastics have a very large band gap and are thus extremely good insulators. The most common strategy to produce a TCO involves selecting a wide band gap insulator, and inducing conductivity in the material by introducing defects. By introducing shallow defects, that is, defects close in energy to either the conduction or valence band, the band gap should not be significantly reduced. While these defects will introduce Drude-like absorption in the infrared and far-infrared portions of the spectrum, they have little effect on the fundamental band gap of the material.

The coexistence of transparency and conductivity has led to TCOs finding widespread use in many modern technologies, including flat/touch panel displays, photovoltaic cells, low-emittance windows, electrochromic windows, transparent window defrosting, and transparent electronics [1–3]. They have also been used for many novel concepts, such as fully Transparent Thin Film Transistors (TTFT) [4, 5], transparent rectifying diodes [6] and windows that would pass visible light yet use Ultraviolet (UV) light to create electricity [7].

The study of TCOs began over a century ago with the first TCO, CdO, discovered
Figure 2.1: The absorption and transmission of light of various energies through a material. The most energetic visible photon (3.1 eV) is unable to promote an electron from the valence band to the conduction band, thus it cannot be absorbed by the material, while an ultraviolet photon, shown in black, has enough energy to promote an electron and so is absorbed. The numbers on each coloured arrow represent the energy (in electronvolts) of a photon with that approximate colour.

Table 2.1: Comparison of basic electrical and optical properties of everyday materials, showing the large spread in their values. The absorption coefficient ($\alpha$) and resistivity ($\rho$) are shown for the most common TCO, Indium Tin Oxide (ITO), in addition to a typical conductor (copper), semiconductor (silicon) and a transparent material (glass). All values are approximate.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha$ (cm$^{-1}$)</th>
<th>$\rho$ ((\Omega) cm)</th>
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<tbody>
<tr>
<td>Glass</td>
<td>$10^{-1}$</td>
<td>$10^{15}$</td>
</tr>
<tr>
<td>Silicon</td>
<td>$5 \times 10^2$</td>
<td>$10^4$–$10^{-4}$</td>
</tr>
<tr>
<td>ITO</td>
<td>$5 \times 10^2$</td>
<td>$10^{-4}$</td>
</tr>
<tr>
<td>Copper</td>
<td>$5 \times 10^5$</td>
<td>$10^{-8}$</td>
</tr>
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in 1907 by Badeker [8]. Since then, a large number of TCOs have been prepared; some of the most common being: fluorine doped tin oxide (SnO$_2$:F or FTO), aluminium doped zinc oxide (ZnO:Al), tin doped indium oxide (In$_2$O$_3$:Sn or ITO$^1$) and indium gallium zinc oxide (IGZO) [9–12]. The intrinsic electrical and optical properties of the most widely used, ITO, are compared with those of common materials in Table 2.1.

The TCOs mentioned above all have one feature in common: they are n-type. It was a full 90 years after the discovery of CdO before a TCO that exhibited p-type conductivity was found. In 1993, Sato et al. prepared unintentionally-doped p-type NiO thin films by magnetron sputtering, but these 110 nm thick films were found to have a high resistivity of $1.4 \times 10^{-1}$ \(\Omega\) cm and to only have an average visible range transmittance of 40% [13]. This compares with n-type ITO, which at that time could easily be grown by spray pyrolysis with a resistivity of $2 \times 10^{-4}$ \(\Omega\) cm and an

$^1$The typical composition for this material is In$_2$O$_3$ 90 wt% / SnO$_2$ 10 wt%. The chemical formula is more accurately written as In$_2$O$_{3-x}$Sn
average visible range transmittance for 92% for films that were 500 nm thick, or spray pyrolysis-grown FTO, which has a resistivity of $4.6 \times 10^{-1}$ Ω cm and a transmittance of 85% for ∼500 nm thick films [14].

Some of the initial attempts at creating p-type TCOs involved attempts at acceptor doping the previously existing n-type TCOs. This was the most straightforward approach, as methods for growing the materials already existed. If successful, it would allow high quality p-n homojunctions to be grown and realise the idea of transparent electronics. Unfortunately, no TCO has yet to be found to be ambipolar.

The most famous example of an n-type TCO that could not be successfully doped p-type is ZnO. It was shown using Density Functional Theory (DFT) that native oxygen vacancies and zinc interstitials form shallow donor levels and act to compensate any potential p-type dopant [15, 16]. Similar results were found for SnO$_2$, where oxygen vacancies were also found to act as a donor species. Unintentionally incorporated hydrogen was also found to be a source of compensation for any potential p-type dopants [17]. The numerous failed attempts at producing ambipolar doping in wide band gap oxides is not coincidental; it has been shown theoretically that successful p-type dopability and n-type dopability require conflicting band structures.

Zunger was able to establish that a material should possesses a small ionisation potential ($I_p$) for successful p-type doping without any compensation, while a material should have a large electron affinity ($\chi$) for n-type doping [18]. These properties are shown for an n-type semiconductor in Figure 2.2. The requirements put forward by Zunger are conflicting as there must always be a gap of 3.1 eV between the Conduction Band Minimum (CBM) and Valence Band Maximum (VBM) for the material to retain visible transparency. If the CBM is suitably located for n-type dopability, then a material with the correct band gap will have too deep of a VBM for facile p-type doping. Empirical estimates have been provided by Arai et al. for both the ionisation potential and electron affinity; the former (for p-type doping) should be less than ∼6 eV, while the latter (for n-type doping) should be greater than ∼4 eV [19]. These are obviously not possible with a band gap of 3.1 eV.

There has however recently been progress in the area, with the demonstration of ambipolar doping in the transparent semiconductor ZrOS [19]. This oxychalcogenide only becomes transparent when synthesised in its tetragonal, rather than cubic crystal structure. It is found to possess a fundamental band gap of 1.5 eV, but as this transition was found to be forbidden its optical band gap is thus 2.5 eV. This band structure allows it to simultaneously possesses an ionisation potential and a electron affinity which fall within the range outlined above for ‘facile’ doping of both polarities. The material showed n-type behaviour when doped with fluorine, and p-type behaviour when doped with yttrium, as determined from Seebeck measurements. Despite showing poor electrical properties (a minimum resistivity of ∼$10^2$ Ω cm and
Chapter 2. Transparent Conducting Oxides

Figure 2.2: A schematic of the energy levels in a degenerate n-type semiconductor. $I_p$, $\chi$, $\phi$, $E_g$, $E_{\text{vac}}$, $E_F$, $E_{\text{CBM}}$, and $E_{\text{VBM}}$ denote the ionisation potential, electron affinity, work function, fundamental band gap, vacuum level, Fermi level, conduction band minimum and valence band maximum, respectively. For successful p-type doping, $I_p$ should be $< 6 \text{ eV}$, while $\chi$ should be $> 4 \text{ eV}$ for successful n-type doping.

a mobility below the limit of both DC and AC Hall effect measurements) and a too small of a band gap for complete visible range transparency, the discovery of this material indicates that an ambipolar TCO is not beyond the realm of possibility.

2.1 p-Type Transparent Conducting Oxides

Kawazoe et al. hypothesised that the lack of p-type TCOs was due to the ionicity of metal oxides which results in the valence band edge of these materials being solely composed of oxide ions [7]. Holes at the valence band edge are strongly localised on these oxide ions, inhibiting conductivity [20]. The idea put forward to counter this was to use a metal cation with $d$-orbitals at the right energy to introduce covalency in the metal-oxygen bonds, resulting in a more disperse mixed metal/oxygen valence band edge. This method is known as Chemical Modulation of the Valence Band (CMVB) and is shown schematically in Figure 2.3. Furthermore, the metal cation should have a closed $d$-shell to avoid strong absorption resulting from $d$-$d$ transitions within the material. The combination of these ideas resulted in the discovery of CuAlO$_2$, which contains the closed shell Cu$^+$ ion which has a $d^{10}s^0$ electronic configuration [7]. This material provided the first glimpse of a large improvement in p-type properties. Discovered in 1997, the undoped CuAlO$_2$ with delafossite crystal structure has a large band gap of 3.5 eV, visible region transmittance of 70% when 500 nm thick, and a carrier mobility of 10 cm$^2$ V$^{-1}$ s$^{-1}$, comparable to ITO [21]. The high transparency and high mobility were highly promising for this material, and for development of a practical p-type TCO. Despite its relatively large resistivity of $\sim 3 \Omega \text{cm}$, it was suggested that this could be improved by up to two orders of magnitude by
Chapter 2. Transparent Conducting Oxides

Change in Valence Band Maximum

Conduction Band Minimum

Cation $d^{10}$  

O $2p^6$

Figure 2.3: Chemical bond between a metal cation and an oxygen anion. The top of the valence band has mixed character consisting of the oxygen $2p^6$ and the metal $d^{10}$. The cation has a closed $d^{10}$ shell, to prevent $d$-$d$ transitions, and thus colouration (visible light absorption) of the material. Adapted from Kawazoe et al. [20].

substitutional doping. The experimental realisation of this unfortunately failed. The original mobility value published was also later revised to a much more modest 0.14 cm$^2$ V$^{-1}$ s $^{-1}$ [21]. Despite these two setbacks, intense research continued into p-type TCOs based on the delafossite structure and on alternate crystal structures.

Other p-type TCOs found that make use of the CMVB method include CuGaO$_2$ with the delafossite structure, and a family of delafossites where Ag$^+$ is the $d^{10}$ cation. These include AgInO$_2$, AgScO$_2$, AgCrO$_2$, and AgGaO$_2$ [22]. SrCuO$_2$ (which is typically doped with potassium for improved conductivity) was also explored [23]. While this material does not have the same delafossite structure as CuAlO$_2$ or CuGaO$_2$, its crystal contains the same $d^{10}$ cation to provide CMVB, and it also has the same rows of O−Cu−O linear chains that are present in the delafossites [24]. This results in the $d^{10}$ cation possessing a small coordination number, which is said to provide a greater mixing of the cation-3$d$ and O-2$p$ states, resulting in a more disperse valence band [20]. However, p-type TCOs which do not follow the CMVB methodology have also been developed.

2.1.1 Spinel Family of Transparent Conducting Oxides

Research has been done on materials with the spinel structure and chemical formula ZnM$_2$O$_4$ where M=Co, Ir, Rh [25–27]. To avoid $d$-$d$ transitions, these group nine cations have filled $d$-$t^6_{2g}$ and empty $d$-$e^0_g$ levels which are split in energy by the octahedral crystal field of the material, and form the valence band and conduction band respectively. This is shown schematically in Figure 2.4. While these materials were shown to possess the expected metal $d$-states at their valence band maximum and conduction band minimum, their band gaps all remained lower than the 3.1 eV
Chapter 2. Transparent Conducting Oxides

Figure 2.4: The formation of a band gap in the ZnM$_2$O$_4$ (M=Co, Ir, Rh) p-type TCOs. The M-$d$ orbitals are split into $e_g$ and $t_{2g}$ states by an octahedral crystal field. The non-bonding $t_{2g}$ orbitals form the valence band, while the hybridised $e_g$ and O-$p$ ligands form an anti-bonding level which forms the conduction band. The M-$d$ electrons must be in the low-spin configuration for a band gap to form. Adapted from [28].

necessary for complete visible region transparency. Their resistivity was also found to not be much improved when compared with the earlier CuAlO$_2$. This, combined with their use of rare, expensive materials prevented their widespread use.

2.1.2 Transparent Conducting Oxychalcogenides

Another material class which has been searched for p-type TCOs is the oxychalcogenides. In these materials, a fraction of the anion sites are occupied by oxygen, with the remainder occupied by a chalcogenide, typically sulfur or selenium. The rationale behind the inclusion of chalcogens is that for a chosen group in the periodic table, as the period increases, the elements within that group will have an increased ionic radius and will simultaneously becomes less ionic. This causes the energy levels of its $p$ orbitals to move closer to the vacuum level. This will result in a more shallow valence band maximum for materials in which the anion has a large contribution towards the density of states at this point, i.e., TCOs [29].

Examples of these oxychalcogenide p-type TCOs include LaCuOS, LaCuO(S$_{1-x}$Se$_x$), LaCuOSe:Mg, BiCuOS, and BiCuOTe [30, 31]. The previously mentioned ZrOS also belongs to this group. Their conductivity arises though CMVB - here the hybridisation of the Cu 3$d^{10}$ orbitals and the chalcogen $p^6$ orbitals provides dispersion in the valence band. Difficulties with these materials include the toxicity of some chalcogenide precursors, the incompatibility of chalcogens with high vacuum systems, and for some synthesised materials, the lack of long term stability upon exposure to air [32].
Chapter 2. Transparent Conducting Oxides

2.1.3 Chromium-Based Transparent Conducting Oxides

One emergent, promising set of transparent conducting materials are those which contain chromium. These include the most conductive p-type TCO to date, CuCrO$_2$:Mg [22] as well as LaCrO$_3$:Sr [33], MnCr$_2$O$_4$:Li [34, 35], Cr$_2$O$_3$:Mg [36], Cr$_2$O$_3$:(Mg,N) [37], and CuCr$_x$O$_2$ [38]. While it might initially seem unusual that such a broad condition of ‘containing chromium’ can lead to favourable p-type TCO properties, several of these TCOs have been shown both theoretically and experimentally to contain chromium states near the top of the valence band [33, 39–41]. This results in a form of CMVB, but rather than the hybridisation of oxygen $2p^6$ and metal $d^{10}$ orbitals, it involves the oxygen $2p^6$ and the filled chromium $t_{2g}$. It was recently shown using resonant valence band photoemission spectroscopy that the upper valence band structure of several chromium containing p-type TCOs is predominantly composed of contributions from Cr 3$d$-states, and that doping these materials does not introduce a significant dispersion within the valence band [39]. This is shown here in Figure 2.5, where the peaks labelled “A” are those determined to be Cr 3$d$-states. It is seen that this feature is at the top of the valence band for both the highly crystalline materials CuCrO$_2$:Mg and Mg$_{0.12}$Cr$_{1.86}$O$_3$ and for the low crystalline quality Cu$_x$CrO$_3$. This suggests that it is the short range, local Cr environment which influences the valence band structure, rather than any long range crystalline order. This local Cr environment is a Cr–O$_6$ octahedron in the above mentioned materials and is shown for Cr$_2$O$_3$ in Figure 2.6(b). As the top of the valence band is composed of these localised Cr 3$d$ states, it is likely that the conduction mechanism for these chromium-based materials is a hopping mechanism between these localised states rather than a band conduction. This mechanism, which is typical of disordered materials, is not a particularly advantageous method of conduction — it typically results in materials with very high carrier concentrations but very low carrier mobilities. This limits the use of these materials in applications where a low carrier mobility is not critical.

2.2 Figure of Merit

While much research has been done on the discovery and development of p-type TCOs in the past three decades, there still remains a large gulf in the performance in terms of transparency, conductivity, and carrier mobility between n-types and p-types. All of the above mentioned p-type TCOs are far from the performance of commercial n-types such as ITO. One way of quantifying the performance of a p-type TCO is by designing a Figure of Merit (FoM) which combines the properties of interest in a certain combination so as to provide a single number with which to benchmark and compare all TCOs.
Chapter 2. Transparent Conducting Oxides

Figure 2.5: The valence band of several Cr-containing p-type TCOs. The feature labelled “A” is assigned to Cr 3d-states. Each valence band was measured with a photon energy of 85 eV. All spectra have been aligned to the VBM of CuCrO$_2$:Mg to facilitate comparison. The data for CuCrO$_2$:Mg is taken from Yokobori et al. [41]. Adapted from Norton et al. [39].

The most obvious choice of FoM would be to combine the most important directly measurable properties of a TCO such as the transmittance ($T$) and sheet resistance ($R_s$) in such a form that a larger FoM indicates a more highly performing TCO. An example of this is:

$$ F = \frac{T}{R_s} \quad (2.1) $$

This FoM was first introduced by Fraser & Cook in 1972 for thin films of sputtered ITO [42]. While this FoM was adequate for such a highly transparent material, in general this FoM will place too much weight on the electrical properties of a sample; while the transmittance varies from 0–100 %, the sheet resistance can vary over many more orders of magnitude for TCOs, leading to this value dominating the FoM. This led to Haacke proposing an alternate form of equation 2.1 [43]:

$$ F = \frac{T^q}{R_s} \quad (2.2) $$

where $q$ is chosen to obtain the correct weighting of importance between optical and electrical properties. Choosing $q$ to have a value of 10 results in a sample obtaining a
maximum FoM when its transmittance is 90%, a value which is perfectly satisfactory for most TCO applications. While this FoM was used for a long time (and still used in certain circumstances today [44]), it has a major drawback in that the parameters used to calculate it are sample dependent rather than material dependent. This would require evaluation of the FoM at several thicknesses to demonstrate the usefulness of TCOs for all applications, as TCOs are used in the range of several nanometres thick to several microns thick. Ignoring reflections, the transmittance of a sample is linked to a material dependent, thickness independent absorption coefficient ($\alpha$) by

$$T = \frac{I}{I_0} = e^{-\alpha t} \quad (2.3)$$

where $I_0$ is the intensity of light incident on a sample, $I$ is the amount of light transmitted through a sample, and $t$ is the sample thickness. The sheet resistance is also linked to a thickness independent variable, the resistivity ($\rho$):

$$R_s = \frac{\rho}{t} = \frac{1}{\sigma t} \quad (2.4)$$

where $\sigma$ is the conductivity of the material. A thickness independent FoM that
utilises equations 2.3 and 2.4 was proposed by Gordon \[45\]:

\[
F = \frac{\sigma}{\alpha} = -\frac{1}{R_s \ln(T + R)}
\]  

(2.5)

where \( R \) is the reflectivity of the material. This FoM has units of Siemens (S), or the equivalent inverse ohms (\( \Omega^{-1} \)). A higher FoM indicates a better performing p-type material. As many researchers who work in the field of TCOs do not have the ability to easily measure the reflectivity of their materials, a simplified FoM is instead used:

\[
F = -\frac{1}{R_s \ln(T)}
\]  

(2.6)

where the symbols have the same meaning as before. This FoM is more often used, yet is inferior to equation 2.5. While it appears to also be thickness independent, it neglects the indirect thickness dependence that is introduced by Fabry-Pérot oscillations. These are oscillations that appear in the transmittance and reflectance spectra of a thin film. The effect of the oscillations can either increase or decrease the calculated visible range transmittance of a material, depending on whether more maxima or minima occur within the visible region. A simulation of this effect is shown in Figure 2.7. Here, the transmission and reflectivity of a 600 nm IGZO film on glass is simulated and shown along with their sum. The Fabry-Pérot oscillations are easily seen, bounded by the dashed lines. The effect of these oscillations is most easily quantified by also measuring a reflectance spectrum of the same sample, but this is absent in the simplified FoM, which makes comparison between TCOs with different thicknesses difficult. The simulated reflectivity shows the same oscillations, but completely out of phase, so that when the transmission and reflectivity are summed, the film shows uniform, unity transmission for photon energies below the band gap. It is seen that the film begins to weakly absorb at \( \sim 2.4 \text{ eV} \) and strongly at \( 3.2 \text{ eV} \). One advantage of measuring Fabry-Pérot oscillations is that they can be used as a quick evaluation of film thickness, as the oscillation maxima/minima spacing varies with film thickness. They can even in some cases provide and estimate for the optical constants (\( n \) and \( k \)) of a weakly absorbing thin film \[46\].

The p-type TCOs with the largest FoMs to date (using the simplified FoM) include CuCrO\(_2\):Mg (5%) with 1600 \( \mu \)S, Cu\(_x\)CrO\(_2\) with 150 \( \mu \)S, LaCrO\(_3\):Sr (25%) with 195 \( \mu \)S and Cr\(_2\)O\(_3\):Mg (8%) with 48 \( \mu \)S \[22, 33, 36, 47\]. The numbers in brackets indicate the doping concentrations. For comparison, the first prominent p-type TCO, CuAlO\(_2\) has been shown to reach a FoM of only 10 \( \mu \)S when doped with 1% magnesium \[48\]. Despite this large increase of over three orders of magnitude in the FoM, the p-type TCOs still trail far behind their n-type counterparts. To compare, the \( \sim 80 \text{ nm} \) thick films of the industry standard TCOs, FTO and ITO, which are
Figure 2.7: Simulated transmission and reflectivity spectrum of a 600 nm IGZO film on glass. The envelopes of the maximum and minimum possible transmission defined by the Fabry-Pérot oscillations are shown to highlight the possible error caused by them. The average visible range transmission is 82%. The structure in the “T+R” spectrum between 2.4–3.25 eV is due to absorption caused by the IGZO film.

used later in this work as a transparent anode for solar cells show measured FoM values of 180 mS and 440 mS respectively.

2.3 Electro-Optical and Crystallographic Properties

While the previously mentioned FoMs provide a useful measure of TCO performance, they do not include every property which knowledge of would be useful when incorporating a TCO into a device. Possibly most importantly, the FoM assumes that the band gap of the material is above 3.1 eV. This is a strict condition and not the case for all reported TCOs; there are many valuable contributions to the field of TCOs that demonstrate materials with band gaps less than this, but with the potential to overcome this barrier through doping or the use of an alternate cation [25, 49]. Even still, some applications do not require UV transparency (e.g., low-emittance windows) and in some applications the improved conductivity that is usually associated with a reduced band gap might be advantageous. Other important material properties which are not included in the FoM include crystallinity, carrier mobility, growth temperature, surface roughness, etc.
The crystallinity of a material can, and usually does play a significant role in determining the properties of a material. This can affect multiple properties in many ways; grain boundaries between crystallites are a common source of carrier scattering, which reduces the carrier mobility and thus conductivity, while grain boundaries are typically associated with an increase in surface roughness, which will increase the amount of diffuse reflection from the surface and lower the transmittance. With traditional semiconductors, an improved crystallinity with minimal defects is usually associated with increased performance e.g., hydrogenated amorphous silicon has an electron mobility of \( \sim 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \), while single crystalline silicon can easily reach electron mobilities of \( \sim 10^3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \) \([50]\). This has turned out to be the opposite for some TCOs.

There has recently been much research into finding new amorphous TCOs since the discovery of amorphous IGZO in 2001 \([12]\). This material is one of the great success stories of TCOs; it has gone from discovery to large scale fabrication and incorporation in consumer devices within 10 years. It has a mobility of \( \sim 10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \), which has allowed it to replace amorphous silicon as an active layer in thin film transistors which are used in large high speed, high resolution displays \([51]\). Other amorphous TCOs include indium zinc oxide (IZO) \([52]\), zinc tin oxide (ZTO) \([53]\), and silicon indium zinc oxide (SIZO) \([54]\). These materials are highly performing in their amorphous phase as their conduction band minima are composed of metal-s orbitals - these spherical orbitals on neighbouring atoms have a large overlap regardless of whether the atoms are in a well ordered crystalline structure or are distributed in such a way that each atom is at a random angle to its neighbour. This is in comparison with, e.g., silicon, where conduction occurs through highly directional \( sp^3 \) orbitals which will have reduced overlap if the atoms no longer conform to a rigid lattice. While there is no a-priori reason that a high FoM amorphous p-type TCO can not be made, it will be a tougher challenge, as the VBM will typically be composed with some fraction of directional O-2p orbitals.

If a material possesses a high carrier mobility it is typically always advantageous, but it is not a critical parameter for certain applications, such as a thin buffer layer in a solar cell, as it would be if the material was to be incorporated into say, a thin film transistor. The conductivity for many p-type TCOs shows an activated behaviour, that is, the acceptor levels due to dopants are not shallow enough that a significant portion of them are ionised at room temperature. This results in low mobility values, typically \(< 0.1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \). Unfortunately, values of mobility this low are extremely difficult to measure experimentally, even when sophisticated AC measurements and high (> 10 Tesla) magnetic fields are employed \([55]\). This difficulty in performing accurate electrical measurements hinders the determination of the exact conduction mechanism in these materials. This is demonstrated by Kehoe
et al., where a measurement of the conductivity as a function of temperature is used to determine the conduction mechanism of Cr₂O₃:Mg [56]. While a thermally activated Arrhenius model does provide the best fit to the data, the differences in the fits obtained by the alternative models are surprisingly minor, despite the large disparity between the physical origins of the models: thermally activated band conduction, variable range hopping, and a small polaron conduction mechanism. Even more difficult is distinguishing between the various hopping mechanisms, as the differences between these models are even more subtle [33, 36].

A lower growth temperature is favourable as it allows the use of temperature sensitive flexible substrates, and allows the material to be incorporated into devices which might contain other heat-sensitive materials. As the field of TCOs has matured, i.e., they are now industrially grown on a large scale and incorporated into consumer devices, more focus has been placed on not just finding new, highly performing materials, but particularly finding materials which improve on or at least match the ‘thermal budget’ of the currently used materials. This thermal budget is proportional to the processing temperature, and the time spent at that temperature that a material requires for manufacturing. This parameter is of particular relevance for industry where the high temperature processing steps play a large part in the final cost of device production.

All the above mentioned properties can also be somewhat dependent on each other, e.g., a lower growth temperature might cause the material to grow in a polycrystalline rather than epitaxial fashion, but the grain boundaries in the material would most likely have a negative effect on the carrier mobility [57]. A similar compromise has to be made with regards to the doping levels of a TCO. Heavily doping a material is usually used to increase the carrier concentration and thus conductivity, often to the point that the material becomes degenerate, e.g., ITO and FTO. This can also prove beneficial to the optical properties of the material; a degenerate material will have free carriers occupying states at the bottom of the conduction band. These filled states result in the lowest unoccupied state being pushed to a higher energy, and thus an increase in the fundamental band gap. This effect is known as the Burstein-Moss shift and, assuming that the conduction band is parabolic, it increases the band gap according to:

$$\Delta E_{BM} = \frac{\hbar^2}{2m^*} \left(3\pi^2 n\right)^{2/3}$$

where $\Delta E_{BM}$ is the magnitude of the Burstein-Moss shift, $m^*$ is the effective carrier mass and $n$ is the carrier concentration. There are, however, negative effects associated with having too high a carrier concentration. If a TCO is doped heavily enough that it begins to exhibit degenerate conduction, then the electrons at the bottom of the conduction band will behave as free carriers, and the plasma frequency will lie in
the infrared, with the material being highly reflective to radiation below this energy. If the carrier concentration is increased further (typically above \( \sim 2 \times 10^{21} \text{cm}^{-3} \) for ITO [58]), this plasma edge will enter the red part of the visible spectrum and the visible range transmittance will be negatively effected. The energy of this plasma frequency is given by:

\[
E_p = \hbar \omega_p = \hbar \sqrt{\frac{ne^2}{m^* \varepsilon}}
\]  

(2.8)

where \( E_p \) is the energy of the plasma frequency and \( \hbar \omega_p \) is the plasma frequency. Above the plasma frequency, the absorption due to these free carriers is [59]:

\[
\alpha = \frac{ne^3}{\pi \varepsilon_0 (m^*)^2 c \mu} \frac{1}{\omega^2}
\]  

(2.9)

where \( \mu \) is the carrier mobility of the material. As the conductivity of a material depends on both the carrier concentration and the carrier mobility by:

\[
\sigma = nq\mu_q
\]  

(2.10)

where \( \mu_q \) is the mobility of a carrier with charge \( q \), it is preferred to keep the carrier concentration low, and achieve a high conductivity by means of a high mobility, as an increased mobility only affects the slope of the change in transmittance/reflectance near the plasma frequency.

Another concern is that as the conduction band is filled, electrons at the Fermi level will be at a large enough energy that they could possibly be excited to the next unfilled band above the conduction band. This is known as the ‘second gap’, and is shown along with the Burstein-Moss shift in Figure 2.8. This second gap must remain above 3.1 eV for the material to remain transparent. The above discussion applies equally well to p-type TCOs, where holes rather than electrons are responsible for conduction [60].

Another effect, known as band gap renormalisation, can occur when the doping level is high enough that the dopant can hybridise with the valence/conduction band and cause the band to “flatten”, moving it away from a simple parabolic shape [61].

In summary, the physical properties of TCO materials are quite interlinked, and it is highly unlikely that one material will fit all applications. Trade-offs must be made in some areas to preserve or enhance the most important physical properties of the material of interest. Perhaps the most important property for a material which is to be used in electronic devices is its charge carrier type, as it can be difficult (or in the case of TCOs, still has yet to be demonstrated) to modify. While basic functionalities can be obtained from a device which contains material of a single carrier type, the vast majority of devices require manipulation of both carrier types to
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Figure 2.8: Band structure of a degenerate n-type and degenerate p-type TCO showing the Burstein-Moss shift and the second gap. The former is shown in blue, and the latter in red. The gray shading represents states occupied by electrons. The Burstein-Moss shift shown here is exaggerated; it typically reaches a value of $\sim 200 \text{ meV}$ in heavily doped ZnO [62].

function. For this reason, research into utilising p-type TCOs in various applications is a vibrant field, despite the existing gulf in performance when compared to their n-type counterparts and the relative infancy of fundamental p-type TCO research.

2.4 Applications for p-Type Transparent Conductors

There are two categories of electronic devices: active and passive. Here, the term active refers to a device where the TCO and its properties play a major role in the behaviour of the device, while in a passive device the TCO plays a secondary role, with the functionality of the device being primarily determined by other layers or materials. The active category can be further divided into transistor-like devices such as a Transparent Thin Film Transistor (TTFT)\(^2\), and p-n, p-i-n diodes and other variations.

The realisation of a p-channel TTFT would be a milestone in the field of TCOs\(^3\). This would represent a huge development in transparent electronics, comparable to the shift from n-type Metal-Oxide-Semiconductor (NMOS) logic to Complementary

\(^2\)Here, a thin film transistor refers to a field effect transistor made solely of thin films.

\(^3\)In the literature, the term Transparent Semiconducting Oxide (TSO) is often used when discussing devices. Here, I will use TCO to cover both conducting and semiconducting transparent oxides.
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Metal-Oxide-Semiconductor (CMOS) logic in traditional integrated circuits. While such a device was demonstrated with p-type SnO as the active layer, it only achieved a mobility of $1.4 \text{ cm}^2\text{s}^{-1}\text{V}^{-2}$ [63]. Furthermore, its band gap is only 2.7 eV, below the criteria for transparency over the full visible spectrum. Manufacturing complementary logic from low performance p-type materials is a significant issue due to the mobility imbalance present between the n and p-type TCOs [64]. For a high performing TTFT, the carrier concentration must also be controllable (typical values are from below $10^{14} \text{cm}^{-3}$ to above $10^{18} \text{cm}^{-3}$), and the native carrier concentration should be low, to achieve a low off-current and a large on/off current ratio. Further progress must be made in the field of p-type TCOs before they have an impact in this area.

Unlike thin film transistors where the mobility of the materials in the active layers have a direct effect on the performance of the device, carrier mobility is of secondary importance in passive applications such as a buffer layer in a solar cell, as there is no high speed switching or amplification. This is also one application where n-type TCOs are not sufficient for every application, as a p-type TCO will be needed for the section of the cell which is involved with hole transport. In this work, p-type TCOs have been incorporated into two simple solar cell architectures: low cost organic solar cells, and n-silicon/p-TCO heterojunction solar cell.

2.4.1 Si Heterojunction Solar Cells

Silicon based solar cells have been studied since the 1940s. The first silicon solar cell was accidentally discovered by Russell Ohl at Bell Labs in 1941 [65]. It was noticed while performing resistivity measurements on a piece of high-purity silicon that the current through the material was being affected by the presence of light emanating from a nearby lamp. It was found that upon illumination, a current flowed through the silicon even when no power source was connected. Ohl had inadvertently created a p-n junction; while cooling down his pieces of molten silicon, impurities fortuitously separated due to their differing atomic weights, with the lighter p-type doping elements (boron, aluminium) remaining at the top and the heavier n-type dopants (phosphorus) settling at the bottom. While an extremely important discovery, the cells produced had an efficiency of less than 1%.

It took until 1954 before what is known as the first 'practical solar cell' was produced by Chapin et al. [66]. This cell was also made at Bell Labs, and achieved an efficiency of 6%. It was produced by diffusing p-type dopants into an n-type silicon wafer. Due to their high cost they were not widely used, but cells of this nature found use in the niche market of satellite power generation; Vanguard 1, the first solar powered satellite was launched in 1958 and made use of a $100 \text{cm}^2$ silicon solar panel which generated 0.1 W.
Shockley-Queisser Limit

While a silicon p-n homojunction is often what is imagined when reading about a solar cell, silicon is also used as an active component in other solar cell architectures. One of the primary reasons that silicon is widely used is due to its nearly-ideal band gap for a cell with a single absorbing layer, as calculated by Shockley and Queisser [67]. Another important reason is due to the abundance, and low cost of high purity silicon\(^4\).

When calculating the Shockley-Queisser the only electron-hole recombination mechanism considered is radiative; this ultimately demonstrates that a single cell utilising an absorbing material with a band gap of 1.1 eV, i.e., silicon, can reach a maximum efficiency of \(\sim 30\%\). It was noted in this paper that recombination caused by the Auger effect could result in lower real-device efficiencies. 23 years later, Green et al. showed that under an illumination intensity equal to that of one-sun, Auger recombination was indeed the dominant loss mechanism in silicon solar cells, and had a detrimental effect on the open circuit voltage [68]. The theoretical efficiency limit has been slightly revised several times [69, 70] since the original estimation by Shockley and Queisser, and currently stands at 29.43\% for a 110 \(\mu\)m thick cell made of undoped silicon [71].

Since the first practical cell of Chapin, silicon p-n homojunctions have improved dramatically, and have now demonstrated efficiencies in excess of 24\% [72]. While their efficiency is heading towards that of the Shockley-Queisser limit, efficiency improvements have stagnated in the past few decades.

Modern Heterojunction Architectures

In light of this stagnation, alternate architectures which still include silicon have begun to be explored recently. One of these is the silicon heterojunction solar cell. These cells are so called due to the heterojunction that is formed between the crystalline silicon wafer substrate and another material; typically amorphous silicon (a-Si) grown on the wafer surface for high performance cells. While they have a complex structure, the cells produced using this architecture are extremely efficient, and have recently demonstrated an efficiency of 26.3\%,\(^5\) the highest of any silicon-based solar cell (excluding those which use concentrated solar radiation) [73]. A schematic of such a cell is shown in Figure 2.9. Many of these cells have a nano-pyramidal texture on their surface to trap light within the cell, reducing reflection losses. One of the main drawbacks of this cell is the chemicals required for growing both the undoped and doped a-Si. Plasma enhanced chemical vapour deposition is

\(^4\)As an example, 99.999\% purity silicon can be purchased for less than €200/kg.

\(^5\)This was improved to 26.6\% and is included in the famous NREL efficiency chart [https://www.nrel.gov/pv/assets/images/efficiency-chart.png](https://www.nrel.gov/pv/assets/images/efficiency-chart.png)
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Figure 2.9: A typical silicon heterostructure solar cell formed from an n-type wafer. The doping of the amorphous and crystalline silicon layers is indicated in brackets. The thickness of the crystalline silicon layer is vastly scaled down for clarity. Efficiencies of up to 25% have been reached using this design.

typically used to grow this material in industrial environments, and this requires the use of gaseous silane (\(\text{SiH}_4\)). This chemical is toxic and pyrophoric, and can ignite upon exposure to air, even when diluted to 1% concentration in nitrogen. The chemicals required to dope the a-Si p-type (phosphorus doping with phosphine (\(\text{PH}_3\))) and n-type (boron doping with diborane (\(\text{B}_2\text{H}_6\))) are also toxic and show similar reactivity.

Si-TCO Solar Cell

Another cell which falls in the same family is the heterojunction between a transparent conducting oxide and silicon. This has been under investigation for at least the past 50 years. One of the first studies was SnO\(_2\) on n-Si [74]. The SnO\(_2\), which was grown in a rudimentary fashion by oxidising SnCl\(_2\) on a heated piece of silicon, was presumed to be n-type, and to be degenerately doped. This was found to produce solar cells with a poor efficiency of one hundredth of that of typical silicon solar cells at the time. Solar cells of similar efficiencies were produced with CdO [75], ITO [76], SrTiO\(_3\) [77], and ZnO [78]. Despite the poor performance of these cells, the results remained promising due to the facile nature of their fabrication. While these papers demonstrated new devices, they did not undertake detailed studies to understand the electrical properties of the cells. As they are n-type TCOs deposited on n-silicon, they were most likely Schottky junction solar cells; the barrier being between semiconducting silicon and “metallic” TCOs. Some evidence for this is provided by the low resistivity and high carrier concentration values provided for the prepared ITO of Matsunami et al., which suggests that their ITO was degenerately doped [79].

A cell with notably improved characteristics was observed when polycrystalline In\(_2\)O\(_3\) [79] was used as the TCO layer. The cell had an efficiency comparable to that of a commercial silicon solar cell when the n-type In\(_2\)O\(_3\) was deposited on a p-type
silicon substrate. The diode and solar cell characteristics were found to be much worse when n-type silicon was used as a substrate. ITO, when grown on n-Si using a variation of spray pyrolysis, was also found to deliver similar performance [80].

Investigations began into the achieving the same efficiencies with indium-free TCOs for the same reason that alternate high-performance n-type TCOs are currently being developed: the high cost and relative rarity of raw indium. One example which combines facile synthesis (spray pyrolysis) with abundant materials is the ZnO/Si solar cell, which achieved an efficiency of 8.5% [81]. Both n and p-type silicon were used as substrates; the n-type was found to produce much better solar cells. These cells however experienced a rapid degradation in their efficiency over a period of five days which was attributed to the formation of an SiO$_2$ layer at the interface between Si and ZnO, which was formed due to atmospheric oxygen diffusing through the ZnO layer along the grain boundaries. Illumination was also found to degrade the cells, a highly undesirable property in solar cell materials.

Various other Si/material heterojunction solar cell systems have been explored recently: a p-type Oxychalcogenide (CuS)$_x$:(ZnS)$_{1-x}$/n-Si cell [82], p-Si and n-Si nanowires with an n-type TiO$_2$ shell deposited on them using atomic layer deposition [83], p-type carbon nanotubes on n-Si [84], vertically aligned nanorods made of (Mg doped, with gold nanoparticles as a catalyst) p-type GaN grown on n-Si [85], and monolayer MoS$_2$ deposited on top of p-Si [86].

One material system which has yet to be explored is the heterojunction between modern high performance p-type TCOs and n-type silicon. Their transparency allows a large proportion of the incident light to reach the silicon layer, while their p-type nature could lead to a p-n junction with silicon which would result in efficient carrier extraction. This device will be explored in this thesis.

2.4.2 Low-Cost Organic Solar Cells

In contrast to silicon solar cells in which the fabrication consists of many steps involving many techniques, Organic Solar Cells (OSCs) are designed to be low-cost, easy, and quick to produce, often employing methods such as roll-to-roll processing, screen printing, and spin coating. Due to this they demonstrate an expectedly concomitant lower efficiency.

In a traditional solar cell, a photon is absorbed in a semiconducting, relatively low band gap layer, leading to a free hole and electron in the valence and conduction band of the material, respectively. The spatial separation of the hole and electron is performed by the depletion region present at the p-n junction. A photogenerated minority carrier (that is, an electron in the p-type side or a hole in the n-type side) will be swept to the opposite side of the p-n junction by the electric field present
within the depletion region, if it diffuses to this region before recombining. This electric field also acts to keep the photogenerated majority carrier from crossing the depletion region. The two photogenerated carriers are then collected by contacts at opposite ends of the cell. This fundamental process is completely different in organic solar cells. The main difference is that in an organic solar cell, the photoactive layer is an organic material, and when a photon is absorbed in this organic material it results in a bound electron-hole pair, known as an exciton, rather than free carriers. Excitons also occur in inorganic semiconductors, but their binding energy is on the order of millielectronvolts, and thus can be dissociated by thermal energy at room temperature. The binding energy of a Coulomb-bound exciton \( E_{eb} \) can be roughly estimated by assuming the electron and hole are separated by a distance \( r \) of approximately 1–5 nm in a material with dielectric constant \( (\varepsilon) \) of approximately 3 [87]:

\[
E_{eb} = \frac{e^2}{4\pi\varepsilon\varepsilon_0 r}
\]  

This gives an exciton binding energy on the order of 0.1–0.5 eV that must be overcome if the carriers are to be separated and extracted from the cell. As this is an order of magnitude larger than room temperature thermal energy, a separate mechanism must be employed to dissociate the exciton and thus generate sufficient amounts of free carriers. The binding energy is much higher in organic materials as their dielectric constant is much lower \((\varepsilon \approx 12\) for silicon\), and the electron and hole wavefunctions are localised on individual molecules which enhances the Coulomb attraction between the two.

While this is a disadvantage compared to inorganic solar cells, OSCs compensate in other areas by using materials which have a very high absorption coefficient (on the order of \(10^4–10^5\) cm\(^{-1}\) which is comparable to metals, cf. Table 2.1) so that only thin (tens of nanometres) active layers are needed, which helps to keep material and thus overall device costs low. OSCs are also usually fabricated with facile synthesis methods such as spin coating or thermal evaporation.

**Organic Solar Cell Variants**

The simplest form of an Organic Solar Cell (OSC) is a single layer sandwiched between two contacts, one with a high work function and one with a low work function. One of these must also be transparent to allow light to reach the organic layer. The difference in work functions of the contacts results in an electric field throughout the organic layer which provides the necessary energy to dissociate the exciton and provide free carriers. This form of OSC is not efficient (with typical power conversion efficiencies \(<0.1\%)\), as the electric field is not sufficiently large enough to provide efficient exciton dissociation before recombination occurs. The rectifying
behaviour of these devices can either be explained through a metal-insulator-metal model, or by considering that the low work function metal and the organic layer can form a Schottky barrier, if the organic layer is p-type [88].

In 1986 Tang demonstrated a cell which consisted of an organic bilayer structure which achieved 1% power conversion efficiency under Air Mass 2 illumination\(^6\) [89]. The organic materials used were copper phthalocyanine (CuPc) which acts as an electron donor and a perylene tetracarboxylic derivative (PV) which acts as an electron acceptor. A film of silver contacted the PV to make the cathode, while In\(_2\)O\(_3\) in contact with the CuPc was the anode. The success of this device was due to the interface between the two organic layers. At the interface, the difference in energy levels between either the Lowest Unoccupied Molecular Orbitals (LUMO) or the Highest Occupied Molecular Orbitals (HOMO) provides a pathway for the exciton to dissociate. This is shown in Figure 2.10. There has been an empirical relationship proposed by Scharber et al. which relates the open circuit voltage to the “fundamental” gap of the donor acceptor system, that is, the difference in energy between the HOMO of the donor and the LUMO of the acceptor:

$$V_{OC} = \frac{1}{q} \left( E_{\text{HOMO}}^{\text{Donor}} - E_{\text{LUMO}}^{\text{Accepto}} \right) - 0.3$$

(2.12)

The numerical factor of 0.3 was chosen as it provided the best fit with the existing experimental data. This was shown to accurately fit a large variety of donor/PCBM systems\(^7\) [90].

The generation and extraction of carriers from the an OSC can be broken down into a five step process, each of which has an associated efficiency [91]:

1. A photon is absorbed, creating a bound exciton within one of the active layers
2. The exciton diffuses towards the donor-acceptor interface
3. The exciton dissociates into a free electron and hole
4. The electron and hole diffuse towards their respective contacts
5. The carriers are collected at the electrodes

External efficiencies such as the transparency of the TCO layer and the reflectivity of the substrate are not considered here. The first step relies on the absorption coefficient, band gap, and thickness of the active layers. The optical electric field intensity in the cell can be modulated so that a maximum in field strength occurs in the active layers; this can be achieved through carefully optimising the thickness\(^6\)\(^\text{The details of various air mass illumination is discussed in Section 3.9.}\)

\(^7\)PCBM is \([6,6]-\text{phenyl-C}_{61}\)-butyric acid methyl ester, a fullerene derivative
Figure 2.10: Exciton dissociation at the interface of a bilayer organic solar cell. The red circles represent holes, while the blue circles represent electrons. (a): The photon is absorbed in the donor, and the LUMO difference at the interface provides the pathway for exciton dissociation. (b): The opposite occurs; the photon is absorbed in the acceptor, and the HOMO difference provides the pathway for exciton dissociation.

of all layers of the device. To maximise the efficiency of this step, an active layer thickness which results in absorption of all incoming photons should be chosen.

A minimal active layer thickness is required to maximise the efficiency of the second step. The exciton diffusion length in the $\pi$-conjugated polymers that are a popular choice for the absorbing layer is on the order of $10\text{nm}$ \cite{92}; this is one of the primary reasons that bilayer OSCs are not currently competitive with other modern solar cell technologies.

The third step, involving the excitonic dissociation is a difficult effect to isolate and estimate the efficiency. While a necessary condition for an efficient cell is that the correct combination of materials have been chosen to ensure that the energy offset at the donor/acceptor interface is larger than the excitonic binding energy, various other effects have to be taken into account such as the interface morphology and the electron affinities and ionisation potentials of the organic materials.

The fourth step relies on the transport properties of the organic materials. The carrier transport mechanism of organic polymers is typically a hopping process between each molecule. This hopping process is associated with a very low carrier mobility which can be as low as $10^{-4}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. The high electric field present within the bulk of the solar cell helps to mitigate this; transport through the active layers can be very efficient once recombination sites and carrier traps such as defects are not present.

The charge collection efficiency at the electrodes can be highly efficient once electrode materials which have a suitable band structure for collection of the relevant carrier have been chosen. It can also depend on the morphology of the interface
between the contacts and the adjacent layers [93].

Due to the competing requirements to maximise efficiency, it is no surprise that bilayer OSCs display low efficiency values of only a few percent. A second architecture, known as the Bulk HeteroJunction (BHJ) has been developed to address these issues. This form of OSC is heavily researched today, and has demonstrated efficiencies over 10% for a single junction [94], over 11% in a multi-junction cell [95], and has been used as a tandem cell with a perovskite solar cell to obtain an efficiency of over 19% [96].

The BHJ avoids the losses present in the bilayer structure that arise from exciton dissociation and exciton diffusion. The structure of an ideal BHJ cell is shown in Figure 2.11 (b). Here, the thickness of each “tooth” in the comb-like structure that both active layers adopt should be less than or equal to twice the exciton diffusion length within the material. This ensures that the vast majority of generated excitons will diffuse to a donor-acceptor interface before they recombine. The effective dissociation efficiency is also much improved as there is a vastly increased interfacial area between the donor and acceptor. This ideal comb-like structure is difficult to realise, as each tooth needs to have a maximum diameter of \( \approx 20 \text{ nm} \) to retain its near unity collection efficiency of photogenerated excitons. This can be accomplished with electron beam lithography, but this process is slow, costly, and not scalable to large areas. Another method would possibly be to grow an ordered structure of vertically oriented nanowires with controllable diameters, and deposit a second material to fill in the voids left by the former process. Such dense, self-assembled nanowire growth has previously been demonstrated with inorganic semiconductors [97], but the specific conditions required for this in addition to the generally reactive and temperature sensitive nature of organic polymers make this method unfeasible.

In reality, the BHJ cells are produced by blending the donor and acceptor, and spin coating this onto the electrode material. This results in a morphology which possesses major drawbacks to the ideal case: there will be a random distribution of donor and acceptor “grain” widths, reducing the probability of an exciton diffusing towards an interface before recombining; there will be isolated grains which do not contact an electrode and so will act as carrier traps; and there will be a proportion of grains which will be in contact with the wrong electrode, which increases recombination in the cell and reduces efficiency. These are shown in Figure 2.11 (c). To overcome the efficiency loss due some of these drawbacks, new complex polymer designs are constantly being discovered and developed [98]. These are typically processed and developed and manufactured on a laboratory scale, making them unsuitable for scaling to commercial levels of production. Despite these large drawbacks, many BHJ cells have been explored, and they generally show a much improved efficiency over bilayer cells [99].
Figure 2.11: Difference in structure between bilayer cell and bulk heterojunction cell. The cells are usually deposited on a glass substrate. (a): A simple bilayer cell, with no buffer layers. (b) A bulk heterojunction cell with the ideal mixing of donor and acceptor. For maximum efficiency, the thickness of each “tooth” in the comb-like structure should be less than or equal to twice the exciton diffusion length within the material. (c): A realistic bulk heterojunction formed by blending the two polymers.

Buffer Layers

Both bilayer and BHJ cells can be improved further by introducing buffer layers. These are typically thin layers inserted between the donor and the anode, or the acceptor and the cathode. In the literature, these buffer layers are also known as hole/electron transport layers, exciton blocking layers, or hole/electron blocking layers. The choice of name typically depends on which effect the author believes is most relevant. Here, the term buffer layer will be used, as the layer typically serves multiple functions. The buffer layer has two primary functions: to aid in extracting carriers from the relevant organic layer to the correct electrode, and to prevent carriers of the opposite type from reaching the wrong electrode, recombining, and reducing the efficiency of the cell.

Buffer layers have also been shown to provide secondary benefits: by choosing the correct thickness they can modulate the optical electric field intensity so that its maximum occurs within the active layers; they can act to smooth the surface of the often-rough electrodes, preventing the cell from shorting which increases the shunt resistance [93]; they can enhance adhesion of the organic layer deposited on it; and they can prevent the organic layers from reacting with the electrodes, reducing the life of the cell.

Buffer layers are not unique to organic solar cells; the inclusion of the organic hole conductor spiro-MeOTAD in a perovskite solar cell with methyl ammonium lead iodide (CH$_3$NH$_3$)PbI$_3$ nanoparticles as the light absorbing material resulted in the perovskite solar cell record efficiency at the time of 9.7% [100].

Here I will focus on Anode Buffer Layers (ABLs), also known as hole transport

---

8C$_{81}$H$_{68}$N$_4$O$_8$, or 2,2',7,7'-tetrakis-(N,N-di-p-4-methoxyphenyl-amine)-9,9'-spirobifluorene
layers, or electron blocking layers, as these are the most relevant to the p-type materials discussed in this work. For an ABL to successfully improve the characteristics of the cell into which it is incorporated, it must have a large work function to aid in hole extraction, have a large band gap so as to not absorb any light before reaching the active layers, be an inefficient conductor of electrons, and be stable enough to not react with any of the other materials used in the cell, particularly the organic materials. Using p-type TCOs as an ABL will satisfy all of these requirements.

Despite this, the most commonly used ABL for OSCs is poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, or PEDOT:PSS. This is easily deposited onto substrates via spin coating, and is a relatively low cost material. It does however possess a low conductivity of \( \approx 1 \text{ S cm}^{-1} \), reacts with common anodes such as ITO \([101]\), and is sensitive to air, water, and ultraviolet radiation \([102, 103]\). This results in cells which have a very short lifetime, and are thus only suitable for laboratory testing.

Many high work function metal oxides such as NiO\([104]\), MoO\(_3\)[105], V\(_2\)O\(_5\)[106], and WO\(_3\)[107] have been shown to improve the efficiency of OSCs when used as an ABL. It was shown in 2011 by Qin et al. that amorphous Cr\(_2\)O\(_3\) \([108]\) and Cr\(_2\)O\(_3\):N \([109]\) could be successfully employed as an ABL in a simple organic solar cell. Both of these materials are insulating, and resulted in increasing the series resistance of the cell, which had a negative effect on the power conversion efficiency of the fabricated cells. It is expected that the much more conductive Cr\(_2\)O\(_3\):Mg will show superior buffer layer properties, and will result in a cell which demonstrates a superior power conversion efficiency.

### 2.5 Cr\(_2\)O\(_3\) & Cu\(_x\)CrO\(_2\)

Of the large variety of TCOs that have been mentioned so far in this chapter, two have been selected for studying their potential use in photovoltaic applications. These are Cr\(_2\)O\(_3\)/Cr\(_2\)O\(_3\):Mg, and the copper deficient Cu\(_{0.4}\)CrO\(_2\). These materials were selected as they are relatively high performing p-type TCOs which have previously been synthesised in our group, are stable to air, and do not require any toxic materials for their synthesis, making them ideal candidates for incorporation into photovoltaic devices \([36, 110]\).

#### 2.5.1 Chromium Oxide (Cr\(_2\)O\(_3\))

Chromium(III) oxide (Cr\(_2\)O\(_3\)) is the most stable of several oxides of chromium, and occurs naturally in the mineral eskolaite. It has the corundum crystal structure, which consists of a slightly distorted hexagonally close packed lattice of oxygen anions, with the chromium cations filling up 2/3 of the octahedral sites. The oxide ions within
the lattice are tetrahedrally coordinated; this is advantageous for p-type conductivity as it helps to reduce the localisation of the O 2p electrons to the oxide ions [20, 111]. The material consists of alternating layers of chromium and oxygen atoms, as can be seen in Figure 2.6(a). The lattice parameters of Cr₂O₃ are \( a = 4.958 \) Å and \( c = 13.594 \) Å. These lattice parameters are favourable for the epitaxial growth Cr₂O₃ on the corundum structured Al₂O₃, which has lattice parameters of \( a = 4.759 \) Å and \( c = 12.992 \) Å. This results in a lattice mismatch of:

\[
\frac{\Delta a}{a} = \frac{a_{\text{film}} - a_{\text{substrate}}}{a_{\text{film}}} = 4.2\%
\]  

which is a large enough mismatch that epitaxial growth would not necessarily be expected. Reciprocal space map measurements show a very broad diffraction peak, with a small signal present at the position expected for strained growth [36]. The presence of this could indicate that the first few atomic layers of the material grow in a strained fashion. On the other hand, Transmission Electron Microscopy (TEM) images from the same work show stacking faults at the Al₂O₃/Cr₂O₃ interface suggesting that the Cr₂O₃ is not growing epitaxially on the Al₂O₃ and is adopting a different in-plane lattice parameter within the first few atomic layers. A misfit dislocation was also seen in the Cr₂O₃ film but as it was found to be located at a large distance from the interface (\( \sim 16 \) nm or \( \sim 70 \) atomic layers), it was assumed to be unrelated to the defective interface.

Cr₂O₃ is chemically stable, hard and brittle. It is also optically transparent due to its large bandgap of 3.4 eV. It has been grown in thin film form by MBE [36, 112], spray pyrolysis [37], magnetron sputtering [113], pulsed laser deposition [56] and chemical vapour deposition [114]. It has also been grown in the form of nanowires [115] and nanoparticles [116].

In its stoichiometric form it is an insulator, often reported to show native, yet very poor p-type conductivity [117]. Despite this report, no intrinsic conductivity was measured in any films grown in this work. The octahedral coordination of the Cr ions (with 3d⁶ configuration) splits these d levels into the \( t_{2g} \) and \( e_{g} \) levels, with the \( t_{2g} \) being occupied and the \( e_{g} \) unoccupied. This gives rise to transitions which are dipole forbidden, but quadrupole allowed, at the typical energies of 2.1 eV and 2.6 eV respectively. Even though these weak transitions give the material a slight green colour, it remains highly transparent throughout the visible spectrum in thin film form.

The conductivity of Cr₂O₃ can be improved dramatically by doping with magnesium [36], to values approaching 0.1 S cm⁻¹, while it has recently been reported that its optical properties can be improved by doping with nitrogen [109, 118]. Co-doping with nitrogen and magnesium has been found to result in an improvement to both
electrical and optical properties [37]. The carrier concentration has been estimated
to be $\approx 10^{22}\text{cm}^{-3}$. It has been shown by density functional theory calculations that
under oxygen rich conditions, magnesium is incorporated into the $\text{Cr}_2\text{O}_3$ lattice as a
substitutional dopant on a Cr site ($\text{Mg}_{\text{Cr}}$) [56]. The neutral state formation energy
of this defect is 0.67 eV, much lower than the n-type magnesium interstitial ($\text{Mg}_i$),
which has a neutral state formation energy of 6.78 eV. The calculations also indicate
that the $\text{Mg}_{\text{Cr}}$ defect remains uncompensated for all values of the Fermi level in the
band gap, implying that $\text{Cr}_2\text{O}_3$:$\text{Mg}$ should show p-type conductivity. In the oxygen
poor regime, the defect calculations predict that the two point defects compensate
each other deep in the band gap (1.92 eV above the valence band maximum), and
either no or very poor conductivity should be observed.

When grown with MBE, the conductivity of $\text{Cr}_2\text{O}_3$:$\text{Mg}$ is found to increase as
the oxygen pressure in the chamber is increased. The conductivity improvements are
seen to continue even up to the highest permissible pressure in the MBE system of
$\approx 5 \times 10^{-5}$ Torr. This is the most likely reason for the improved electrical properties
of the material when it is grown by pulsed laser deposition, as oxygen pressures
greater than $7.5 \times 10^{-2}$ Torr can be employed during growth. This behaviour is
expected for p-type oxides, as an increase in oxygen pressure can typically suppress
the formation of compensating defects, such as oxygen vacancies.

Despite the prevalence of $\text{Cr}_2\text{O}_3$ (commonly used as protective coatings for steel,
and as a constituent of green pigment), there are still open questions about the exact
value of the fundamental band gap of the material, and what the exact conduction
mechanism for Mg-doped $\text{Cr}_2\text{O}_3$ is. When thin films of doped or undoped $\text{Cr}_2\text{O}_3$
are grown, they take on a slight green colouration. This indicates the presence of
transitions within the material being approximately 2.1–2.5 eV, which corresponds
well with the forbidden transitions between the crystal split $d$-orbitals. When
undertaking measurements of the optical absorption coefficient of $\text{Cr}_2\text{O}_3$, the $\approx 3.4$ eV
transition is easily seen to be dominant, but the weak forbidden transitions can
also be observed$^9$. DFT calculations vastly underestimate the band gap of many
transition metal oxides due to their localised $d$-electrons which have a strong on-site
Coloumb interaction. These interactions are described by a $U$ parameter, the value
of which is chosen to match the DFT predicted band gaps to the experimentally
measured gap. This erodes the predictive power of DFT, and instead pushes the
problem of determining the band gap to the experimentalists. Work currently in
preparation by Norton et al. has combined high resolution UPS, absorption coefficient
measurements, and an ab-initio calculated $U$ parameter to find the fundamental gap
of $\text{Cr}_2\text{O}_3$. When the ab-initio $U$ parameter is utilised in standard DFT calculations,
a band gap of 2.1 eV is predicted. This agrees very well with the experimental results.

\footnote{$^9$an example of this measurement is shown in Figure 4.10 in Section 4.3.2.}
The conduction mechanism of Cr$_2$O$_3$ has been assigned as small polaron hopping by Farrell et al. [36], and as thermally activated band conduction by Kehoe et al. [56]. Theoretical calculations suggest that it is a heavy hole band conductor [119], but Cr$_2$O$_3$ fits the description of materials which usually possess small polaron hopping: strongly correlated transition metal oxides which have a multi-valence cation. As mentioned previously, distinguishing between these mechanisms is tough, due to the low mobility and conductivity of Cr$_2$O$_3$.

### 2.5.2 Copper-Chromium Oxide (Cu$_x$CrO$_2$)

The delafossite CuCrO$_2$ is a p-type TCO that has been reported to have a large conductivity of 220 S cm$^{-1}$ when doped with magnesium [22]. A related compound is the copper-deficient Cu$_x$CrO$_2$; this is simply CuCrO$_2$ but with a large amount of copper vacancies. Either stoichiometric or copper deficient material can exist as a rhombohedral polymorph with with space group R$ar{3}$m, or as a hexagonal polymorph with space group P6$_3$/mmc. Both forms can be described with a hexagonal unit cell with a similar $a$ lattice parameter (2.9734 Å for the rhombohedral polymorph, 2.9740 Å for the hexagonal polymorph [120, 121]) but with significantly different $c$ lattice parameters (17.100 Å for the rhombohedral polymorph, 11.400 Å for the hexagonal polymorph). The difference in $c$ lattice parameters arises due to the stacking sequence of the chromium layers in each polymorph; the chromium layers form an ABCABC stacking sequence in the rhombohedral structure but form an ABAB stacking sequence in the hexagonal structure. This results in the hexagonal structure having a $c$ lattice parameter equal to 2/3 of that of the rhombohedral one. This crystal structure combines several of the aspects which favour p-type conductivity: Cr−O$_6$ octahedra, tetrahedrally coordinated oxygen atoms, and O−Cu−O chains. These features can be seen for both stoichiometric and copper deficient material in Figure 2.12.

Doped and undoped CuCrO$_2$ have been grown by magnetron sputtering [22], chemical vapour deposition [122], spray pyrolysis [123], by a sol-gel process [124], atomic layer deposition [125], or by pulsed laser deposition [126]. In spite of the fact that the aforementioned magnetron sputtered films could reach the anomalous conductivity value of 220 S cm$^{-1}$, other attempts to grow this material with the same method resulted in conductivity values two orders of magnitude lower [127]. The only other report of highly performing CuCrO$_2$ was when it was doped with 10% magnesium and grown by pulsed laser deposition. Even so, these films only reached a conductivity of $\sim$67 S cm$^{-1}$; all other deposition methods resulted in a conductivity closer to 1 S cm$^{-1}$, even when doped with magnesium [123] or zinc [128].

One particularly interesting variant of CuCrO$_2$ is the copper deficient Cu$_x$CrO$_2$,
Figure 2.12: Crystal structure of the rhombohedral polymorph of CuCrO$_2$ and Cu$_{0.4}$CrO$_2$. The black line indicates the boundary of the unit cell. Four unit cells are shown. Several atoms in neighbouring unit cells are included so as to not leave any incomplete octahedra. Chromium atoms are shown in green, copper atoms in blue, and oxygen atoms in red. (a) Delafossite CuCrO$_2$. The Cr–O$_6$ octahedra and O–Cu–O chains are easily visible. (b) The same structure, but with approximately 60% of the copper atoms removed at random to give Cu$_{0.4}$CrO$_2$.

where $x \approx 0.4 - 0.5$. This material, despite any extrinsic doping, has a conductivity of 12–17 S cm$^{-1}$ [38, 129], greater than the undoped material. It has also recently been shown that a conductivity of up to 100 S cm$^{-1}$ is achievable with this material when grown on single crystal substrates [130]. Despite this high conductivity, the measured hole mobility was still approximately 0.1 cm$^2$ V$^{-1}$ s$^{-1}$, with a concomitant high carrier concentration of $10^{21}$ cm$^{-3}$. It has been grown by both spray pyrolysis [38, 110] and chemical vapour deposition [129, 131], although in the spray pyrolysis paper by Farrell et al., it was noted that the growth of the material proceeds even when the direct line of sight from spray nozzle to substrate is blocked, indicating that the growth might actually be proceeding in a chemical vapour deposition-like fashion [110]. The best performing films were found to have a copper/cation ratio, Cu/(Cu+Cr) of 30-40%, where a ratio of 50% would indicate a stoichiometric material.

The copper deficient material is grown at a low temperature of $\sim 345$ °C to inhibit the formation of the spinel phase CuCr$_2$O$_4$. This parasitic phase is easily detected as it has a high optical absorption coefficient, and will produce noticeably darker films. This low growth temperature is advantageous as it allows the growth on flexible polyimide substrates, which begin to degrade above 400 °C. The growth kinetics of the material are unusual - at a substrate temperature of 345 °C the growth is controlled by the amount of copper precursor in the growth solution - if no copper is
present, no film growth occurs. Once copper is introduced, film growth begins, and the copper content of the films (as measured by x-ray photoelectron spectroscopy) is larger than that expected if the film grew with the same cation stoichiometry of the growth solution. The copper content of the grown films saturates at about 30%, corresponding to a stoichiometry of $\text{Cu}_{0.43}\text{CrO}_2$. This type of growth implies that the chromium chemical precursor has a very low sticking coefficient on a chromium terminated surface at a temperature of 345°C, but will readily decompose on a copper terminated surface. The introduction of copper enables the crystal structure to grow in an $A$-$B$ stacking sequence (where $A$ are chromium containing layers and $B$ are copper containing layers) similar to Figure 2.12(a).

It would be expected from the presence of a significant amount of copper vacancies and the low growth temperature that the grown films would be amorphous, but the growth kinetics suggest that the growth should grow in an $A$-$B$-$A$... sequence, which should introduce some order and thus crystallinity. It is seen that the grown material’s overall structure is an unconventional combination of both - Raman spectroscopy results suggest that there is a large amount of disorder in the inter-atomic bonds, as would be expected for an amorphous material, but x-ray diffraction results show that there is some long-range crystallographic order, and furthermore, that the grown films have an average coherent domain size of $7 \pm 3$ nm. Materials which possess these extremely small crystalline domains are termed nanocrystalline.

Recent work by Popa et al. demonstrated the growth of $\text{Cu}_x\text{CrO}_2$ by chemical vapour deposition on single crystal $\text{Al}_2\text{O}_3$ substrates, which resulted in films with improved crystallinity [130]. This could be improved further still by high temperature annealing (900°C) in an argon atmosphere. They found through elemental analysis performed via electron energy loss spectroscopy that while the grain boundaries of a film contained stoichiometric $\text{CuCrO}_2$, within the individual crystal grains of their deposited films there was in fact an excess of chromium in addition to a copper deficiency, resulting in a stoichiometry of $\text{Cu}_{0.66}\text{Cr}_{1.33}\text{O}_2$. X-ray photoelectron spectroscopy measurements (which provides a stoichiometry value averaged over a large amount of crystal grains) supported this result. Atomically resolved scanning transmission electron microscopy was able to show that rather than a random distribution of copper vacancies throughout the material, as is shown in Figure 2.12(b), rows of many adjacent copper atoms were missing from the crystal structure. The high conductivity of these crystalline samples was suggested to result from the rows of these copper vacancies. Further evidence was provided by examining the films which had been annealed at high temperatures; the rows of copper vacancies had disappeared, and resulted in a concomitant large reduction in the conductivity, from $10^2$ S cm$^{-1}$ to $10^{-4}$ S cm$^{-1}$.

Whether the film is grown in its nanocrystalline or normal crystalline form, it
is one of the highest performing p-type TCOs to date, with the synthesis of the nanocrystalline material being particularly facile and suitable to upscaling.
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Chapter 3

Experimental Methods

3.1 Molecular Beam Epitaxy

Molecular Beam Epitaxy (MBE) is a technique used for growing thin films of various materials, with precise control over properties such as thickness, stoichiometry, and crystal phase. In essence, the materials of choice are evaporated in Ultra High Vacuum (UHV)\(^1\), and the resultant evaporant flux impinges on a substrate, which is typically a single crystal held at high temperature. A wide range of materials, from simple metals to quaternary oxides have been synthesised using MBE (a paper by Schlom alone gives examples of \(\sim 100\) oxides grown by MBE in the past 40 years [1]). What distinguishes MBE from other growth techniques is its low growth rate, typically 1-10 monolayers per second, and precise control over the starting and stopping of growth. This low growth rate, combined with the UHV conditions and short evaporation source to substrate distances of \(\sim 0.2\) m result in the evaporated species being in the molecular flow regime. Molecules and atoms are said to be in this regime when the mean free path of these evaporated species is larger than the distance from the evaporation source to the substrate, i.e., the atoms in the evaporated flux can be considered to be non-interacting.

The term ‘Molecular Beam Epitaxy’ was first coined in 1970 by Alfred Cho, a man who is known as the father of MBE [2]. The phrase ‘Molecular Beam’ refers to the fact that the constituents of the evaporated species are in the molecular flow regime, while ‘epitaxy’ originates from the Greek words \(epi\), which means ‘above’ and \(taxis\), which means ‘in an ordered manner’ [3].

Epitaxy comes in two forms: homoepitaxy, where the substrate and grown film are the same material (e.g., GaAs on GaAs), or heteroepitaxy, where the substrate and film are different materials (e.g., \(\text{Cr}_2\text{O}_3\) on \(\text{Al}_2\text{O}_3\)). True epitaxy is only achieved when the crystal lattice parameters of the substrate and film are equal or very close.

---

\(^1\)Ultra High Vacuum is typically considered as pressures lower than \(1 \times 10^{-9}\) Torr
Figure 3.1: Three of the different forms of epitaxy. Each block represents a unit cell of the substrate (white) or film (grey). The substrate shown here is cubic with lattice parameter \(a\). (a) Homoepitaxial film. The overlayer has the same lattice parameters as the substrate (b) Strained heteroepitaxial film. Here the overlayer has its in-plane lattice parameter fixed to that of the substrate’s, while it retains its intrinsic out-of-plane lattice parameter (c) Fully relaxed heteroepitaxial film. In this example, the film has as an in-plane lattice parameter equal to 90\% of the substrate’s.

The lattice mismatch between the two is defined as

\[
\frac{\Delta a}{a} = \frac{a_{\text{substrate}} - a_{\text{film}}}{a_{\text{substrate}}} \tag{3.1}
\]

where \(a_x\) refers to the in-plane lattice constant. If the lattice mismatch is negligible, the film will grow epitaxially on the substrate. For many film/substrate combinations, the film will grow with its lattice parameter strained to that of the substrate until a certain critical thickness, where it then becomes more energetically favourable to form defects such as edge dislocations, screw dislocations, or grain boundaries than for the film to be strained by the substrate. An example of homoepitaxy and heteroepitaxy is shown in Figure 3.1.

Ideally, the growth of a thin film would proceed in a layer by layer fashion, where a complete layer is fully formed before the growth of a subsequent layer commences. This is known as Frank-van der Merwe growth. This growth mode occurs if the force between atoms that have landed on the surface (adatoms) and the atoms that are part of the surface is stronger than the force between adatoms. Alternatively, the inter-adatom force can be greater, which lead to adatoms agglomerating to form 3-dimensional islands. This is known Volmer-Weber growth. There is also an intermediary growth mode known as Stranski-Krastanov growth. This occurs when a film begins to grow layer by layer, but after a critical thickness begins to form islands. This critical thickness is similar to the ‘defect formation’ critical thickness, but it depends on other factors such as surface and interface formation energies as well as strain, so that the two are not necessarily the same [4].

Growth of thin-film oxides was carried out in a DCA M600 MBE system with a
base pressure of $5 \times 10^{-10}$ Torr, and the ability to grow on substrates up to 1 inch in diameter. A schematic of this MBE is shown in Figure 3.2.

The system has two chambers: a load-lock, which is used for loading samples, and a main deposition chamber, where deposition is performed. In the main chamber there is a four pocket electron beam evaporator with each pocket holding up to 7 cm$^3$ of material, a large 25 cm$^3$ single pocket electron beam evaporator, and the capability to install up to five Knudsen-cells. The power supplies for both electron beam evaporators can deliver up to 1 A of current at 8 kV. Each evaporation source has a pneumatically controlled shutter to allow precise stopping and starting of layer growth, and there is also a pneumatically controlled main shutter to shield the substrate from all evaporation sources simultaneously. Both of the electron beam evaporators have a water-cooled quartz crystal monitor positioned above them in such a way that the evaporation rate can be measured without having to open the shutter that would expose the substrate to the evaporating material flux. Each crystal monitor has its own shutter to prolong the life of the crystal. There is a separate crystal monitor attached to a UHV-compatible linear drive, which allows movement of the crystal monitor to the typical substrate growth position. This enables growth rates from the Knudsen cells to be measured. In this work, only electron beam evaporators were used, as the high oxygen pressures necessary for the growth of p-type oxides could oxidise and damage the filaments of the Knudsen cells.

In addition to this, the main chamber is equipped with a large volume cryopanel, and a water cooled panel between the top and bottom halves of the chamber to help prevent thermal cross-talk between components. The substrate manipulator provides linear motion, rotation via a magnetic coupling, and contains an oxygen-resistant high temperature heater capable of reaching $\sim 850^\circ$C. In-situ monitoring tools include a Reflection High Energy Electron Diffraction (RHEED) set-up and a residual gas analyser.

Pumping for the system is completely oil-free, and in the main chamber consists of a 5001 s$^{-1}$ triode ion pump, a 10001 s$^{-1}$ turbomolecular pump, and a scroll pump which acts as a roughing pump and a backing pump for the turbomolecular pump. The load-lock has a base pressure of $\sim 1 \times 10^{-7}$ Torr and is pumped by a 701 s$^{-1}$ turbomolecular pump, and also has a scroll pump for rough pumping and to back the turbomolecular pump. Pressure measurement is performed by means of a hot-cathode ionisation gauge in the main chamber, and a pirani and hot-cathode ionisation gauge in the load-lock.

Introduction of gas into the main chamber, such as oxygen for metal oxide growth, is performed by opening a manual leak valve connected to a high-purity gas supply until the desired gas flow/chamber pressure was reached. This leak valve is connected to a microwave plasma source. This source creates a high density plasma
by generating 2.45 GHz microwaves and coupling these microwaves into a coaxial feedthrough structure which guides the microwaves into an alumina plasma chamber, which is inside the UHV environment of the main chamber of the MBE. External gas is fed into this plasma chamber through a capillary. This plasma chamber is surrounded by magnets in a quadrupole configuration which generate an 87 mT field inside the chamber. This field strength causes electrons in a 2.45 GHz microwave field to undergo electron cyclotron resonance motion. By having the electrons move in this spiralling motion, the electron path length and thus probability of collision with molecules in the plasma chamber is greatly enhanced, helping to keep the plasma ignited. The plasma primarily serves to split molecular oxygen into the more reactive atomic oxygen and to produce oxygen ions.

The plasma source function is primarily determined by the nature of the aperture placed between the plasma chamber and the MBE main chamber. By using an aperture with small enough holes, the oxygen ions produced in the plasma chamber will be thermalised on contact with the boundaries of these holes when exiting the plasma chamber and continuing to travel towards the substrate. This results in a beam of oxygen atoms.

If instead an aperture with large holes is used, oxygen ions can directly exit the plasma chamber without becoming neutralised. The ion flux is typically enhanced by extracting the ions using a high voltage applied to a grid above the aperture. Typical aperture hole diameters are 0.2 mm for atomic mode and 2 mm for ion mode. The number of holes in the aperture depends on the flux/pressure requirements, but a typical value is 20–100 holes in a 5 cm diameter circular aperture. The plasma source in this work is a hybrid source, that is, it has the small hole aperture used to create an atomic beam, but is also equipped with an ion extraction grid, allowing the addition of a small component of ions to the atomic beam. The ratio of ions to atoms in the produced flux can be somewhat controlled by altering the incoming gas flow; at high gas flows many of the ions produced will either be scattered or neutralised. When an MBE is equipped with such a plasma source, the technique is often referred to as Plasma Assisted Molecular Beam Epitaxy, or PA-MBE.

During the project the gas delivery system to the MBE was improved upon by introducing two mass flow controllers into the gas supply system. This has the advantages of increased accuracy and repeatability, and allows the introduction of two gases simultaneously into the growth chamber. If the plasma source is not turned on, the gas introduced simply leaves the alumina plasma chamber through the aperture and arrives at the substrate. A gas flow of $\sim2 \text{ cm}^3 \text{ min}^{-1}$ results in a chamber pressure of $\sim4 \times 10^{-5} \text{ Torr}$. 

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Figure 3.2: A schematic of The DCA M600 MBE system. Here, the main shutter is closed, interrupting any growth. The shutter for the multi-pocket electron beam evaporator is open, while the shutter to the single pocket evaporator is closed. For clarity, some features such as the load-lock chamber and Knudsen cells are not shown.

3.2 Spray Pyrolysis

Spray pyrolysis is a much less sophisticated growth technique than MBE, but while it lacks precise control UHV conditions and typically produces polycrystalline/amorphous films, its strength lies in its cost effectiveness, simplicity, and speed. In its simplest form, spray pyrolysis is a process where a thin film is deposited by spraying a solution onto a heated substrate. The spraying can be performed in atmosphere, or under a controlled gas or vacuum environment. The chemical precursors used are chosen so that any unwanted by-products that form on the substrate are volatile at the chosen deposition temperature [5]. Typical chemical precursors are metal salts, which are dissolved in water or an organic solvent, diluted to low molarities of less than 0.1 mol.

The spray pyrolysis system used was home built. The deposition was performed in a large (18×18×18 inch) cubic stainless steel chamber with an air assisted atomiser nozzle placed at a distance of 30 cm from a large area hot plate. Despite the large area of the hot plate (∼10 × 10 cm), slight temperature differences were present across the heated surface. The growth position which provided the best thin film properties was found by growing on multiple substrates simultaneously to locate this position. Liquid flow to the nozzle was controlled by a peristaltic pump, typically...
operating with a flow rate of 1.66 ml min$^{-1}$. Mass flow controllers were used to regulate gas flow to the nozzle. By mixing compressed air and nitrogen, the oxygen concentration within the chamber could be controlled. An oxygen sensor was used to monitor the oxygen concentration. The deposition temperature was measured by means of a type K thermocouple inserted into a copper block which was in contact with the surface of the hotplate. The hotplate temperature was held within 10°C of the chosen setpoint by a Proportional-Integral-Derivative (PID) controller which regulated the power delivered to the hotplate.

### 3.3 Photoelectron Spectroscopy

The photoelectric effect is one of the key experimental observations which demonstrate the failure of classical physics and necessitates quantum theory to fully understand it. Experiments in the late 19th and early 20th century found that when light was shone on a piece of metal placed in a vacuum enclosure, electrons would be emitted from the surface. The maximum energy of these electrons could be measured by biasing a metal collecting plate held near the electron-emitting metal, and electrically connecting the two via an external circuit. At zero bias, some emitted electrons would arrive at the collector, resulting in a measurable current. As the collector bias was made increasingly negative, there would be a point where none of the emitted electrons would have enough energy to overcome the potential difference between the emitter and collector. The voltage at this point is equal to the maximum kinetic energy of the emitted electrons. An example schematic of the apparatus used is shown in Figure 3.4.

Reasoning at the time would have predicted that if the intensity (i.e., the energy)
of the incident light was increased, then a similar increase in the energy of the
electrons emitted from the surface would be observed. This was found to not be true;
instead, only an increase in the number of electrons emitted from the surface was
detected. It was in 1902 that Lenard found that the energy of the emitted electrons
increases with the frequency of the incident light [6]. In 1905, Einstein expanded
on the earlier work of Planck, and devised a theory for the photoelectric effect by
viewing light as discrete quanta of energy rather than waves. This earned him the
1921 Nobel Prize\(^2\). These discrete quanta of energy were given the name photons,
where the energy \(E\) of a photon is given by

\[
E = h\nu = \hbar\omega
\]

(3.2)

where \(h\) is Planck’s constant, \(\nu\) is the frequency of the light, \(h = h/2\pi\) and \(\omega = 2\pi\nu\).

It was also assumed by Einstein that it takes a certain minimum amount of energy
for an electron to escape a material (now know as the work function, \(\phi\)) and that
the difference between this and the energy of the incident photons will be given to
the electrons as kinetic energy, \(E_{\text{kin}}\). Thus, for the most energetic electrons emitted
from a sample:

\[
\hbar\omega = E_{\text{kin}} + \phi_{\text{sample}}
\]

(3.3)

Modern Photoemission experiments are not too dissimilar from the experiments
performed in the early 20\(^{th}\) century, although the apparatus has been much improved.
The three main differences are:

1. The incident photon source used is now an x-ray source, leading to the technique
   being named X-ray Photoelectron Spectroscopy (XPS). The x-ray emission
   from either aluminium or magnesium is the most common source, and it is

\(^2\)http://www.nobelprize.org/nobel_prizes/physics/laureates/
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Figure 3.5: The inelastic mean free path of electrons in various material classes. The curves shown are obtained by finding the least squares fit of the general equation $AE^{-2} + B\sqrt{E}$ to measured data. $A, B$ are material-class dependent constants, $E$ is electron energy. Adapted from Seah & Dench [7].

often monochromated at the $K_\alpha$ energy, to provide improved resolution. This gives a light source with an energy of 1253.7 eV for magnesium or 1486.7 eV for aluminium.

2. Photoemission is usually performed under UHV conditions. The majority of photoelectrons which escape the material originate in the topmost few nanometres, as can be seen by the electron Inelastic Mean Free Path (IMFP). This is the average distance an electron of a given energy can travel between inelastic collisions and is shown in Figure 3.5 as a function of electron energy. Approximately 68% of all photoelectrons originate from a depth of one IMFP, while 99.7% originate from a depth of three IMFPs. This requires a clean surface and thus UHV conditions, as any surface contaminants will produce photoelectrons from undesired material.

3. Electron energy analysers have been developed which allow the measurement of the energies of all emitted photoelectrons, not just the most energetic ones. Typical energy resolution is better than 1 eV.

The use of an X-ray photon source enables the excitation of electrons which originate from the core levels of the materials under investigation. If this core level is at a binding energy $E_B$ relative to the Fermi level of the material, then Equation 3.3 is modified to

\begin{align}
    \hbar \omega &= E_{\text{kin}} + \phi_{\text{sample}} + E_B \quad (3.4a) \\
    E_B &= \hbar \omega - E_{\text{kin}} - \phi_{\text{sample}} \quad (3.4b)
\end{align}
Figure 3.6: X-Ray photoelectron spectra of a silicon sample with a small amount of surface oxidation. The x-ray energy is 1486.7 eV. The main spectral features are highlighted. The large signal within the light grey rectangle is due to the low kinetic energy secondary electrons.

Hence by measuring the kinetic energy of the photoelectrons, their binding energy can be easily calculated. Core levels occur at certain specific energies for each element, so by analysing the binding energy of the electrons originating from these core levels and comparing them to tabulated values, the elemental composition of a material can be measured [8]. Furthermore, quantitative elemental analysis can be performed by comparing the photoemission signal intensities of each element present (weighted by their respective relative sensitivity factors).

While the binding energy of an electron depends on which core level it originates from, it also depends on the oxidation state of the atom from which it originates, and its chemical environment. These result in small shifts in the binding energy of an electron; the ability to detect these shifts is one of the major strengths of XPS.

A typical x-ray photoelectron spectra is shown in Figure 3.6. Here, the material under investigation is silicon, with a small amount of surface oxide present. The main core levels are highlighted. Other features in the spectrum include a continuous background which is due to secondary electrons, minor peaks due to electrons arising from auger emission, ‘plasmon’ peaks which occur from photoelectrons which have lost energy to the conduction electrons in the material, and shake-up and shake-off structures which are related to the resulting ionisation state of the atom after the photoelectron is ejected [9].

While $E_{\text{kin}}$ is the kinetic energy of the electron after leaving the sample, it will in general not be equal to the kinetic energy measured by the electron analyser, $E'_{\text{kin}}$. This is because the analyser will have a work function that will most likely not be the same as the sample under analysis. This leads to a contact potential between sample and analyser. From Figure 3.7 it can be seen that:

\[ E_{\text{kin}} = E'_{\text{kin}} - \phi \]
Chapter 3. Experimental Methods

Figure 3.7: Energy level diagram for a metallic specimen in electrical contact with a spectrometer. The red line indicates the total energy of the electron. The core level to Fermi level distance in the sample has been vastly decreased for clarity. An analogous diagram exists for semiconducting and insulating samples; the difference being that the Fermi level would be located within the band gap.

\[ \phi_{\text{analyser}} + E'_{\text{kin}} = \phi_{\text{sample}} + E_{\text{kin}} \]  
\[ E'_{\text{kin}} = E_{\text{kin}} - (\phi_{\text{analyser}} - \phi_{\text{sample}}) \]

Where \( \phi_{\text{analyser}} \) is the analyser work function. The \( E_{\text{kin}} \) term can be removed by modifying Equation 3.4b to \( E_{\text{kin}} = h\omega - E_B - \phi_{\text{sample}} \) and substituting this to obtain:

\[ E'_{\text{kin}} = h\omega - E_B - \phi_{\text{sample}} - (\phi_{\text{analyser}} - \phi_{\text{sample}}) \]

\[ E'_{\text{kin}} = h\omega - E_B - \phi_{\text{analyser}} \]

Thus only the analyser work function, and not the sample work function needs to be known [10].

In fact, Equation 3.6 can be simplified by measuring the Fermi edge of a metallic sample, and defining this as \( E_{\text{kin}} = h\omega \), or equivalently, \( E_B = 0 \). This calibration places all features of the spectrum at their kinetic energies before they left the sample. The electron kinetic energy and binding energy are then related by

\[ E_{\text{kin}} = h\omega - E_B \]
The work function of a sample can be determined by measuring the energy of the lowest kinetic energy electrons. These will be secondary electrons which have lost all their energy through inelastic collisions save for just enough to overcome the work function and leave the surface with approximately zero kinetic energy\(^3\). While XPS can be used to measure the work function of a sample, Ultraviolet Photoelectron Spectroscopy (UPS) is more commonly used for this task due to its inherent higher resolution.

### 3.3.1 Ultraviolet Photoelectron Spectroscopy

Ultraviolet Photoelectron Spectroscopy is essentially the same technique as XPS, but with a different photon source energy. The most common ultraviolet source used is the He I line from a helium discharge lamp, which has an energy of 21.2 eV. Gas discharge lamps are used as they provide a very high intensity and high resolution. Due to the low photon energy, UPS is used to analyse electrons that originate in the valence band, and very shallow core levels of the material.

When examining the secondary edge region of a sample with UPS to determine its work function, two secondary edges will in fact be seen, making it difficult or impossible to determine the position of the secondary edge of the sample. While one of these is from the sample, the other is due to secondary electrons produced in the analyser itself, originating from collisions of photoelectrons with the analyser surfaces. These secondary electrons will not be affected by the contact potential between sample and analyser, and so will appear at lower kinetic energies. They can however be removed from the spectra by applying a bias of a few volts (typically 5 V or 10 V) between the sample and the analyser. This will accelerate all photoelectrons emitted from the sample, but will have no effect on the analyser secondary electrons as they originate from the analyser. This serves to ‘separate’ the analyser secondary edge from that of the sample, making work function measurements possible.

### 3.3.2 Omicron Multiprobe XPS

XPS measurements were performed on an Omicron Multiprobe XPS system, shown schematically in Figure 3.8. It consists of a fast entry load lock for loading samples, along with a sample preparation and analysis chamber, both with base pressures better than \(3.75 \times 10^{-11}\) Torr. The preparation chamber contains facilities for high temperature sample annealing, low energy argon ion sputtering, low energy electron diffraction and thin film growth. The main features of the analysis chamber are a dual filament X-ray source with aluminium anode, a quartz crystal monochromator, and a dual channeltron detection system.

\(^3\)The secondary edge is not shown in Figure 3.6. The edge is usually very intense, and as these high count rates will age the channeltrons this portion of the spectrum is generally not measured.

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Cross section of Hemispherical Analyser

Figure 3.8: A schematic of the Omicron Multiprobe XPS highlighting its main features

hemispherical electron energy analyser. The sample, x-ray source and monochromator crystal all lie on a 500 mm diameter Rowland circle. The monochromater is aligned to select the aluminium $K_{\alpha1}$ emission line.

The generated photoelectrons enter a dual electrostatic lens system before entering the HemiSpherical Analyser (HSA). The first of these lenses selects the analysis area of the sample, and defines the angular acceptance of the analyser. The second lens retards the photoelectrons by an certain amount set by the lens voltage. The electrons then enter the HSA, which consists of two concentric hemispheres of radii $R_1$ and $R_2$, with a mean radius of $R_0$ as shown in the inset of Figure 3.8. The inner hemisphere is negatively biased and the outer positively with respect to $V$, the median equipotential surface between the hemispheres. This results in an inverse square field between the hemispheres. The HSA thus acts as a bandpass filter, only allowing electrons with the pass energy $E_p$ to reach the detector. The pass energy is given by:

$$E_p = \frac{eV}{\left(\frac{R_2}{R_1} - \frac{R_1}{R_2}\right)}$$

(3.8)

Typical values of the pass energy are between 20–50 eV depending on the required resolution (with lower pass energy providing better resolution). By varying the voltage on the retarding lens, the amount of retardation is changed, and electrons
possessing the kinetic energy of interest can be made to have an energy equal to the pass energy and subsequently reach the detector, while all other electrons are rejected. This mode of operation is known as constant analyser energy mode.

The electron detector is a set of five electron multipliers (channeltrons) placed across the exit plane of the analyser, which provide a gain of $10^7$–$10^8$. The binding energy scale of the system is calibrated by measurement of the Fermi edge of a silver single crystal.

### 3.4 Band Alignment

Knowledge of the surface band structure is paramount when forming heterostructures of materials. During the Nobel lecture of Herbert Kroemer, he explicitly defined a heterostructure as a structure in which the interface which plays an essential role in a device’s operation. It is in this lecture that he also famously coined the phrase ‘the interface is the device’ [11]. The development of MBE helped to spur experimental and theoretical interest in the electronic structure of such abrupt interfaces [12].

The technique of photoelectron spectroscopy readily allows the measurement of the valence band maximum, work function and ionisation potential of a material, providing insight into the band structure of a material at its surface. Of interest is the valence band offset (VBO) or conduction band offset (CBO) between two materials, as this offset will establish the charge carrier transport properties across the interface between the two materials. Knowledge of these offsets can aid device design through correct material choice.

One way of predicting the band offset between two materials is known as Anderson’s rule. This states that the conduction/valence band offset should be equal to the difference in electron affinity between the two semiconductor surfaces [13]. While it provides a reasonable estimate, it rarely agrees with experiment, even failing for the prototypical heterojunction of GaAs/Al$_x$Ga$_{1-x}$As. As an example, the difference in VBO measured by photoelectron spectroscopy and calculated by Anderson’s rule for films of silicon and germanium on various substrates is shown in Figure 3.9. The typical measurement accuracy is $0.1\text{ eV}$ or better. In most cases there is a large discrepancy between Anderson’s rule and experiment, with some cases having a predicted offset which would result in completely different heterojunction behaviour to that observed. Reasons for this inaccuracy include not taking into account the chemical bonding or the lattice matching at the interface, and also that the electron affinity is defined as between a material and vacuum, not between a material and the interface with another material.

The most simple form of measuring the VBO would be to measure the energetic position of the valence band maximum relative to the Fermi level of the chosen
substrate, then perform the same measurement as the overlayer thickness is increased, to gain a picture of the valence band maximum evolution with thickness. This, however, can not be performed on all material systems; once a portion of the overlayer has been deposited, the valence band maximum measurement will contain contributions from both materials. Only when materials have their valence band maximum separated by a significant energy (∼1 eV) will the two separate valence band maxima be able to be deconvoluted. A heterojunction where this method proves useful is Si on CdS, as seen in Figure 3.10 [14].

The alternative, and more often used way of measuring band offsets is through the Kraut Method [15, 16]. This is a method which relies on core level measurements of the materials, and infers the valence band maximum position through these measurements. This can be understood by referring to Figure 3.11. It can be seen that the core level to valence band maximum separation ($E_{CL} - E_{VBM}$) of a material is a quantity that remains constant as the interface is developed. Thus, by starting with a measurement of the core level and valence band maximum position in the bulk material/substrate and then measuring the binding energy of the core level as the interface is grown, the valence band maximum position can be calculated as ($E_{CL} - E_{VBM}$) remains constant:

$$E_{CL}(i) - E_{VBM}(i) = E_{CL} - E_{VBM}$$ (3.9a)

$$E_{VBM}(i) = E_{CL}(i) - (E_{CL} - E_{VBM})$$ (3.9b)

This can be measured for both substrate and overlayer as long as the overlayer thickness is small enough to allow photoelectrons from the substrate to escape. From this, values for the VBO, and for the band bending, $V_{BB}$ can be calculated. The valence band offset ($\Delta E_{VBM}$) between say, material $x$ and material $y$ is given by
Figure 3.10: The Band Alignment of Si on CdS. (a) The valence band maxima of a clean CdS surface and the same surface with increasing thicknesses of Si deposited on the surface. The Fermi level is at a binding energy of 0 eV. The VBM is found from the intersection of the leading edge of the spectra and the background, and is marked by thick black bars. The VBM can be resolved for each material at intermediate thicknesses. (b) The variation in VBM position of both Si and CdS, calculated from the data in panel (a). The band bending at the interface is indicated by dashed lines and arrows. (c) The resulting band diagram of the CdS/Si interface. Adapted from Katnani & Margaritondo [14].

\[ \Delta E_{\text{VBM}}(i) = (E_{\text{CL}} - E_{\text{VBM}}^y) - (E_{\text{CL}}^x - E_{\text{VBM}}^y) - \Delta E_{\text{CL}} \]  
\[ (3.10) \]

where

\[ \Delta E_{\text{CL}} = E_{\text{CL}}^y(i) - E_{\text{CL}}^x(i) \]  
\[ (3.11) \]

Measurements of the VBO are ideally carried out at various overlayer thicknesses, to study how the band bending progresses as the heterojunction is formed. The band bending is due to the charge distribution that will occur at the formation of an interface (whether it is with another material or with vacuum), and Poisson’s equation predicts that all bands and energy levels will bent by the same amount. This allows the CBO to be calculated by measuring the bulk band gap of each material, typically with ultraviolet-visible spectroscopy. Combining Equation 3.9b with the bulk band gap produces:

\[ E_{\text{CBM}}(i) = (E_{\text{CL}} - E_{\text{VBM}}) + E_k - E_{\text{CL}}(i) \]  
\[ (3.12) \]
Figure 3.11: Band alignment of a material near its interface. The hatched rectangle represents an interface with vacuum, metal, semiconductor, or insulator. \( E_{\text{CL}}^x, E_{\text{VBM}}^x, E_{\text{CBM}}^x \) represent the core level, valence band maximum, and conduction band minimum measured relative to the Fermi level, \( E_F \). Values measured at the interface are marked with \( (i) \). The fundamental band gap is indicated by \( E_g \), and the band bending by \( qV_{\text{BB}}^x \). The width, i.e., the spatial extent of the band bending in the material, is represented by \( W \). Adapted from Kraut et al. [15].

The original paper by Kraut [15] uses a theoretically calculated, broadened density of states which is fit to the edge of the valence band to determine the valence band maximum. While theoretically ideal, this approach is very computationally expensive for many materials, especially those where dopants are present with a concentration of a few atomic percent, as is the case for many functional oxides. This necessitates the use of a large supercell during calculations to correctly include the effect of the dopant, making these calculations unfeasible. The alternative method is to fit a line to the leading edge of the valence band, and take the intercept of this with the background as the valence band maximum. In fact, this method, despite its apparent crudeness, has been shown for several oxides to give more physically reasonable results when compared to the original Kraut method [17]. The measurements in this paper also include only one measurement to determine the VBO, where the overlayer has a thickness of \( 20 \, \text{Å} \). This is justified in this case as for the materials chosen for the band alignment demonstration (germanium on gallium arsenide), the
spatial extent of the band bending can be predicted from the carrier concentration of the overlayer to be on the order of $\sim 1000\,\text{Å}$, making a measurement at 20 Å close to the true ‘interface’ value. This will not be true for all materials; the band offset should be measured as a function of overlayer thickness to see the full extent of the band bending. Here, the term ‘band alignment’ will refer to when the band offset is measured as a function of overlayer thickness near the interface, while ‘band offset’ will be used for when a band offset measurement is performed at a single overlayer thickness.

### 3.5 Portable UHV Transfer System

It can be shown from kinetic gas theory that the impingement rate ($\Phi$) of a gas on a surface can be given by

$$\Phi = \frac{P}{\sqrt{2\pi mk_B T}} \left( \text{cm}^{-2}\text{s}^{-1} \right) \quad (3.13)$$

Where $P$ is the gas pressure, $m$ is the mass of an impinging gas atom, $k_B$ is Boltzmann’s constant, and $T$ is the temperature of the gas. By assuming that every impinging gas atom sticks to the surface and has a molecular diameter of 300 pm, the time to form a monolayer can be expressed as [18]

$$\text{Monolayer formation time} = 2.5 \times 10^{-6} \frac{P(\text{torr})}{s} \quad (3.14)$$

It can be seen that to keep a surface free from contaminants for a period of one hour, it must be in a vacuum better than $7 \times 10^{-10}\text{Torr}$ or $1 \times 10^{-9}\text{mbar}$. Keeping a clean surface is vital when using XPS to measure the band alignment of a pair of materials; any surface adsorption can have a major effect on the band bending at the surface and will lead to an incorrect interpretation of band alignment results [19, 20]. Typical surface contaminants include surface oxidation (for metal, or metal terminated surfaces), adsorbed carbon compounds, and adsorbed hydroxide species.

To move samples from the MBE to the XPS system without breaking vacuum a portable UHV transfer system was developed. It consists of a magnetically coupled linear/rotary drive with a stroke of 609 mm, a 20 l s$^{-1}$ Ion Pump, a gate valve and a port aligner. A gripping mechanism is attached to the end of the linear drive and is actuated by rotating the drive. The mechanism engages or unlocks when there is resistance during rotation, i.e., when the sample holder is being held in free space it will rotate with the linear drive, but if the sample holder is held against a surface the increased resistance will cause the drive rotation to lock/unlock the gripping mechanism. The sample holder is gripped by its ‘nipple’, which is shown
Figure 3.12: Photographs of (a) the original MBE sample holder for 10x10mm substrates, (b) the new, modified MBE sample holder (c) the original XPS sample holder, (d) the newly designed XPS sample holder, (e) the backside of the new XPS sample holder.

circled in Figure 3.12(c). All components are connected with ConFlat (CF) 35 mm inner-diameter flanges. The transfer system connects to the load lock on both the MBE and XPS. As the MBE and XPS are in the same room, the ion pump can remain powered during movement of samples from one system to the other. As the ion pump provides a pressure reading by measuring the current in the pump, a separate pressure gauge is not necessary. In future, a non-evaporable getter pump will be added to the system. This will aid the base pressure of the transfer system and will enable the transfer of samples between systems which are located in other rooms, such as the scanning tunneling microscope and magnetron sputtering tool. The transfer system has a base pressure better than $1 \times 10^{-9}$ mbar after bake-out. A sample spends approximately 1–2 h in the transfer system. While this includes the time to vent the loadlock of the MBE so that the transfer system can be removed, and the physical movement and attachment of the transfer system to the XPS, the majority of the time is spent waiting for the XPS loadlock to be pumped down to an acceptable pressure ($<1 \times 10^{-7}$ mbar) to minimise the risk of contaminating the transferred sample.

A picture of the original sample holders for the MBE and XPS and their sizes
are shown in Figures 3.12(a) and 3.12(c) respectively. The MBE sample holder shown is made of 1.5 mm thick molybdenum and is designed to hold 10x10mm square substrates. The substrate sits in the recess of the sample holder and remains face down through all manipulation in the MBE. It is held by gravity, resting only by its corners on four metal clips. This shields as little of the substrate surface as possible from the deposition, and provides the radiant heater with a direct line of sight to the substrate backside.

In comparison, the XPS is designed for much smaller flag-shaped sample holders, as seen in Figure 3.12(c). The sample is usually secured to the sample holder with UHV-compatible conductive copper tape, or held in by spot welded tantalum brackets if the sample is to be heated. The sample must be held securely as it is rotated upside down as it moves from the load lock to the analysis chamber of the XPS.

A new XPS sample holder was designed which was compatible with both systems, and is shown in Figure 3.12(d) and 3.12(e). It is constructed out of molybdenum so as to be suitable with high temperatures. As in the MBE, the sample is secured only at its corners, but a 1 mm diameter molybdenum wire bent into a ‘U’- shape (not shown in Figure 3.12) is placed against the sample backside and held in by its natural springiness. This is used to prevent the sample from falling out of the holder and also forces the substrate into contact with the sample holder to provide electrical contact with the XPS. This is necessary to prevent substrate charging, which makes determination of binding energy shifts extremely difficult. Substrates used with this sample holder had ∼50 nm of gold deposited onto their corners to provide this electrical contact from film to XPS.

While this sample holder is naturally compatible with the internal mechanisms of the XPS, a piece had to be designed for the MBE to allow the sample holder to be moved between the load lock and main chamber. This is shown in Figure 3.12(b). It was originally a holder for 1” wafers; it has now been modified by removing a portion of the holder and adding two molybdenum supports that are attached to the sample holder with screws. The supports allow the new XPS sample holder to rest on its edges, with the sample facing down. The portion which has been cut out allows an XPS sample holder which is attached to the linear drive to be placed into this sample holder. A piece of bent tantalum foil acts as a spring to hold an XPS sample holder in place.

To demonstrate the effectiveness of the transfer system and the detrimental effect that surface contamination can have on XP spectra, XPS was performed on two samples of Mn$_2$Au. One was moved from the MBE to the XPS using the vacuum transfer system, while the other was removed from the dry nitrogen-vented MBE loadlock, mounted on an XPS sample plate, and inserted in the XPS loadlock as quickly as possible. This resulted in an air exposure of approximately 15 minutes. A
Figure 3.13: XP survey spectra of vacuum transferred and air exposed Mn$_2$Au samples. The intense peaks originating from Mn are shown in purple (—), those from Au are shown in gold (—), while those from contaminants are shown in blue (—). Inset: High resolution XPS of the O 1s peak showing the large amount of oxide species that accumulate on an air-exposed sample.

A comparison of the two XP survey spectra is shown in Figure 3.13. Typical spectral features due to the aforementioned contaminants appear as features in the O 1s peak at 530 eV and C 1s peak at 284 eV.

The material shown here (Mn$_2$Au) is more suitable to highlight contamination than the p-type metal oxides which this thesis is based on, as the O 1s core level present in all oxides can obscure any oxygen-containing contaminants such as adsorbed hydroxide or carbon monoxide. For the vacuum transferred sample, less than 10% of the signal originates from surface contaminants, while for the air exposed sample, the signal is dominated by contaminants, with only 20% of the signal originating from the Mn$_2$Au.

The Mn and Au core levels are seen to be sharper and more intense, and some features such as the Au 4p$_{3/2}$ at 546 eV are highly obscured in the air-exposed sample. As can be seen in the inset of Figure 3.13, the oxygen content of the vacuum-transferred sample is minimal. There is also no detectable carbon on the surface of this sample.

### 3.6 Ultraviolet-Visible Spectroscopy

In 1966, Tauc, Grigorovici & Vancu proposed a method for determining the band gap of a semiconductor from the material’s absorbance as a function of energy [21]:

\[
(\alpha \hbar \omega)^{1/n} = A (\hbar \omega - E_g)
\]  

(3.15)
where $\alpha$ is the absorption coefficient of the material, $A$ is a proportionality constant, and $n = 1/2$ for direct, optically allowed transitions. The band gap can be obtained from the intercept of the graph of $(\alpha \hbar \omega)^{1/n}$ against $\hbar \omega$. The value of $n$ takes on different values if the optical transition is indirect or forbidden. The absorption coefficient can be obtained by measuring the fraction of transmitted light ($T$) through a material as a function of energy. If Fabry-Pérot oscillations are present in the data, the reflectance ($R$) of the sample as a function of energy must also be measured if the correct band gap is to be obtained. This is obtained from the equation

$$\alpha = -\ln \left( \frac{T + R}{d} \right)$$

(3.16)

where $d$ is the sample thickness.

The instrument used for UV-Vis spectroscopy is a PerkinElmer 650S. This spectrophotometer has two light sources; a deuterium lamp for high energies in the ultraviolet range and a tungsten halogen lamp for the visible energies. There are dual holographic grating monochromators to provide high resolution. At each wavelength, the instrument measures the intensity of the light after passing through the sample, the intensity of light which has travelled an identical path length but not through the sample, and a dark reading. The transmission is calculated from these values. The typical wavelength range measured is 315–830 nm corresponding to an energy range of 1.5–3.9 eV which is a sufficient range to excite electrons across the band gap of most semiconductors. The spectrometer also has an integrating sphere which allows the measurement of diffuse transmission and reflection. The substrate (typically glass or $\text{Al}_2\text{O}_3$) contribution to all of the optical measurements performed is not subtracted from any of the data shown in this thesis.

### 3.7 X-Ray Diffraction

X-rays typically have a wavelength on the order of 1 Å, which is a comparable dimension to the inter-atomic distance in most materials. If the material has a crystalline structure, the periodic features of the crystal will act as a three dimensional diffraction grating to x-rays. The smallest repeating unit in a crystal structure is known as the unit cell. If x-rays are incident on a surface of a crystalline material with all crystal planes parallel to the surface, separated by a distance $d$, then at certain incident angles the path difference between x-rays diffracted from each plane will be such that constructive interference between the diffracted x-rays will occur. The angle between the x-ray and the surface normal at which constructive interference
occurs \((\theta)\) is given by Bragg’s Law

\[ n\lambda = 2d\sin \theta \]  

(3.17)

where \(n\) is the order of diffraction, and \(\lambda\) is the wavelength of the incident x-rays. Thus the measurement of \(\theta\) gives \(d\). In practice, the x-ray source and detector are aligned to both make an angle \(\theta\) to the surface of the sample; the angle of both is then increased in a coupled fashion while the diffraction intensity is measured. This is demonstrated in Figure 3.14(a) and is known as a symmetric scan.

Measurement of the parallel-to-surface crystal plane spacing will give a value for the lattice constant in this direction. If the other lattice constants of the crystal are to be found, then the Bragg angle for other crystal planes that are not parallel to the surface must be measured. For these crystal planes, the source and detector need to be positioned symmetrically about the normal of the chosen crystal plane, then have the angle of both source and detector with respect to the crystal plane increase in the same coupled fashion as the previous case. This is not possible for all crystal planes as the source and detector can not be rotated to every angle due to their finite size. X-ray diffraction can be used to distinguish between single crystal, polycrystalline and amorphous materials; an amorphous material will show no intense diffraction pattern, only a broad diffuse background. A polycrystalline film consists of a huge amount of randomly oriented crystal domains. For each crystal plane, a small percentage of crystallites will be in the correct orientation to satisfy the Bragg condition (Equation 3.17). Every plane will thus be visible in a symmetric scan.
If a symmetric scan is performed on a single crystal or an epitaxial film, only the
diffraction peaks for the crystal plane parallel to the surface will be seen. For an
epitaxial film, this will be set by the crystal structure of the underlying substrate.
Other crystal planes can be detected by rotation of the sample about different axes.
The large amount of perfectly aligned crystal planes in an epitaxial or single crystal
sample will result in very narrow diffraction peaks. By analysing the exact position
and width of the peaks, information on the strain and the lattice constants of the
film can be obtained.

The primary uses for XRD include lattice constant determination, texture analysis,
and phase identification. Each crystal structure will produce diffraction peaks at
different angles, so by comparing a measured diffraction pattern with a reference
database pattern the crystal structure of the measured material can be determined4.

The x-ray diffractometer used is a Bruker D8 Advance with a Cu anode operated
at an accelerating voltage of 40 kV and emission current of 40 mA, a Göbel mirror to
manipulate the x-ray emission into a parallel beam, a 2-bounce monochromator to
select the $K_\alpha$ (with a wavelength of 1.54 Å) from the Cu x-ray emission spectrum, and
a solid state detector with 192 one-dimensional linear detecting elements of 0.075 mm
width. The detector is oriented so that each element is spaced along the $\theta$ direction.
The detector measures 2.6° along this direction simultaneously which enables faster
measurements compared to a point detector. The sample stage is an Euler cradle
which allows a full 360° rotation about the sample normal ($\phi$), a 90° rotation about
an axis perpendicular to the sample normal ($\chi$), and has three translational axes
of movement ($x, y, z$), enabling precise sample alignment. The diffractometer and a
schematic showing these axes of movement is shown in Figure 3.14.

3.8 X-Ray Reflectivity

If x-rays are incident on the surface of a sample that consists of one or more thin layers
on a substrate, with the layer(s) having different electron densities, the x-rays reflected
from the surface and from the interfaces between the layers will undergo interference
and oscillations will appear in the reflectivity as a function of incidence angle profile.
The measurement of this reflectivity profile is known as X-Ray Reflectivity (XRR).
At very shallow angles, x-rays undergo specular reflection from a surface. This occurs
as the refractive index for solid materials is typically less than 1 at x-ray energies.
This can be seen by looking at the classical theory of dispersion [22]. Electrons within
a material can be considered as a negative shell of charge attached to stationary
positive nucleus by ‘springs’. When light (a time varying electric field of amplitude

4An example of a freely accessed crystal structure database is the Crystallographic Open
Database (www.crystallography.net)
$E_0$ is incident on a material, it drives these oscillators sinusoidally at the frequency of the light ($\omega$) with amplitude

$$A = \frac{eE_0}{m_e} \frac{1}{\omega_0^2 - \omega^2}$$

(3.18)

where $e$ is the charge of the electron, $m_e$ is the mass of the electron and $\omega_0$ is the resonant frequency of the electron-nucleus oscillator. For simplicity, damping is neglected here. The dielectric constant of the material containing these bound electrons can be determined by relating the induced electric field to the incident field, and from that the refractive index ($n$) as a function of frequency can be shown to be

$$n^2 = 1 + \frac{N e^2}{\varepsilon_0 m_e} \left( \frac{1}{\omega_0^2 - \omega^2} \right)$$

(3.19)

where $\varepsilon_0$ is the permittivity of free space and $N$ is the electron density within the material. If $\omega \gg \omega_0$, as will be the case with high energy x-rays, then the refractive index in the material becomes less than one. As the material then has a lower refractive index than air for x-rays, they will undergo total external reflection at low incidence angles.

An example of an XRR measurement is shown in Figure 3.15. The measured reflected intensity is seen to be approximately constant until $\sim 0.5^\circ$. At higher angles there is a rapid decrease of specular reflection intensity with incidence angle $\theta$, proportional to $\theta^4$ [23]. The critical angle is defined as the angle where the intensity falls to half of its maximum value. Figure 3.15 also shows some of the physical parameters that can be obtained from XRR data. Surface and interface roughness can cause intensity and oscillation decay rates to change at higher angles, but are not seen in the data presented here due to the high quality of the MBE grown film. XRR can measure film thicknesses in the range 1–250 nm. It also provides information on the electron densities and surface and interface roughnesses of the layers. If the surface of the sample is too rough, there will be no specular reflection and an alternative method must be used to measure the film thickness. A thick film will have a very small separation between oscillation maxima and will need a high resolution x-ray source to resolve these, while a thin film will have a large spacing between oscillation maxima requiring a highly intense source to detect reflection at large angles. This requires compromise in the experimental set up, as in general, the more highly monochromated an x-ray source is, the lower its intensity.

XRR was performed using the same machine as for XRD, the Bruker D8 Advance, but with the x-ray optics configured to provide linear, high dynamic range x-ray detection. This is due to the large variation of count rates involved in measuring XRR, typically spanning five or more orders of magnitude. This was done by rotating the
Figure 3.15: A typical X-Ray Reflectivity curve with physical properties that can be extracted from the measurement highlighted. The sample is an MBE-grown thin film of Cr$_2$O$_3$ on an Al$_2$O$_3$ substrate, with a thickness of 48.7 nm, a density of 5.23 g cm$^{-3}$, a surface roughness of 0.2 nm and an interface roughness of 0.02 nm. The critical angle for this sample is 0.66°.

detector 90°, so that the reflected beam is incident on all detecting elements rather than a single one. This removes the need to use absorber slits at high intensities to prevent the detector saturation that would result if a single detecting element was used. High resolution is achieved by means of a slit (0.1 mm width) placed in front of the detector. The set-up used allowed accurate film thickness determination in the range 5–120 nm. A knife edge collimator was used to keep the illuminated area identical for each sample. Layer thicknesses for all measured samples were initially estimated by taking a fast Fourier transform of the XRR data; this was then used as the starting point for a model which was fit to the data using a genetic algorithm. The parameters extracted from this model include the thickness, density and roughness of each layer. The accuracy of these parameters depends on how good of a fit is achieved with the model. The thickness of a film can typically be estimated to a precision of less than one nanometre.

### 3.9 Solar Cell Characterisation

A solar cell, while not under any illumination, can be seen to have the Current-Voltage ($IV$) characteristics of a diode, as it is effectively just a pn-junction. The current through the cell is given by the Shockley diode equation [24]:

$$I = I_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right]$$  \hspace{1cm} (3.20)

where $I_0$ is the (dark) reverse saturation current, or the diode leakage current in the absence of light, $q$ is the charge of an electron, $V$ is the voltage across the terminals
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of the diode/solar cell, \( n \) is the ideality factor, typically between 1 and 2 and is determined by the defects responsible for causing recombination, \( k \) is Boltzmann’s constant, and \( T \) is the temperature of the cell.

When the solar cell is exposed to light, it begins to generate power. This can be represented by a current source (providing current \( I_{ph} \)) in parallel with the cell/diode, with the total current now given by:

\[
I = I_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] - I_{ph}
\]

The power generated not only depends on the intrinsic properties of the cell, but also depends on the emission spectrum of the illumination source. Ideally all cells are characterised using a standard, easily reproduced illumination source. One option would be to use a monochromatic source such as a laser, however, this does not represent everyday working conditions. The more obvious choice would be to test all cells with the emission spectrum of that of the sun. Fortunately, the spectrum of the sun closely resembles that of a black body with a temperature of 5777 K, as can be seen in Figure 3.16; this can be reproduced in a lab using a hot cathode, such as a halogen lamp, or a xenon arc lamp. The solar emission spectrum measured just out side of the Earth’s atmosphere is known as AM 0 (Air Mass of zero atmospheres).

While close, this does still not represent the typically daily illumination that a solar cell on Earth will receive, as the atmosphere contains many compounds (\( \text{H}_2\text{O}, \text{CO}_2, \) etc.) which absorb potentially useful light. Moreover, the thickness of atmosphere that the sunlight has to travel through before reaching the cell will depend on the latitude of the cell. To alleviate this problem, solar cell properties are typically measured under AM 1.5 conditions. This corresponds to a solar zenith angle of \( \sim 48^\circ \). All cells fabricated in this thesis have been measured using a laboratory source with an AM 1.5 spectrum.

A real solar cell however, does not act like an ideal current source in parallel with a diode. To be modelled accurately, the parasitic resistances that are present within a real solar cell must be considered. One of these loss mechanisms can be modelled by a resistor in series with the solar cell and the external circuit, and is known as the series resistance \( (R_S) \). The physical causes of this series resistance are the movement of carriers from the active layer through to the buffer layers, the contact resistance between the buffer layers and the active layers, and the resistance of the external contacts. This is equal to zero in an ideal solar cell. Another loss mechanism can be modelled by a resistor in parallel with the solar cell, and is known as the shunt resistance \( (R_{SH}) \). The shunt resistance represents unwanted current paths within the solar cell. These can be formed by having a rough substrate; the deposited organic layers might not completely cover the rough substrates, thus leaving a highly
Figure 3.16: Comparison of the spectral irradiance of a black body at 5777 K with the AM 0 and AM 1.5 spectra from 280–3000 nm. The chemical symbols indicate the molecules responsible for absorption at the approximate wavelength of their position. The black body spectrum is calculated from Planck’s law, while the air mass spectra are taken from the standard table ASTM G173-03 (2012) [25].

conductive short circuit path between anode and cathode. This will reduce the overall efficiency of the cell. This shunt resistance is infinite in an ideal solar cell. Taking these loss mechanisms into account, Equation 3.21 is modified to:

\[ I = I_0 \left[ \exp \left( \frac{q(V + IR_S)}{nkT} \right) - 1 \right] - I_{ph} + \frac{V + IR_S}{R_{SH}} \]  (3.22)

It is seen that the equation for an ideal cell (Equation 3.21) is obtained if the series resistance and shunt resistance are set to their ideal values of zero and infinite, respectively. The effect that these resistances have on the \( IV \) characteristics of a solar cell are shown in Figure 3.17.

There are several ways to determine the intrinsic resistances of a solar cell. The most simple method is to measure the \( IV \) curve of the cell, and find the inverse of the slope at the open circuit voltage to obtain \( R_{SH} \) and at the short circuit current to obtain \( R_S \) [26]. This method is shown in Figure 3.18, where the accuracy is seen to be satisfactory for both cells considered. This accuracy is only achieved for cells for which \( R_{SH} \gg R_S \), which, while satisfied by most modern solar cells, is not always the case for low-efficiency OSCs.

A more complex but still straightforward method is to fit Equation 3.22 to the measured data using the method of least squares. As this equation is transcendental, it cannot be solved explicitly, however, the current and voltage can be separated by
Figure 3.17: Equivalent circuit diagrams and associated $IV$ curves for Equations 3.20–3.21. (a) corresponds to Equation 3.20, (b) corresponds to Equation 3.21, and (c) corresponds to Equation 3.22, with $R_S = 5 \, \Omega$ and $R_{SH} = 100 \, \Omega$. The filled orange rectangle meets the $IV$-curve at the maximum power point. The hatched rectangle indicates the maximum power that could be obtained an ideal cell with the same values of $V_{OC}$ and $I_{SC}$, i.e., if the fill factor was unity.

re-writing the equation in terms of the Lambert W-function\(^5\) [27]. Algorithms exist for solving finding numerical solutions to this function.

There are several values used to characterise the properties of a solar cell; the short circuit current ($I_{SC}$), the open circuit voltage ($V_{OC}$), the fill factor (FF), and most importantly, the efficiency ($\eta$). The short circuit current is defined as the current through the solar cell when the voltage across the cell is zero. It can be seen as the largest current which may be drawn from a solar cell, and can be experimentally determined by performing an $IV$ measurement on the solar cell, and noting the current value at the point where the $IV$ curve crosses the current axis, e.g., as shown in Figure 3.17(e). The open circuit voltage is the maximum voltage available from a solar cell, occurring when the net current through the cell is zero. Similarly to the short circuit current, it can be experimentally determined by performing an $IV$ measurement on the solar cell, and noting the voltage value at the point where the $IV$ curve crosses the voltage axis, again as shown in Figure 3.17(e).

The fill factor of a solar cell is defined as the ratio of the maximum power available from a solar cell to the product of $V_{OC}$ and $I_{SC}$. As power is simply given by $P = IV$, the maximum power point of a solar cell can be determined by differentiating this

\[^5\text{The Lambert-W function is the inverse function of} f(W) = W \exp(W)\]
Figure 3.18: Simple determination of the intrinsic resistances of a silicon solar cell from its $IV$ curve. The simulated $IV$ curve 1 (shown in red) has $R_S = 5 \Omega$ and $R_{SH} = 100 \Omega$. The inverse slopes provide values of $R_S = 5.8 \Omega$ and $R_{SH} = 105 \Omega$. The simulated $IV$ curve 2 (shown in blue) has $R_S = 2 \Omega$ and $R_{SH} = 5000 \Omega$. The inverse slopes provide values of $R_S = 2.77 \Omega$ and $R_{SH} = 5002 \Omega$.

with respect to either $I$ or $V$, and finding where this equals zero:

$$\frac{d(IV)}{dV} = 0$$

(3.23)

The fill factor is then given by the ratio of the area bounded by the rectangle with corners at the origin and the maximum power point, and the ratio of the area bounded by the rectangle with corners at $V_{OC}$ and $I_{SC}$. This is shown in Figures 3.17(e) and 3.17(f); the fill factor is the ratio of the solid orange rectangle to the hatched orange rectangle. In Figure 3.17(e) the fill factor is approximately 65%, while in Figure 3.17(f), the resistances of the cell have reduced this to 26% (as well as reducing $V_{OC}$ and $I_{SC}$). The fill factor can be thought of as the “squareness” of the $IV$ curve.

Combining Equation 3.20 or 3.22 with Equation 3.23 results in an equation that can not be solved analytically and makes determination of the maximum power point non-trivial. When the effect of the resistances on the cell operation are small, an accurate empirical formula can be used to calculate the fill factor [28]:

$$FF = \frac{V_{OC}^* - \ln(V_{OC}^* + 0.72)}{V_{OC}^* + 1}$$

(3.24)
where

\[ V_{OC}^* = \frac{qV_{OC}}{nkT} \]  (3.25)

Once the fill factor is calculated, the maximum power obtainable from a solar cell can be determined:

\[ P_{\text{max}} = V_{OC}I_{SC}\text{FF} \]  (3.26)

and the efficiency of a solar cell is given by the ratio of this to the input power

\[ \eta = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{V_{OC}I_{SC}\text{FF}}{P_{\text{in}}} \]  (3.27)
Bibliography


25. *Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface*


Chapter 4

p-Type Transparent Conducting Oxides as Buffer Layers in Organic Solar Cells

In the first section of this chapter, the preparation of the anode materials ITO and FTO, commonly used in organic solar cell fabrication, is described. The epitaxial growth of \( \text{Cr}_2\text{O}_3 \) and the p-type transparent conducting oxide \( \text{Cr}_2\text{O}_3:\text{Mg} \) is described, as are the necessary modifications to the growth procedure to grow these materials on ITO and FTO.

Results obtained from utilising \( \text{Cr}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3:\text{Mg} \) as a buffer layer in a simple organic solar cell are presented. The effect of the buffer layer is shown on two common anode materials: ITO and FTO, with the latter being used with a view towards moving away from indium containing TCOs. Comparisons are made towards the current state of the art. In the second half of this chapter, a combination of x-ray and ultraviolet photoelectron spectroscopy is used to measure the band offsets to understand the difference between \( \text{Cr}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3:\text{Mg} \) as an anode buffer layer, while band alignment between \( \text{Cr}_2\text{O}_3:\text{Mg} \) with both FTO and ITO are performed to determine how the anode choice affects the buffer layer performance. This required use of the ultra high vacuum suitcase which was constructed specifically for these measurements. Band offset measurements are performed on an ITO/\( \text{Cr}_2\text{O}_3 \)/CuPc structure to determine the potential barriers for hole transport throughout the whole device. These spectroscopy results are used to understand the mechanism behind how \( \text{Cr}_2\text{O}_3:\text{Mg} \) can act as an anode buffer layer in organic solar cells.
4.1 FTO and ITO substrates

For initial measurements ITO was used as an anode for our solar cells. Indium oxide and its variants have been a popular choice for the anode (hole collecting side) of organic solar cells, even being used in the first high performance two-layer organic solar cell device demonstrated by Tang in 1986 [1]. Its high visible region transparency, relatively high work function, and chemical stability have resulted in it being incorporated in many types of solar cell to date [2, 3].

Despite the near-ideal properties of ITO, there is a push in the TCO community to move away from materials which require a large proportion of rare and costly materials in their fabrication, such as indium [4]. For this reason, FTO was also used as an anode in the fabricated solar cells. This material has a similarly high work function, typically has three times the sheet resistance of ITO for the same thickness, and shows slightly lower visible range transmittance, particularly above wavelengths of 500 nm.

The ITO coated glass substrates used were obtained from Solems, and were prepared by physical vapour deposition. They have a thickness of 80–100 nm, a lower sheet resistance of 25–35 Ω/□ and a visible range transmittance of 82–86 % as specified by the manufacturer. The FTO coated glass substrates used for solar cell buffer layer growth were also obtained from Solems. They are prepared by chemical, rather than physical vapour deposition, have a thickness of 80–100 nm, a sheet resistance of 80–120 Ω/□ and a visible range transmittance of 78–91 % as specified by the manufacturer. For both the FTO and ITO the sheet resistance was found to vary by only ∼5 % between different samples from the same batch, while multiple sheet resistance readings taken from different areas on the same sample were in close agreement (<1 %), verifying that the material is homogeneous. A cross section of the film imaged by scanning electron microscopy is shown in Figure 4.1. This imaging technique is expanded upon in Appendix B.1.

The ideal growth conditions for Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg grown by MBE have been shown by Farrell et al. to be at a substrate temperature of 600 ºC, and an oxygen pressure of $4 \times 10^{-5}$ Torr [5]. Exposing the FTO and ITO to these conditions was found to have a detrimental effect on the sheet resistance of both substrates. This is shown for the case of FTO in Figure 4.2. FTO/glass substrates were annealed in the main growth chamber of the MBE, under identical conditions to which they would be exposed to if a Cr$_2$O$_3$/Cr$_2$O$_3$:Mg layer was to be grown on them. It is seen from Figure 4.2 (a) that exposure to a temperature of 600 ºC for a brief period of time of 9 minutes was enough to increase the sheet resistance of the FTO by a factor greater than two. This large increase in the sheet resistance will have a detrimental effect on the series resistance, and thus the ultimate efficiency of a solar cell which
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**Figure 4.1:** Scanning Electron Microscope image of the as-received FTO/glass substrate. The bottom of the image is glass and the thin, lighter layer is FTO. The average thickness of the layer is $101 \pm 17$ nm. The white bar has length of 200 nm.

makes use of this FTO as a contact. An example of a heating and cooling cycle that each substrate is exposed to is shown in Figure 4.3 for the case of a 9 minute, 600°C anneal.

A compromise between the electrical properties of the FTO and the ideal growth conditions for $\text{Cr}_2\text{O}_3$ was reached by growing all buffer layers on FTO at 500°C. The same procedure was followed for ITO substrates and as a result, all buffer layers were grown on ITO at a temperature of 400°C. As can be seen in Figure 4.2 (a), the sheet resistance increased by only 5% after 9 minutes, and only 15% after a longer anneal of 18 minutes. The relative percentage changes compared to un-annealed FTO are shown in Figure 4.2 (b). To understand whether any of the annealing treatments cause the film to undergo any crystalline structure modification, XRD was performed. As can be seen in Figure 4.2 (c), no change in peak shape, relative intensity, or peak position is seen when the FTO undergoes different annealing treatments. All peaks are referenced to the $\text{SnO}_2$ cassiterite phase, from the international centre for diffraction data file: PDF 00-041-1445. Annealing in air has been previously shown to increase the average crystallite size in $\text{SnO}_2$, but the same effect would not necessarily be expected here due to the much lower oxygen partial pressure used. A possible reason for the sheet resistance increase which would remain undetectable by XRD could be dopant redistribution/clustering within the material upon annealing, as has been observed in $\text{Cr}_2\text{O}_3$ [6]. While this effect could usually be measured with XPS, the low cross section of fluorine to x-rays make any meaningful quantitative measurements extremely difficult for FTO. As a general rule in crystalline TCOs, vacuum annealing improves the electrical properties of n-types and diminishes the electrical properties of p-types, while annealing in an oxygen rich atmosphere has the opposite effect. This effect also applies to the oxygen pressure present during growth [7]. This is due to the formation/removal of oxygen vacancies which act as electron donors [8, 9].
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Figure 4.2: Effect of annealing on an FTO substrate. The annealing was carried out in the MBE with an O\textsubscript{2} partial pressure of \(4 \times 10^{-5}\) Torr and with the temperature indicated in the graph. (a) Sheet resistance as a function of temperature for the FTO substrates before and after annealing. (b) Relative sheet resistance change after annealing. (c) XRD patterns of the FTO substrates after annealing. No difference is seen in peak positions or relative intensities. Peak positions are taken from PDF 00-041-1445 (SnO\textsubscript{2}, cassiterite).

Bierwagen & Speck have shown that by annealing films of In\textsubscript{2}O\textsubscript{3} at 700°C in vacuum or oxygen, the carrier concentration can be altered from \(1.5 \times 10^{21}\) cm\textsuperscript{-3} to \(2.7 \times 10^{20}\) cm\textsuperscript{-3} respectively. This reduced carrier concentration upon oxygen annealing, which is performed at similar conditions to that used for the growth of Cr\textsubscript{2}O\textsubscript{3} was found to be due to oxygen interstitials [10, 11]. A similar mechanism could be present in the films of FTO and ITO; the increase of sheet resistance with annealing time at a constant pressure supports the idea that the FTO is being oxidised, deteriorating its n-type conductivity.

4.2 Substrate Preparation

Prior to buffer layer deposition, the as-received substrates with an area of (3×3)cm\textsuperscript{2} were cut into pieces measuring (3×1)cm\textsuperscript{2} with a diamond saw. One third of the FTO/ITO was then etched away, leaving the substrates as shown in Figure 4.4(b). This etching was performed by covering two thirds of the substrate with sticky tape, and exposing the uncovered section to a solution of HCL and zinc powder. Complete etching of the film took approximately ten minutes. This method was compared with
Figure 4.3: Heating/cooling cycle in the MBE main chamber. Here a 9 min anneal is shown. The heating rate is linear at 50 °C min⁻¹. The cooling is limited at 50 °C min⁻¹ until the sample temperature reaches ~275 °C, after which the heater power is set to zero and the temperature of the sample exponentially approaches room temperature.

removal of the FTO/ITO film via a physical etching process. Here, the substrate was placed in a cryo-pumped high vacuum chamber with a base pressure of 10⁻⁷ Torr. Polyimide tape was used to cover two thirds of the substrate, while the other third was exposed to a 300 W argon plasma, which etched the substrate at a rate of 1–2 nm min⁻¹. The etching for both methods was considered to be complete when the exposed area became fully insulating. Both methods were found to result in sharp TCO/glass boundaries, and complete removal of the film. Due to its facile nature, the first method was adopted for all cells which were grown in this work.

Figure 4.4: Substrate preparation process. (a) The as-received substrate. (b) The substrate after etching. (c) The full organic solar cell. Each subsequent layer is deposited slightly offset from the previous layer to ensure that no short circuits occur throughout the cell. A description of each layer and its thickness is given in Figure 4.15 on page 99.
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Figure 4.5: AFM scan of a chemically etched FTO/glass boundary. (a) A 3D scan of the boundary. A 2nd order polynomial background has been subtracted from the data to minimise the effects of thermal drift and piezo creep in the instrument. (b) A single line scan taken from the image in (a). The step height (and FTO thickness) is seen to be approximately 90 nm.

A representative AFM image of a Zn/HCL etched FTO film is shown in Figure 4.5. Here, the AFM tip was scanned across an area which contained both FTO/glass and glass after FTO removal. The etching is seen to produce a very sharp boundary; the difference between 10% and 90% of the maximum step height is less than 1 µm.

After etching, the substrates were cleaned first with soap and rinsed with deionised water, followed by a 15 minute clean in an ultrasonic bath in each of acetone, propan-2-ol and deionised water. The substrates were then loaded into the loadlock of the MBE.

Prior to growing Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg buffer layers on the FTO/ITO substrates, several films were grown on (10×10)mm$^2$ Al$_2$O$_3$ (0001) substrates, to check the growth rate and doping concentration. Each substrate underwent 15 minutes of ultrasonic cleaning in each of acetone and propan-2-ol, before being inserted into the loadlock of the MBE. Each Al$_2$O$_3$ substrate was then UHV annealed in the main chamber of the MBE at 600 °C for 30 minutes, followed by annealing in an oxygen pressure of 4 × 10$^{-5}$ torr at 600 °C for a further 30 minutes. These conditions were sufficient to remove all contaminants from the substrate surface to below the detection limit of XPS (≈1%), and were found to produce substrates which demonstrated a sharp RHEED pattern, indicating a highly ordered surface. Figure 4.6 shows representative RHEED images taken along the [1T00] azimuthal direction after both annealing steps. The Kikuchi lines present in both images are indicative of a high degree of crystalline order within the bulk of the substrate. After oxygen annealing, the diffuse background, which is a sign of disorder present on the surface of the substrate, is found to reduce in intensity in comparison with a vacuum annealed substrate.
Figure 4.6: RHEED images of an Al₂O₃ substrate after (a) a 30 minute, 600 °C UHV anneal and (b) a subsequent oxygen anneal. The Kikuchi lines present in both images are indicative of a high degree of crystalline order within the bulk of the substrate. Images were taken at an accelerating voltage of 20 kV along the [1100] azimuthal direction.

4.3 Growth of Cr₂O₃ and Cr₂O₃·Mg

The Cr₂O₃ films were grown by evaporating Cr₂O₃ pieces (99.9% purity) in an electron beam evaporator in the presence of an oxygen partial pressure in the MBE main chamber. Cr₂O₃·Mg films were grown by simultaneously evaporating Cr₂O₃ pieces and MgO pieces (99.95% purity) in separate electron beam evaporators. Both evaporators have independent water-cooled quartz crystal monitors, allowing the evaporation of each material to be separately measured during growth. These two crystal monitors are positioned in such a way that no crosstalk is present between them. The crystal monitors were calibrated by comparing the indicated thickness with the thickness of grown samples, as measured by XRR. The growth rate of all films was fixed at 0.2 Å s⁻¹, while the MgO rate was varied until the optimum doping concentration was found. The determination of this optimum Mg concentration is discussed in Section 4.3.2. Optimisation was carried out at the temperature which the buffer layer would be grown at, i.e., 400 °C for ITO and 500 °C for FTO. All samples were grown at an oxygen pressure of 4 × 10⁻⁵ torr. This pressure was set by opening a leak valve which is connected to a high-purity oxygen gas bottle. All growth parameters were set to the required values before the substrate temperature was increased to growth temperature, in order to expose it to high temperatures for as little time as possible. After growth, all samples were cooled down immediately in the same oxygen pressure that was used during growth, until the substrate temperature was below 75 °C. The heating cycle of each growth thus followed the graph of Figure 4.3.
4.3.1 RHEED study of Cr\textsubscript{2}O\textsubscript{3}

The initial stages of growth of a Cr\textsubscript{2}O\textsubscript{3} film grown at 600 °C was monitored by RHEED, and is shown in Figure 4.7. Here, images are shown from along the [1\bar{T}00] azimuthal direction and the [10\bar{T}0] azimuth. The Kikuchi lines in the RHEED images are seen to persist until a thickness of 12 Å, approximately one unit cell of Cr\textsubscript{2}O\textsubscript{3}. Along both directions, a streaky pattern is observed soon after growth begins, and persists up to thicknesses greater than 50 nm. The streaks are non-uniform in intensity along their length; this intensity modulation is indicative of a surface which is not atomically flat, and displays a small roughness. This modulation is also present in much thicker films.

The variation in RHEED streak spacing is inversely proportional to the distance between the surface features which are causing the surface diffraction. Assuming an oxygen terminated surface [12] which does not undergo any reconstruction as the growth proceeds, measuring the streak spacing allows a determination of the in-plane lattice parameter of the Cr\textsubscript{2}O\textsubscript{3} film as a function of layer thickness. This is shown in Figure 4.8 for RHEED streak spacing along the [10\bar{T}0] azimuthal direction. All images were taken at 600 °C and at an electron energy of 20 keV. The in-plane lattice parameter of the grown film is seen to immediately relax to a value 3.2 % larger than the Al\textsubscript{2}O\textsubscript{3} substrate. This relaxation occurs within the first 4 Å of growth, which is approximately one third of a unit cell of Cr\textsubscript{2}O\textsubscript{3}, or two monolayers. It is possible that the first or second monolayer grow fully strained and the film immediately relaxes upon growth of the third monolayer, but the RHEED streaks become difficult to distinguish from the diffuse background at these small thicknesses. The more likely scenarios are that the Cr\textsubscript{2}O\textsubscript{3} film does not grow strained in any way, or that the first few monolayers contain a large amount of point defects to mitigate the strain energy from reaching a high value.

In Figure 4.8 (b), the in-plane lattice parameter of Al\textsubscript{2}O\textsubscript{3} has been set to the bulk value of 4.7587 Å. This is the value at room temperature and will differ at the high temperatures at which the images were taken due to the thermal expansion coefficient of Al\textsubscript{2}O\textsubscript{3}. This is a small effect, on the order of 10\textsuperscript{−6}–10\textsuperscript{−5}°C\textsuperscript{−1}. Thermal expansion will also affect the absolute lattice parameter shift, as both materials will most likely have different thermal expansion coefficients. While values for these coefficients are available for both bulk materials, the results here have not been corrected for this, as the thermal expansion coefficients of surfaces have been shown to vary by a large amount when compared to bulk values [13, 14].

Similar incomplete relaxation has been observed previously. Chambers, Liang & Gao found that when growing Cr\textsubscript{2}O\textsubscript{3} on Al\textsubscript{2}O\textsubscript{3}, the RHEED streak spacing gradually
Figure 4.7: RHEED Images of an Al$_2$O$_3$ substrate and different layer thickness of Cr$_2$O$_3$. The cross sectional data was Fourier filtered to remove noise and normalised to the central peak intensity. The centre position of each peak was determined by fitting a Lorentzian function. The shift in the first order peaks is indicated by a solid line. The RHEED images were taken at 20 keV.
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Figure 4.8: Directions along which RHEED images were taken and the change in streak spacing with Cr$_2$O$_3$ deposition. (a) Directions in the basal plane of the hexagonal crystal system. RHEED images were taken along the azimuthal directions marked in blue. (b) The change in RHEED streak spacing along [10\bar{1}0] with increasing Cr$_2$O$_3$ thickness. This was calculated from the cross sections in Figure 4.7, by averaging the first order streak spacing on both sides of the main streak.

decreased by 2.6% after growth of $\sim$53 monolayers, or 120 Å [15]$^1$. Furthermore, periodic intensity oscillations were observed for the first 16 monolayers, indicating a layer-by-layer growth mechanism during this time. This, and the slower relaxation are indicative of a film with higher crystalline quality than the films grown in this work. This higher crystalline quality might be expected as in the aforementioned paper a slower growth rate of 0.12 Å s$^{-1}$ was used, as was activated oxygen generated by an oxygen plasma source. This supports the idea that the films grown in this work have a higher defect density in the first few monolayers, which causes the film to relax to a value near its bulk lattice parameter almost immediately after growth begins, rather than the fast relaxation being due to the Cr$_2$O$_3$-Al$_2$O$_3$ in-plane lattice mismatch.

4.3.2 Mg doping of Cr$_2$O$_3$

Doping the insulating Cr$_2$O$_3$ with magnesium is found to induce p-type conductivity within the material. As the inclusion of the magnesium dopant only has a minor effect on the optical properties of the material, the optimum doping level is simply identified by finding which magnesium concentration results in the films with the

$^1$While the growth of Cr$_2$O$_3$ was stopped before the lattice parameter had stopped decreasing, fitting a simple exponential decay to their RHEED streak spacing as a function of time data gives a maximum relaxation of 2.9%.
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Figure 4.9: Variation of $\text{Cr}_2\text{O}_3$:$\text{Mg}$ resistivity as a function of magnesium dopant concentration. Here, two different source materials were used to grow the films, Cr and $\text{Cr}_2\text{O}_3$. As $\text{Cr}_2\text{O}_3$ was found to produce more conductive films, it was used in this work. All samples in this graph were grown at a temperature of $600^\circ\text{C}$. The resistivity is found to vary greatly around the optimum magnesium concentration of 9-10%. Adapted from [5].

The highest conductivity. This was previously performed by Farrell et al.; the results are shown in Figure 4.9 [5]. The optical transmission, reflection and absorption coefficient of a $\text{Cr}_2\text{O}_3$ and a $\text{Cr}_2\text{O}_3$:$\text{Mg}$ film, both grown on $\text{Al}_2\text{O}_3$ are shown in Figure 4.10. The $\text{Cr}_2\text{O}_3$:$\text{Mg}$ film has a nominal doping concentration of 10% - the value which results in the highest conductivity. The $d - d$ transitions at 2.1 eV and 2.6 eV appear to be slightly reduced in intensity upon doping. The band gap of both the $\text{Cr}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$:$\text{Mg}$ films were determined to be $3.1 \pm 0.1$ eV.

Epitaxial samples of $\text{Cr}_2\text{O}_3$:$\text{Mg}$ were grown on $\text{Al}_2\text{O}_3$ with varying magnesium concentrations, at $600^\circ\text{C}$ for comparison with previous results, at $500^\circ\text{C}$ for optimisation of growth on FTO, and at $400^\circ\text{C}$ for optimisation of growth on ITO. The resistivity of each of these epitaxial samples was measured so that the optimum doping could be found. Selected samples had their magnesium concentration measured with XPS. This optimum magnesium concentration was found to be between 9% and 10%. Here, this concentration represents the ratio of magnesium ions to total cations within the samples, i.e.,

$$[\text{Mg}] = \frac{\text{Mg}^{2+}}{\text{Cr}^{3+} + \text{Mg}^{2+}} \quad (4.1)$$

As it has been shown with density functional theory that magnesium most likely is incorporated into $\text{Cr}_2\text{O}_3$ as a substitutional dopant on a chromium site [16], $\text{Cr}_2\text{O}_3$:$\text{Mg}$
Figure 4.10: Optical properties of both undoped Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg doped with 10\% Mg. The Mg concentration is nominal, and is the value which results in the most conductive Cr$_2$O$_3$:Mg. (a) The transmission, (b) reflectance, (c) absorption coefficient and (d) a Tauc plot for both samples. The Cr$_2$O$_3$ film has a thickness of 56 nm and the Cr$_2$O$_3$:Mg film has a thickness of 58 nm.

can also be written as Mg$_x$Cr$_{2-x}$O$_3$ where $x$ is related to the above magnesium concentration [Mg] by

$$x = \frac{[\text{Mg}]}{1 - [\text{Mg}]}$$

(4.2)

For example, if [Mg] = 20\% the resulting chemical formula is Mg$_{0.25}$Cr$_{1.75}$O$_3$.

As 600 $^\circ$C was previously found to result in Cr$_2$O$_3$:Mg films with the optimum electrical properties [5], the samples grown at lower temperatures were investigated with XRD, XPS, and resistivity measurements to determine what effect the growth temperature had on the samples. A summary of the results is shown in Table 4.1. Most importantly, the resistivity of the films is not seen to increase as the growth temperature is reduced to 400 $^\circ$C, the growth temperature required for buffer layers on ITO, and the lowest growth temperature for Cr$_2$O$_3$ used in this work.

While it appears that the lower growth temperature is actually beneficial for the resistivity of the samples, there is a slight difference in doping concentration between each sample. As can be see in Figure 4.9, the conductivity of Cr$_2$O$_3$:Mg is extremely sensitive to the magnesium concentration, and can change by an order of
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Figure 4.11: Effects of growth temperature on the properties of \( \text{Cr}_2\text{O}_3:\text{Mg} \). (a) XPS spectrum of the Mg 2s and Cr 3s of the samples in Table 4.1. Here the data has been normalised to the lower binding energy doublet of the Cr 3s. The multiplet splitting of 4.0 eV agrees well with the previously reported value of 4.1 eV. (b) XRD scans of the same samples. The sample grown at 600 °C has a slightly elongated \( c \) lattice parameter compared to the lower temperature samples, and the bulk value. The bulk values of the peaks are indicated by dashed lines.

Table 4.1: Variation of \( \text{Cr}_2\text{O}_3:\text{Mg} \) resistivity as a function of growth temperature. Magnesium concentrations were measured by XPS, temperatures were read from the MBE thermocouple which is between the substrate heater and the substrate, while the resistivity was determined from a combination of sheet resistance and x-ray reflectivity measurements.

<table>
<thead>
<tr>
<th>Growth T (K)</th>
<th>Mg Conc. (%)</th>
<th>Resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>9</td>
<td>29</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>29</td>
</tr>
<tr>
<td>400</td>
<td>9.5</td>
<td>23.5</td>
</tr>
</tbody>
</table>

magnitude if the magnesium doping concentration changes by as little as 1%. While the technique of MBE offers the utmost control over the growth rates of the individual source materials, the electron-beam evaporators used provide a less consistent/stable growth rate than Knudsen cells. Electron-beam evaporators are necessary for both MgO and \( \text{Cr}_2\text{O}_3 \) due to the low vapour pressure of both materials. This lower stability, combined with the extremely low growth rates of MgO of \( \approx 0.02 \text{ Å s}^{-1} \) will inevitably result in a slight deviation of the magnesium concentrations between samples. Through XPS analysis of many samples, the reproducibility of the doping concentration is estimated as \( \pm 0.25\% \).

The XPS measurements used to determine the doping concentration of the samples from Table 4.1 are shown in Figure 4.11(a). This is performed by finding the relative ratio of the areas (weighted by their respective sensitivity factors) of the
Cr 3s and the Mg 2s peaks. The area of each peak is highly sensitive to the chosen background region, especially at the low count rates observed, where the Mg 2s has a peak intensity on the order of 10 counts per second. Typical atomic concentration values are also only typically accurate to 0.5% when obtained from XPS data. The combination of MBE reproducibility, the low XPS count rates, and the XPS accuracy strongly suggests that the improved conductivity of the sample grown at 400 °C is due to it possessing a magnesium concentration which is closer to the ideal value than the 500 °C and 600 °C samples, providing evidence that this ideal value is 9.5%.

An interesting feature seen in the XPS data in Figure 4.11(a) is that the chromium 3s core level appears in the spectrum as a doublet. Splitting of XPS core levels into a doublet feature is typically due to the spin-orbit interaction, where the spin of the remaining core level electron couples to the orbital angular momentum. This should not occur for s orbitals, as they possess no orbital angular momentum. Instead, the splitting seen here is due to multiplet splitting, which is caused by the unpaired d electrons of the chromium species. Within Cr$_2$O$_3$, the chromium cation is in a Cr$^{3+}$ ($d^3$) configuration, with the spins of the d electrons aligned. After photoemission of a 3s electron, there are two possible final states with the 3s$^1$3d$^3$ configuration, one with the 3s electron having its spin aligned parallel to those of the 3d electrons or one with antiparallel alignment. In the case where the spins are parallel, it results in this state having a lower energy by approximately 4.0 eV, which is observed as two peaks at separate binding energies separated by this amount when performing XPS [17]. This agrees with previous data from Cr$_2$O$_3$, where the splitting was found to be 4.1 eV [18]. The theoretical intensity ratio between the two components of 5/3 is also well replicated by the experimental data. The multiplet splitting of Cr$_2$O$_3$ is most noticeable in the Cr 2p core level; the Cr 2p$_{3/2}$ component can be de-convoluted into 6 multiplet split components.

For films grown at each temperature, 2θ – ω scans were performed to assess the effect of temperature on the crystalline quality. This is shown in Figure 4.11(b). At each temperature, only the (0006) and (00012) diffraction peaks were observed, indicating epitaxial growth. While the samples grown at 400 °C and 500 °C show a c lattice parameter almost identical to that of bulk Cr$_2$O$_3$, the 600°C sample shows an elongation along the c-axis of 1.3%. Minor crystallographic differences such as this would not expected to be replicated in the buffer layer films, due to the crystal structure mismatch between FTO/ITO and Cr$_2$O$_3$.

It should be noted that while the growth rate of the film does not decrease as the growth temperature is changed from 600 °C to 400 °C, there is a difference in the incorporation rate of the evaporated MgO. At 400 °C, the MgO evaporation rate must be decreased by 18% to result in films which contain the same magnesium concentration as samples grown at 600 °C, as measured by XPS. This was taken into
account to produce the samples shown in Table 4.1. Furthermore, several samples
grown at room temperature (which were not used in this work) were grown, and it was
found that the evaporation rate of both $\text{Cr}_2\text{O}_3$ and MgO must be changed. Here, the
$\text{Cr}_2\text{O}_3$ evaporation rate needed to be decreased by 21%, while the MgO evaporation
rate needed to be decreased by 56%. The difference in the rate modifications
with temperature between the two materials implies that at the high temperatures
some volatile magnesium containing species are forming and re-evaporating. The
MgCr$_2$O$_4$ phase has been observed in as-deposited $\text{Cr}_2\text{O}_3$:Mg films in the form of
nanoclusters [6]. Raman spectroscopy shows that it remains incorporated within the
films to some extent. The post-annealing treatment which results in an improved
conductivity is reported to dissociate these clusters, resulting in a more homogeneous
magnesium distribution in the films. This spinel phase is also stable at temperatures
up to 900 °C [19], making it is unlikely to re-evaporate at $\text{Cr}_2\text{O}_3$ growth temperatures.
The only other stable ternary compound is magnesium chromate, MgCrO$_4$. Similarly
to the spinel, this material was synthesized at temperatures of 1600 °C, suggesting
that it is stable at high temperatures, and unlikely to re-evaporate [20]. Direct
detection of re-evaporating species can be performed with a line-of-sight quadrupole
mass spectrometer, but in the MBE system used the mass spectrometer is located
in a fixed position at the perimeter of the main chamber, and is used solely for
background gas analysis. The line-of-sight technique has previously been used to
study the sub-oxide formation and subsequent desorption during growth of SnO$_2$,
Ga$_2$O$_3$, and In$_2$O$_3$ [21]. Magnesium is not known to form any suboxides and so
is ruled out as a potential desorbing species. The most likely candidate is thus
re-evaporation or desorption of elemental Mg from the surface of the growing film.
Magnesium is a high vapour pressure element, and so would be expected to be
volatile at a temperature of 600 °C.

It is seen in Figure 4.9 that subjecting grown samples to a post-growth anneal at
700 °C for 2 hours in 1 atm of oxygen is found to improve the conductivity of the
material, typically by 50%, yet not have a detrimental effect on the optical properties
of the film. This results in a FoM improvement by a factor of approximately 3. While
the most conductive material is desirable for buffer layer applications, post-growth
annealing was not explored further due to the temperature sensitivity of the FTO
and ITO substrates used.

### 4.3.3 $\text{Cr}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$:Mg on ITO and FTO

After the ideal growth conditions were established on Al$_2$O$_3$ substrates, $\text{Cr}_2\text{O}_3$ films
were grown on both ITO and FTO, to determine how these substrates affect the
crystal structure and growth rates. The ITO substrates had a low enough surface
roughness (<1 nm) that XRR could be performed on the Glass/ITO/Cr$_2$O$_3$ samples. An example of such a measurement is shown in Figure 4.12. It was found that the film grew at the same rate on ITO and FTO as it did on Al$_2$O$_3$.

No oscillations could be detected when performing XRR on FTO or FTO/Cr$_2$O$_3$, implying that the surface roughness is quite high (>2 nm). Instead, a combination of AFM and profilometry was used to determine the thickness. To estimate the surface roughness of the FTO substrates, AFM was performed as shown in Figure 4.13. The roughness is seen to be on the order of 5–6 nm. While the roughness calculated from AFM is taken over a much smaller area than XRR (a factor of ~10,000 in the surface area scanned), the two values are typically within reasonable agreement, e.g., the ITO in Figure 4.12 had a surface roughness of 0.7 nm, while AFM measurements on other ITO substrates were found to have a surface roughness of less than 1.5 nm.

It is seen that the deposited Cr$_2$O$_3$ has approximately the same roughness as the underlying substrate. This also occurs when Al$_2$O$_3$ is used as the substrate; epitaxial Cr$_2$O$_3$ films have a roughness on the order of 0.1–0.2 nm. In some cases, the ABL can fill in the voids present on the surface of a rough substrate and produce a “smoothed” out surface. This is important as just as in the case of Cr$_2$O$_3$, the surface can influence the morphology of the next layer. For the case of the ABL the next layer is one of the active organic layers. This continuation of morphology has been shown for ultra-thin films of gold, where it acted to smooth out the surface of ITO [22]. A study of this kind was performed by Dahou et al., where it was shown that for three types of FTO with roughness values of 5, 20 and 35 nm, only the smoothest substrates could produce cells which demonstrated efficiencies over 1% [23].

Figure 4.12: XRR measurement of a Glass/ITO/Cr$_2$O$_3$ sample. The high frequency oscillations are due to the ITO (measured as 94 nm thick), while the low frequency oscillations are due to the Cr$_2$O$_3$ (measured as 6.5 nm thick).
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Figure 4.13: AFM images of an FTO substrate before and after deposition of a 7 nm thick Cr₂O₃ layer. (a) FTO substrate. Image is (2.5 × 2.5)µm² in size. RMS roughness is 5.84 nm. (b) The same FTO substrate with 7 nm Cr₂O₃ deposited on top. Image is (2.5 × 2.5)µm² in size. RMS roughness is 6.34 nm.

XRD was performed on both Cr₂O₃:Mg/FTO and Cr₂O₃/ITO samples but no diffraction peaks originating from the Cr₂O₃ were found, implying that the material grows in an amorphous fashion when deposited on ITO/FTO.

As light must pass through the ABL before entering the active layer, the ABL must be transparent to the visible spectrum so as not to reduce the quantum efficiency of the cell. To quantify the amount of light absorbed by Cr₂O₃:Mg, films of thicknesses ranging from 7–20 nm were grown on FTO, and the transmission spectrum of the samples measured using UV-Vis spectroscopy. This is shown in Figure 4.14. The Cr₂O₃:Mg is seen to be highly transparent in the thicknesses grown here, with the 20 nm layer only reducing the amount of light that will reach the active layers by ∼10%.

4.4 Solar Cell Fabrication and Characterisation

Thin layers of Cr₂O₃ and Cr₂O₃:Mg in the thickness range of 5–20 nm were grown on pre-prepared ITO and FTO substrates. After this, the combined anode and ABL were shipped to the laboratory of Prof. Cattin and Prof. Bernède in Nantes, France. The samples were not shipped in vacuum, nor was any protective layer applied to the surface. The remainder of the solar cell was fabricated in Nantes. There, the shipped samples were cleaned with propan-2-ol before being inserted into a vacuum deposition chamber. The chamber has a base pressure of 7.5 × 10⁻⁷ Torr. All the remaining layers of the solar cell were deposited in this chamber without exposing the sample to air. The final structure of the solar cell is Glass/TCO/ABL/CuPc/C₆₀/Alq₃/Al. Here, the TCO anode is either FTO or ITO, and the ABL is either Cr₂O₃ or Cr₂O₃:Mg. CuPc acts as the electron donor, while C₆₀ is the electron acceptor. A
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Figure 4.14: Transmission spectra of FTO/Cr$_2$O$_3$ with various Cr$_2$O$_3$ thicknesses. (a) The transmission is seen to slowly decrease as the Cr$_2$O$_3$ buffer layer thickness is increased. (b) The average transmission in the visible range as a function of Cr$_2$O$_3$ thickness. The average was taken in the range 1.5–3.1 eV (800–400 nm).

schematic, and the physical structure of the cell are shown in Figure 4.15(a) and Figure 4.15(b) respectively, while the chemical structure of the organic compounds is shown in Figure 4.16. The relevant energy levels for the operation of the cell for the donor, acceptor, and anodes are shown in Figure 4.17. The thickness and deposition rates of the layers grown in this vacuum deposition system have been previously optimised [24], they are 35 nm at 0.5 Å s$^{-1}$ for CuPc, 40 nm at 0.5 Å s$^{-1}$ for C$_{60}$, and 9 nm at 1 Å s$^{-1}$ for Alq$_3$. The deposition rates of each layer are monitored by a quartz crystal monitor, similar to that used in the MBE growth of Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg.

A mask to define the active area is then moved in front of the cell, and the aluminium back contact is deposited. The effective area of each cell is (2×5)mm$^2$, or equivalently 0.1 cm$^2$. As a final step, approximately 100 nm of amorphous selenium is deposited on the cell. This layer encapsulates the device, and has been shown to protect the sensitive organic layers and the aluminium layer of the device from oxygen and water vapour present in the air [26]. The effect of this is to produce a cell which has a markedly improved lifetime when compared with cells which have no encapsulation layer. A commonly used definition of the lifetime of a cell is the time taken for the efficiency of the cell to reduce to half of its original value in standard atmospheric conditions and lighting. Typical lifetimes for organic cells are on the order of several minutes to months.

The “standard” ABL in many OSCs is PEDOT:PSS, due to its high performance. In a similar manner, Bathocuprione (BCP) is a very commonly used cathode buffer layer in many cells. Here, aluminium tris(8-hydroxyquinoline), or Alq$_3$ is instead used as the cathode buffer layer as cells which incorporate this buffer layer have been
Figure 4.15: Schematic and physical structure of the organic solar cells produced. The selenium encapsulating layer is not shown for clarity. (a) Light enters through the front contact, which is shown at the bottom in this picture. Each layer thickness is drawn approximately to scale. (b) The glass substrate is shown as a white-filled rectangle. Each subsequent layer is deposited slightly offset from the previous layer to ensure that no short circuits occur throughout the cell.

shown previously to have a much longer lifetime [27]. In cells which had the same structure as those used in this work (but without encapsulation), the cell fabricated with Alq3 was found to have a lifetime of over 150 times that of a cell which contained BCP as the cathode buffer layer (159 hours vs 23 minutes). Similar to the ABL, the cathode buffer layer must be chosen carefully to ensure that it works effectively with the chosen active layers.

The IV characteristics of the cell were measured with a calibrated solar simulator (Oriel 300W) at 100 mW cm\(^{-2}\) light intensity, adjusted with a reference 0.5 cm\(^2\) Copper Indium Gallium Selenide (CIGS) solar cell which was previously calibrated at the National Renewable Energy Laboratory, USA. Measurements were performed in ambient atmosphere, under standard AM 1.5 conditions, with the samples having been exposed to atmosphere for the minimum amount of time.

4.5 Characterisation of Cells With Cr\(_2\)O\(_3\) and Cr\(_2\)O\(_3\):Mg as a Buffer Layer

It was shown in 2011 by Qin et al. that amorphous Cr\(_2\)O\(_3\) [28] worked well as an ABL in a bulk heterojunction OSC, with the optimised buffer layer thickness of
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(a) Aluminium tris(8-hydroxyquinoline) or Alq₃

(b) CuPc

(c) C₆₀

Figure 4.16: The organic compounds used in the fabrication of the organic solar cells used in this work.

Figure 4.17: Notable energy levels of the materials used in the OSCs in this work. The vacuum level is set to 0 eV for all materials. The black lines farthest from the vacuum level represent the VBM for FTO/ITO and the HOMO for CuPc/C₆₀, while the black lines closer in energy represent the CBM and LUMO respectively. Green lines represent the Fermi level. The work functions of FTO/ITO were measured with UPS, as described in a later section. Remaining data taken from [25].

10–14 nm producing a cell with an efficiency of ∼3%, similar to a cell which had a PEDOT:PSS buffer layer. Unfortunately, no data on a cell without an ABL was produced for comparison. They also demonstrated that optimisation of the buffer layer thickness was crucial to obtain a high efficiency cell; a reduction in the buffer layer thickness by as little as 4 nm reduced the cell efficiency to 2.5%, while reducing it a further 4 nm reduced the cell efficiency to 2%. This was one of the primary reasons for choosing to grow the Cr₂O₃ and Cr₂O₃:Mg buffer layers by MBE; highly precise thickness control is more easily achieved compared to other growth methods such as magnetron sputtering. Such a strong dependence of efficiency on buffer layer thickness has been previously observed by Shrotriya et al. [29], who argued that while a minimum thickness of ABL is required to form a uniform contact (to reduce leakage current), too thick of an ABL will increase the series resistance of the cell.
Table 4.2: Effect of Cr$_2$O$_3$ buffer layer on the properties of OSCs with an ITO anode. $t$ is the ABL thickness.

<table>
<thead>
<tr>
<th>$t$ (nm)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$R_S$ (Ω)</th>
<th>$R_{SH}$ (Ω)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.157</td>
<td>2.18</td>
<td>118</td>
<td>86</td>
<td>26</td>
<td>0.09</td>
</tr>
<tr>
<td>5</td>
<td>0.467</td>
<td>3.50</td>
<td>3100</td>
<td>220</td>
<td>20.5</td>
<td>0.333</td>
</tr>
<tr>
<td>8</td>
<td>0.440</td>
<td>4.38</td>
<td>4000</td>
<td>154</td>
<td>19</td>
<td>0.365</td>
</tr>
</tbody>
</table>

and result in a lower cell current. Shrotriya et al. further found that for their bulk heterojunction cells with an ITO anode, the optimum thickness was 3 nm for a V$_2$O$_5$ ABL and 5 nm for an MoO$_3$ ABL.

While the results published by Qin et al. were promising, the only cells fabricated were heterojunction OSCs, making the exact mechanism of the efficiency improvement provided by the Cr$_2$O$_3$ layer difficult to determine. Furthermore, the films grown in that study possessed a resistivity as low as $2.5 \times 10^1$ Ω cm; the same order of magnitude as the intentionally doped and optimised Cr$_2$O$_3$:Mg films presented in this work. The authors attributed this anomalous high conductivity to chromium vacancies. While this defect would be expected to produce p-type conductivity, DFT calculations have shown that chromium vacancies have a high formation energy, and would be unlikely to form [16]. One possibility is that the films produced were not phase pure; CrO$_2$ is a well-known half metal with a high conductivity. Hall effect measurements on the most conductive sample show a low carrier concentration of $5.73 \times 10^{19}$ cm$^{-3}$ and a Hall mobility of $4.7 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ suggest that erroneous resistivity data were published. Similar results were shown for Cr$_2$O$_3$:N [30], where an efficiency of $\sim 3\%$ was demonstrated, with the Cr$_2$O$_3$:N films showing the same low resistivity. The combination of using a bulk heterojunction solar cell architecture and using unintentionally conductive Cr$_2$O$_3$ leads to complexities in the analysis on the role which Cr$_2$O$_3$ plays in these cells; in this section both insulating Cr$_2$O$_3$ and conductive Cr$_2$O$_3$:Mg are investigated as a buffer layer in an OSC to elucidate the mechanism behind how it provides efficiency improvements.

4.5.1 Cells Fabricated on ITO

Measurements were initially performed using ITO as an anode and Cr$_2$O$_3$ as a buffer layer to determine whether it possessed the necessary band structure to improve hole extraction from the active layers of the fabricated cells. ITO was chosen for initial measurements as there exists a larger amount of literature data with which to compare it to in comparison to FTO. The properties and parameters extracted from least-squares fitting of the $IV$ curves of all fabricated cells with ITO anodes are shown in Table 4.2.
It is seen that in the case of an ITO anode, introduction of the insulating \( \text{Cr}_2\text{O}_3 \) layer results in a large increase in the series resistance of the cells produced. This is to be expected, as the introduction of any extra layers in the cell will increase the resistance of the whole device; this will be exacerbated in the case of a highly resistive layer. Despite this, there is a large enough improvement in the \( V_{\text{OC}} \) and \( I_{\text{SC}} \) of the cells that the efficiency increases by over a factor of 3, from 0.09% for a cell with no buffer layer present to 0.365% for a cell with an 8 nm \( \text{Cr}_2\text{O}_3 \) ABL. The measured \( IV \) curves are shown in Figure 4.19 (a).

As seen in Figure 4.17 the HOMO-LUMO separation of the CuPc/\( \text{C}_60 \) system is \( 5.2 \text{ eV} - 4.5 \text{ eV} = 0.7 \text{ eV} \); using this in Equation 2.12 gives a predicted open circuit voltage of 0.4 V, which agrees well with the open circuit voltages of \( \sim 0.45 \text{ V} \) measured in the cells containing a \( \text{Cr}_2\text{O}_3 \) ABL. This is much larger than the \( V_{\text{OC}} \) value of 0.16 V obtained when the anode consists of ITO with no ABL. This large increase in \( V_{\text{OC}} \) is indicative than \( \text{Cr}_2\text{O}_3 \) possesses a band structure which can more easily facilitate extraction of holes from CuPc when compared with ITO alone as an anode.

The shunt resistance of the cell is seen to increase by a factor of two when the \( \text{Cr}_2\text{O}_3 \) ABL is present. An increase in shunt resistance has been previously linked with a decrease in roughness of the anode [23]; this implies that the \( \text{Cr}_2\text{O}_3 \) is acting to smooth out the surface of the ITO. The increase in shunt resistance is however only moderate, with the value for ITO alone being particularly low. Analysis of AFM images shows that the ITO substrates have an average root mean squared roughness of 1.4 ± 0.3 nm (3 samples) while the ITO/\( \text{Cr}_2\text{O}_3 \) samples have a roughness of 1.1 ± 0.5 nm (9 samples) where here the error represents the standard deviation. While this low roughness would not be expected to produce cells with such low shunt resistances, AFM, shown in Figure 4.18, reveals that the ITO surface consists of an extremely smooth surface with numerous large grains with heights greater than 100 nm. This detail is lost when only considering the root mean square roughness of a surface. These grains will clearly not be completely covered deposition of several nanometres of \( \text{Cr}_2\text{O}_3 \) and are likely to cause short-circuits in the cell, reducing the shunt resistance of the device.

The short circuit current density is seen to increase with increasing \( \text{Cr}_2\text{O}_3 \) buffer layer thickness, indicating that the \( \text{Cr}_2\text{O}_3 \) in its function as a buffer layer, is acting to improve the collection of light-generated carriers within the cell. This can be either due to the \( \text{Cr}_2\text{O}_3 \) transporting holes more efficiently to the anode, preventing electrons from reaching the anode, or a combination of the two. If the thickness of the \( \text{Cr}_2\text{O}_3 \) layer would be increased much further, it would be expected that the increased resistance the \( \text{Cr}_2\text{O}_3 \) layer from would begin to outweigh the advantage gained by the increased carrier collection.

In Figure 4.19 (b) and (c), the decay in the efficiency of the cell is seen to be
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Figure 4.18: (a) AFM image of an ITO surface. The image is \((10 \times 10)\mu\text{m}^2\) in size. (b) The profile along the white line present in (a). Several large protrusions such as that shown in the line profile are present in the image.

predominantly due to the decay in the short circuit current of the device with time. The power output of the cell drops to half its original value after 46 hours. This degradation is inherent in the vast majority of OSCs, and is an obstacle to be overcome if they are to see widespread adoption. Previous measurements on cells with the same materials have suggested that the lifetime of the cell is limited by the degradation of the C\(_{60}\) layer in ambient conditions [31], and is not dependent on the illumination conditions. The C\(_{60}\) layer reacts with O\(_2\) and H\(_2\)O present in the air, which increases its resistivity and decreases the current flowing through the cell. While all cells produced were capped with a layer of amorphous selenium, it has been shown previously [32] that CuPc is seen to degrade under UV illumination, resulting in a decrease in the efficiency of cells using it as a donor layer. A minor difference in the morphology of the CuPc was measured at its surface after UV exposure, and was proposed as the mechanism of degradation.

One notable feature present in both IV curves in Figure 4.19 is the “S”-shape or kink which is present. While a low performance cell with a large series resistance and low shunt resistance will possess an IV curve with a very low fill factor, it will still retain a similar shape to the ideal case, with an increasing slope as the voltage is increased (see Figure 3.17(f)). The physical reason for this unusual IV curve shape is highly debated, and has been observed in many OSCs containing a large variety of materials. Many possible explanations have been put forward: Säve et al. attributed it to hindered charge carrier transport at the organic/cathode interface [33], Ecker et al. attributed it to highly resistive TiO\(_x\) ABL [34] while Wagner et al. also attributed the effect to a high cell series resistance [35]. Tress et al. was able to show with drift-diffusion simulations that large differences in carrier mobilities between the two active materials produces an S-shaped curve [36], while
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**Figure 4.19:** (a) The measured $IV$ curves of the samples listed in Table 4.2. The dark curves are shown as dashed lines. (b) The change in shape of the $IV$ curve of the sample ITO+5 nm Cr$_2$O$_3$ with time. (c) The decay of the efficiency and short circuit current of the same solar cell with time.

Finck & Schwartz used similar simulations to show that a drop in conductivity at either one of the cell contacts, modelled by largely different carrier mobilities at each end of the cell produced similar $IV$ curve shapes.

The S-shaped curves present here cannot be modelled by an equivalent circuit with a single diode and two intrinsic resistances. Instead, to accurately reproduce the shape of the curves of the cells with an ITO anode, a second diode (and an associated shunt resistance for this diode) must be added to the equivalent circuit model, as shown in Figure 4.20. This second diode can be thought to represent a barrier for

**Figure 4.20:** Equivalent circuit of a cell that is represented with the double-diode model.
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![](image)

charge carriers existing within the cell. This model assumes that conduction across this diode is due to thermionic emission, where the hole current can be written as [38]

\[
I = -I_0 \left[ \exp \left( \frac{qV_b}{kT} \right) - 1 \right]
\]  

(4.3)

where the saturation current \( I_0 \) depends on the Richardson constant, temperature and the Schottky barrier height between the anode work function and the energy level where holes are being extracted from, that is, the HOMO of the electron donor if no ABL is present, or the VBM if a hole conducting ABL is used. Equation 4.3 can be added to the single-diode model and solved. While the model assumes a Schottky barrier, the various aforementioned works can reproduce the same \( IV \) characteristics with the presence of a low conductivity/mobility section in the cell, possibly indicating that it is not the nature of the barrier which is important, but any difficulty in carrier extraction will lead to an S-shaped \( IV \) curve.

Many of the previously published results attribute the S-shaped characteristics to the existence of some form of difficulty in extracting carriers from the cell, be it through a barrier at the anode, cathode, or the active layers. Godoy et al. has shown that for the situation where ITO without an ABL is used as an anode, the double-diode model is necessary to accurately fit the \( IV \) curve, but single-diode \( IV \) characteristics are obtained again when an ABL consisting of a thin layer of gold is used in the cell [24]. As these results were obtained using the exact same cell architecture and show that the effect resides purely at the anode, here it will be assumed that the barrier lies at the anode sections of the cell. When a buffer layer is present, the barrier could exist at either ITO/ABL, the ABL/organic interface, or both.

While simulations show that the barrier causing this problem is due to a low conductivity/mobility at one contact of the cell, it is also a possibility that there is an extraction barrier present caused by a difference in energy between the valence band maximum of the ABL and the conduction band minimum of the anode. Both are possible with insulating \( \text{Cr}_2\text{O}_3 \), but using the much more conductive p-type \( \text{Cr}_2\text{O}_3:\text{Mg} \) should elucidate which of the mechanisms is causing the cells to show less than ideal characteristics. This was tested by growing cells on FTO, with some having a \( \text{Cr}_2\text{O}_3 \) ABL and some having a \( \text{Cr}_2\text{O}_3:\text{Mg} \) ABL. Cells containing \( \text{Cr}_2\text{O}_3:\text{Mg} \) as an ABL on an ITO anode have yet to be fabricated; these measurements are planned as future work.

### 4.5.2 Cells Fabricated on FTO

FTO was chosen as the anode to compare both \( \text{Cr}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3:\text{Mg} \) as an ABL. The primary reason for choosing FTO as an anode for OSCs is that it possesses similar
properties to ITO, but does not include expensive and rare indium. While ITO is the most widely used transparent electrode in modern organic optoelectronics [39] and often demonstrates OSCs with superior properties, using expensive/rare materials removes the low-cost element of these cells, which is one of their primary advantages over mature silicon solar cell technology.

The properties and parameters extracted from least-squares fitting of the $IV$ curves of all fabricated cells with FTO anodes are shown in Table 4.3 and the measured $IV$ curves are shown in Figure 4.21 (a).

The effect of using undoped Cr$_2$O$_3$ as an ABL on FTO shows similar results to what was obtained on ITO; the series resistance of the cell remains high, yet an increase in both short circuit current and open circuit voltage provide an overall efficiency increase in the cell of a factor of $\sim 2$. On the other hand, when Cr$_2$O$_3$:Mg is employed as the ABL the series resistance is seen to decrease in comparison with no ABL. A concomitant improvement in the efficiency by a factor of 3 is also observed. Despite this, there is little improvement in the other cell parameters, which leads to Cr$_2$O$_3$:Mg providing approximately the same increase in efficiency as Cr$_2$O$_3$. This provides evidence that there is an offset between either the Cr$_2$O$_3$:Mg VBM and the CuPc HOMO, or there is an offset between the same VBM and the CBM of FTO.

The shunt resistance values obtained from the measured $IV$ curves indicate that the Cr$_2$O$_3$:Mg is possibly not providing complete coverage at low thicknesses; the 20 nm thick ABL provides a notable increase in shunt resistance. While thicker layers could be grown, this will continue to lower the short circuit current, offsetting

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2The solar cell measurements utilising Cr$_2$O$_3$ (and the 0 nm reference cell) were carried out at a different point in time to the cells utilising Cr$_2$O$_3$:Mg (and the 0 nm reference layer). The $IV$ testing apparatus was calibrated in between these sets of measurements, resulting in each reference cell showing slightly different $IV$ characteristics. For this reason, the Cr$_2$O$_3$-containing and Cr$_2$O$_3$:Mg-containing cells are only compared to their respective 0 nm reference measurement, and not directly to each other.
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Figure 4.21: *IV* measurements of cells with an FTO anode and a Cr$_2$O$_3$:Mg buffer layer. (a) The measured *IV* curves. The dark curves are omitted for clarity. A cell with a 3 nm MoO$_3$ buffer layer is included for comparison (b) The efficiency of the OSCs produced as a function of the Cr$_2$O$_3$:Mg buffer layer thickness. The maximum is seen to lie in the range 10–15 nm.

Any efficiency gains provided by an increased shunt resistance. Both anode and cathode buffer layers in OSCs have to have their thickness optimised; the competing behaviour of an increased series resistance due to the addition of extra material and the increase in efficiency due to improved carrier extraction must be balanced. This is shown for the case of Cr$_2$O$_3$:Mg in Figure 4.21 (b), where the ideal buffer layer thickness is found to lie between 10 and 15 nm.

If the anomalous *IV* curve of the sample with a 10 nm Cr$_2$O$_3$:Mg ABL is ignored, the change in the short circuit current is seen to vary with ABL thickness in the same way as the efficiency does. The reason for the unusual shape of the 10 nm Cr$_2$O$_3$:Mg ABL is currently unknown. The cell with a MoO$_3$ ABL is seen to possess much improved characteristics in every aspect when compared to Cr$_2$O$_3$:Mg. While the fill factor of the MoO$_3$-containing cell is 53% which is far from ideal, it does not demonstrate the same S-shaped characteristics as the other cells. MoO$_3$ is another oxide which possess a high work function of 6.6 eV and demonstrates n-type conductivity, although this conductivity heavily depends on the stoichiometry as it is due to oxygen defects [40].

To demonstrate the importance of a highly conductive anode and ABL for cell performance, several FTO substrates were annealed to increase their sheet resistance, after which solar cells including a Cr$_2$O$_3$:Mg ABL (all of the same conductivity) were fabricated on them. The results, shown in Figure 4.22 show that there is a direct link between the sheet resistance of the anode and the series resistance of the cell,
Figure 4.22: Variation of measured solar cell series resistance with sheet resistance of the FTO anode. A clear correlation is seen between the sheet resistance of the anode and the cell series resistance, and thus overall efficiency.

demonstrating the necessity of a conductive anode and ABL to achieve the maximum performance.

In summary, Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg were shown to act as effective ABLs in the OSCs fabricated in this work. Cr$_2$O$_3$ was seen to provide a slight smoothing of the ITO surface, although the large height grains present on the ITO surface lead to a low shunt resistance regardless of the Cr$_2$O$_3$ thickness. The optimum thickness of a Cr$_2$O$_3$:Mg ABL for an FTO anode was determined to be 10–15 nm. A linear dependence was shown between the sheet resistance of an FTO anode and the resulting series resistance of a cell fabricated from the same anode.

Using more conductive Cr$_2$O$_3$:Mg is seen to results in cells with a lower series resistance than those fabricated with Cr$_2$O$_3$. Despite this, the improvement in $I$V characteristics expected by using the much more conductive Cr$_2$O$_3$:Mg over Cr$_2$O$_3$ was not observed. There are two possibilites for this, either that the Cr$_2$O$_3$:Mg used still possesses too low of a conductivity or mobility to be able to efficiently transport holes to the FTO, or there is a non-ideal line up of the VBM of Cr$_2$O$_3$:Mg with either the HOMO of CuPc or the CBM of FTO. To determine whether this was the case, band offset measurements were performed on the interfaces between Cr$_2$O$_3$:Mg, Cr$_2$O$_3$ and ITO/FTO to directly measure the potential barriers to hole transport that could be present. Following this, more detailed band alignment measurements were performed to see how band bending at the interface could modify the original alignment. Band offset measurements were then performed Cr$_2$O$_3$:Mg/CuPc interface to understand the complete hole transport through the cell.

The band alignment of Cr$_2$O$_3$:Mg/FTO is first discussed to demonstrate and explain how these measurements are performed.
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4.6 Band Alignment of Cr$_2$O$_3$:Mg and FTO

As discussed in Section 3.4, XPS and UPS can be used to measure the energetic position of the VBM, Fermi level, and vacuum level of a material. Band alignment is the measurement of these levels as one material is progressively deposited on top of the next, allowing detection and quantitative determination of band offsets, and band bending as a function of the thickness of the deposited layer. From these measurements, any barriers for hole transport between FTO and Cr$_2$O$_3$:Mg can be identified. When combined with a band gap measurement (or values taken from literature) conduction band offsets can also be determined.

UPS measurements are extremely surface sensitive due to the low photon energy used, so any determination of the work function will depend strongly on how the surface was treated or cleaned before the measurement. In addition, the act of performing a UPS measurement involves exposing the sample to a high intensity ultraviolet photon source with photon energy 21.2 eV; the act of performing this measurement has been seen to modify the work function of certain materials which are sensitive to ultraviolet radiation [41]. For the measurements shown in this work, the substrates were cleaned exactly as they would be before insertion into the UHV XPS/UPS system and exposed to the UV source for as little time as possible.

A piece of first FTO was inserted into the UHV XPS/UPS system to measure its pseudo-bulk properties$^3$. This includes the work function, the difference in energy between the Fermi level and VBM ($E_F - E_{VBM}$) and the energetic position of selected core levels in the material. Following this, the FTO was transferred to the MBE using the UHV transfer system described in Section 3.5. In the MBE, a thin layer of 4 Å of Cr$_2$O$_3$:Mg was grown on the FTO, in a similar manner to how the ABLs discussed in the previous section were grown. The sample was transferred back to the XPS using the UHV transfer system where selected core level spectra of both FTO and Cr$_2$O$_3$:Mg were measured. This was repeated for Cr$_2$O$_3$:Mg thicknesses of 8 Å, 15 Å, 25 Å, and 30 Å. Finally, Cr$_2$O$_3$:Mg was grown until the film had a total thickness of $\sim$30 nm so that pseudo-bulk measurements could be performed. This thickness is much greater than the escape depth of electrons in the material to ensure that no photoelectrons originating from the FTO are detected. Following all photoemission experiments, the sample is removed from vacuum and XRR is performed to measure the total thickness of the Cr$_2$O$_3$:Mg layer. The thickness at each step is extrapolated from this value. When transported in the UHV transfer system, the sample is kept in vacuum of approximately $5 \times 10^{-9}$ Torr. When being moved from the transfer system, through the loadlock and into the UHV main chambers in each system, the thickness at 80–100 nm thick, any band bending that is present at the interface is expected to be negligible at this thickness.

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$^3$At 80–100 nm thick, any band bending that is present at the interface is expected to be negligible at this thickness.
Figure 4.23: Work function and valence band maximum of FTO as determined by UPS and XPS respectively. The UPS was performed with a bias of 5 V applied to the sample to shift the secondary edge of the analyser; this has been subtracted on the scale here. Both values were determined by fitting lines to the relevant leading edge and the background, and finding the point of intersection between the two.

The UPS measurements of FTO are shown in Figure 4.23. The work function of FTO that has been cleaned first with soap and rinsed with deionised water, followed by a 15 minute clean in an ultrasonic bath in each of acetone, propan-2-ol and deionised water is found to be 4.1 eV while its VBM is 4.1 eV. Varying the doping level and the surface treatment can vary the work function by a large amount; previous results have shown that by just varying the cleaning chemicals used, a variation in the work function by 0.35 eV could be achieved [42]. The same publication also attributes the highest intensity peak, which is at the top of the valence band to the O 2p band of SnO$_2$. What appears to be a finite density of states above the marked VBM in Figure 4.23, between 2–4 eV, has been previously observed and attributed to He I$\beta$ satellite of the O 2p band [42]. The same feature is seen in the XPS-measured valence band in this work, refuting this idea. This feature is more likely to be caused by secondary electrons associated with electrons in the conduction band/at the Fermi level. The signal due to these electrons is shown (magnified by a factor of 5) in Figure 4.23. The Fermi level is seen to lie at 0 binding energy of the spectrometer, assuring accurate calibration has been performed.

The same measurements are shown for bulk Cr$_2$O$_3$:Mg in Figure 4.24. The work function is 5.8 eV, much larger than that of FTO. The VBM is seen to lie 0.6 eV
Figure 4.24: Work function and valence band maximum of Cr$_2$O$_3$:Mg as determined by UPS and XPS respectively. The UPS was performed with a bias of 5 V applied to the sample to shift the secondary edge of the analyser; this has been subtracted on the scale here. Both values were determined by fitting lines to the relevant leading edge and the background, and finding the point of intersection between the two.

For the steps of intermediate Cr$_2$O$_3$:Mg thickness, the Sn 3$d$, Cr 3$p$, and the O 1$s$ core levels regions were analysed to measure any shifts in the binding energy present in these regions. The Cr 2$p$ was also measured, but was not used in the band alignment analysis due to it’s complex multiplet split core level, which involves up to 11 peak components. This core level, in addition to the Sn 3$d$ was used to determine the relative proportion of FTO and Cr$_2$O$_3$:Mg at each growth step as both peaks are close in binding energy and can be captured in a single measurement. This was performed by comparing the areas of the core levels and is shown in Figure 4.25. The Sn 3$d$ core level has become practically undetectable at Cr$_2$O$_3$:Mg thicknesses greater at 5 nm, justifying the use of 30 nm as a bulk sample of a material. The amount of hydroxide (OH) present on the surface of the sample is initially high, accounting for 50 % of the O 1$s$ core level by area. The hydroxide component was then found to generally reduce in intensity as the Cr$_2$O$_3$ layer was grown thicker. This is most likely due to two causes: The Cr$_2$O$_3$ layer is grown at elevated temperatures, which would likely cause some desorption of the OH species from the surface of the material. The initial FTO surface also did not undergo extensive UHV surface treatment, such as annealing or sputtering. Whatever OH species remain on the surface which were due to atmosphere exposure before loading in the UHV chamber could remain bonded to
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the FTO interface, and the signal due to this species would reduce in intensity as the Cr$_2$O$_3$ overlayer is made thicker.

The stoichiometry of FTO was determined by XPS to be 75% tin and 25% oxygen respectively. While this is far from the perfect stoichiometry of 33% tin and 66% oxygen, an excess of tin is to be expected in such conductive FTO. The conductivity of FTO arises from oxygen vacancies, and is typically increased by F$^-$ anions, which substitute for a O$^{2-}$ anion, creating a shallow donor level [43, 44]. In its stoichiometric form, SnO$_2$ is found to be highly resistive [45]. Due to the low formation energy of Sn interstitials and O vacancies, SnO$_2$ would be expected to have a stable, natural oxygen deficiency [46]. The presence of the fluorine dopant would also be expected to contribute towards some of the non-stoichiometry, but due to its low x-ray capture cross section and low atomic weight, determination of its presence is difficult with XPS.

While XPS data is typically fit using a number of components which are a convolution of Gaussian and Lorentz functions, this makes exact binding energy determination imprecise for broad core levels, and when the spectra show a considerable amount of noise. To accurately determine the position of the Sn 3$d_{3/2}$, 3$d_{5/2}$, and the Cr 3$p$ core levels for band alignment purposes, the raw data was first smoothed using a Savitzky-Golay filter, using enough points (typically 8-15) to ensure a smooth curve at the maximum in intensity at each core level. The raw data is shown in Figure 4.26. In this figure, all spectra have been shifted to their respective bulk values, so any band bending will not be seen. This allows us to compare the data at each step to ensure that there is no interdiffusion between the two materials at the interface, as this would present itself as a modification of the lineshape of each spectrum.

The O 1$s$ peak was fit by assuming three components: Cr-O, Sn-O and a hydroxide peak (OH). The positions were left unconstrained, as they will vary as the Cr$_2$O$_3$:Mg thickness is changed if there is any band bending present. The FWHM of the Sn-O and the Cr-O peaks were found from the bulk films to be 1.045 eV and 1.33 eV respectively. The FWHM of the OH component was found to be 2.04 eV on the bulk FTO and 2.25 eV on the bulk Cr$_2$O$_3$. The FWHM for the intermediate steps was allowed to vary between these values. Each bulk oxide O 1$s$ core level could be fit with two components - the main metal-oxide peak and a hydroxide peak, as seen in Figure 4.27. For the steps where both materials were simultaneously present, the FWHMs of these peaks were initially constrained to the bulk values, then allowed to vary by up to $\pm$0.025 eV; this small relaxation of constraints was allowed to account for the possibility of Cr-O-Sn bond formation at the first few atomic layers of the interface. This would likely produce a shifted, low intensity peak within the O 1$s$ region. Due to its low intensity, and small separation from either Sn-O or Cr-O, it
would effectively act to broaden the FWHM of the combined Metal-O1s component. This procedure was found to produce an excellent fit to the data, as can be seen in figure 4.27.

Combining the measurement of the bulk VBM position of both materials with the binding energy shifts of the selected core levels produces the band alignment diagram for the FTO/Cr$_2$O$_3$:Mg interface, and is shown in Figure 4.28. The error associated with each point on this graph is $\pm 0.1$ eV. As we move from bulk towards the interface, the VBM of Cr$_2$O$_3$:Mg is seen to bend downwards (away from the vacuum level). The bending has magnitude $0.6$ eV, as determined by taking the average of the shift of the Cr-O component of the O 1s core level and the Cr 3p core level. No band bending is seen to occur within the FTO, regardless of the Cr$_2$O$_3$:Mg thickness. While the Sn-O component of the O 1s core level does show a large shift at relatively large (5 nm) Cr$_2$O$_3$:Mg thickness, this has been ignored here as at this thickness the Sn-O component is extremely low intensity and the quality of fit obtained in Figure 4.27 does not depend strongly on the position that the component is placed. This is in contrast to the Sn 3d core level where a shift is easily detectable yet no shift is seen for any thickness of Cr$_2$O$_3$:Mg.

Figure 4.25: The relative proportion of FTO and Cr$_2$O$_3$:Mg at each growth step measured by XPS. This was calculated from the relative ratios of areas of the Sn 3d and Cr 2p core levels. The proportions have been calculated from the raw data and do not take the IMFP of the electrons in each layer into account.
4.6.1 Band Diagram of FTO/\(\text{Cr}_2\text{O}_3\cdot\text{Mg}\)

To construct the full band diagram of FTO, \(\text{Cr}_2\text{O}_3\cdot\text{Mg}\), and the interface between the two from the above information, the band gap of each material must be known.

As discussed in Section 2.5.1, work in preparation by Norton et al., titled “Fundamental Band Gap of \(\text{Cr}_2\text{O}_3\) and \(\text{Cr}_{2-x}\text{Mg}_x\text{O}_3\)” provides strong evidence that the fundamental band gap of \(\text{Cr}_2\text{O}_3\) is \(2.1\) eV, a significant decrease over the often reported value of \(3.4\) eV \([47, 48]\). As the value of the band gap is not essential to the conclusions made here, and the work determining the new value has yet to be published, the value used in this work is \(3.4\) eV.

The band gap of FTO is taken as \(3.2\) eV, the same as undoped \(\text{SnO}_2\) \([42, 49]\). Due to the heavy fluorine doping it is possible for the band gap to vary due to combination of the Burstein-Moss shift and band gap renormalisation. With this in mind an error of \(\pm0.2\) eV is assumed for this value.

The full band diagram is presented in Figure 4.29. The conduction band offset between the FTO and \(\text{Cr}_2\text{O}_3\cdot\text{Mg}\) is seen to be very large at \(3.1\) eV. If the revised band
gap for Cr₂O₃:Mg of 2.1 eV is used, this reduces this offset to 1.8 eV. The relevant barrier for hole transport between the two materials is that where conduction takes place in both materials, i.e., the CBM of FTO and the VBM of Cr₂O₃:Mg. Without band bending present, there is a barrier for hole transport at this interface equal to 0.3 ± 0.1 eV. Previous work has indicated that a barrier of 0.5 eV is enough to significantly affect the fill factor of a CdTe cell and introduce S-shaped characteristics in the IV curves, but not have a major effect on the open-circuit voltage of the cell [38]. This has been demonstrated in the cells fabricated on FTO; the fill factor and thus efficiency of cells with a Cr₂O₃:Mg anode was significantly lower than those with a MoO₃ anode, but both cells showed the same open circuit voltage. The experimentally determined barrier height combined with the uncertainty in the band gap of FTO leads to the strong possibility of the barrier equalling this magnitude. This strongly suggests that this barrier is responsible for the inhibited hole transport from the Cr₂O₃:Mg to the FTO.

When band bending is taken into account, the barrier height is effectively reduced.
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Figure 4.28: Relative change of core level positions (and thus VBM position) in FTO and Cr$_2$O$_3$:Mg as a function of Cr$_2$O$_3$:Mg layer thickness.

Figure 4.29: The band alignment of FTO and Cr$_2$O$_3$:Mg. (a) The bulk energy levels of each material are highlighted. Respective band gaps are shown in red, work functions in blue, and VBM levels relative to the Fermi level in black. (b) The bending and offsets that are produced at the interface between FTO and Cr$_2$O$_3$:Mg. The offset between the VBM of Cr$_2$O$_3$:Mg and the CBM FTO is highlighted in red.
Figure 4.30: Applying Anderson’s rule to the FTO/Cr$_2$O$_3$:Mg interface. (a) All the band bending is present in the Cr$_2$O$_3$:Mg, similar to the band alignment measurements. (b) There is equal band bending in both materials.

to zero. While this might imply that hole transport across this interface should be facile, Figure 4.29 does not accurately represent the spatial extent of the band bending. In traditional semiconductors such as germanium or gallium arsenide, band bending can typically be detected over a thickness of $\sim 100$ nm [50]. Here, due to the large carrier concentrations of both materials, the bands are seen to return to their bulk values after moving 5–10 nm away from the interface, over an order of magnitude greater than typical semiconductors. While the barrier effect will possibly be slightly reduced, this relatively large change in band energy over such a short distance will resemble a localised barrier of height close to that in the case where band bending is not present.

Figure 4.30 shows the interface alignment between FTO and Cr$_2$O$_3$:Mg predicted by Anderson’s rule. While this model does not predict in which material the bending will occur, estimates can be made by considering the carrier concentrations in each material. Two situations have been considered here: the case where the bands do not bend in FTO and the the bending is restricted to the Cr$_2$O$_3$:Mg as is seen in the band alignment measurements, and the case where the band bending is shared equally between the two materials, as they both possess high carrier concentrations. In both cases a larger barrier from the CBM of FTO to the VBM of Cr$_2$O$_3$:Mg is predicted at the interface, and the predictions for $\Delta E_{CB}$ and $\Delta E_{VB}$ are very different to the experimentally determined values. This highlights the necessity of experimental determination of the band alignment, rather than using a simple physical model.
4.6.2 Band Offset Measurements

Measuring the band alignment between two interfaces is time consuming as it requires XPS measurements at many different values of overlayer thickness. A much faster method, more suitable to screening of materials for potential uses as an ABL is the band offset method. This has been performed for both \( \text{Cr}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3:\text{Mg} \) on both ITO and FTO. The results are presented in Figure 4.31. The error in these energy level determinations is \( \pm 0.1 \text{ eV} \).

The similarities of the offsets present for both \( \text{Cr}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3:\text{Mg} \) on ITO and FTO correlate well with the similar cell properties obtained for the various anode/ABL combinations studied. This measurement serves to demonstrate that the choice of \( \text{Cr}_2\text{O}_3 \) or \( \text{Cr}_2\text{O}_3:\text{Mg} \) is not critical when performing measurements on the energetic position of the bands with the materials, as both materials show an extremely similar band structure.

For both ITO and FTO, the VBM of \( \text{Cr}_2\text{O}_3:\text{Mg} \) is 0.1 eV closer to the Fermi level than the VBM of \( \text{Cr}_2\text{O}_3 \). While this shift lies within the error of the measurement, if this shift is really present, in the case of FTO using \( \text{Cr}_2\text{O}_3:\text{Mg} \) over \( \text{Cr}_2\text{O}_3 \) as an ABL would increase the hole transport barrier by 0.1 eV, possibly offsetting the improvement that would be gained by the reduced series resistance provided by the \( \text{Cr}_2\text{O}_3:\text{Mg} \).

In the case of ITO, the separation between the VBM of \( \text{Cr}_2\text{O}_3:\text{Mg} \) and CBM of ITO is 0.7 eV. This energetic difference is a step, rather than a barrier that is present in the case of FTO, implying that hole transport between \( \text{Cr}_2\text{O}_3:\text{Mg} \) and ITO should not be inhibited.
As significant band bending was seen at the FTO/Cr$_2$O$_3$:Mg interface, the same band alignment measurements were repeated but with ITO as the substrate to determine if a large amount of band bending is present at the interface, possibly resulting in a barrier to hole transport.

### 4.6.3 Band Alignment of ITO/Cr$_2$O$_3$:Mg

Similar to Cr$_2$O$_3$:Mg, the band gap of ITO is still studied and under debate. Despite the early discovery and industrial use of ITO, the band gap of In$_2$O$_3$ was calculated using DFT by Walsh *et al.* in 2008, approximately 50 years after its commercialisation. This was further confirmed by x-ray emission and photoemission spectroscopy results. The fundamental band gap had erroneously assumed to be $\sim$3.7 eV, as this was the energy where a strong onset of optical absorption could be seen. Calculations showed that the VBM in fact lies $\sim$0.8 eV above the previously assumed VBM, reducing the band gap to 2.9 eV [51]. Transitions from this new VBM to the CBM were found to be forbidden as both states posses the same parity, while the crystal structure of In$_2$O$_3$ only allows transitions between states of opposite parity.

Due to the heavy doping with tin to form ITO, the band gap is likely to change due to combination of the Burstein-Moss shift and band gap renormalisation, in a similar manner to FTO. For this reason, the fundamental band gap used here is 2.9 eV, with the potential for it to be shifted by 200 meV in either direction.

The band alignment of ITO/Cr$_2$O$_3$:Mg is shown in Figure 4.32. The separation between the VBM of Cr$_2$O$_3$:Mg and CBM of ITO is seen to be 1.3 eV when band bending is considered and 0.7 eV when band bending is not taken into account$^4$. While the energetic difference between the VBM of Cr$_2$O$_3$:Mg and the CBM of ITO is larger when band bending is considered, it is still an energetic step which is present rather than a barrier, implying that this interface should not impede hole transport by a significant amount. In the case of using ITO as a substrate, this points towards a barrier existing at another interface in the cell. To this end, the interface between Cr$_2$O$_3$ and CuPc was investigated with XPS and UPS to determine if a barrier for hole collection was present.

### 4.6.4 Band Offsets with CuPc

While ideally band offset measurements are performed between two materials when the energetics at the interface between two materials is of interest, this is not always possible as band alignment measurements require the ability to transfer between XPS/UPS and growth chambers with the sample remaining in UHV conditions.

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$^4$This is the band bending value after subtracting the 0.2 eV bending in the ITO and the 0.4 eV bending in the Cr$_2$O$_3$:Mg.
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Figure 4.32: The band alignment of ITO and Cr$_2$O$_3$:Mg. (a) The energy levels of each material are highlighted. Respective band gaps are shown in red, work functions in blue, and VBM levels relative to the Fermi level in black. (b) The bending and offsets that are produced at the interface between ITO and Cr$_2$O$_3$:Mg. The offset between the VBM of Cr$_2$O$_3$:Mg and the CBM FTO is highlighted in red.

at all times. As there were no facilities available to deposit CuPc in-situ on top of Cr$_2$O$_3$/ITO, samples consisting of 7 nm of Cr$_2$O$_3$ on ITO were shipped to the laboratory of Prof. Cattin and Prof. Bernède in Nantes, France, where samples of pseudo bulk CuPc and a thin, 5 nm layer of CuPc were deposited on them. As CuPc is sensitive to oxygen, the samples were returned in vacuum for XPS and UPS analysis. The samples were exposed to air for as little time as possible while transferring them from a shipping container to the XPS system.

The work function, HOMO and a survey spectrum of bulk CuPc are shown in Figure 4.33. Two potential HOMO energies are detected, at 1.5 eV below the Fermi level and at 0.6 eV below the Fermi level. The shipping in vacuum is seen to be effective at preventing the sample from reacting with oxygen; the O 1s peak at 530 eV has a very low intensity compared to both the C 1s at 284 eV, the N 1s at 399 eV and the Cu 2p at ∼ 940 eV. The energetic positions of the Cu 2p core levels were used to calculate the value of the HOMO-valence band offset at the interface between CuPc and Cr$_2$O$_3$, using Equation 3.10. The HOMO-LUMO separation of CuPc used is 1.7 eV [52]. The band offset diagrams for the two potential HOMO positions are shown in Figures 4.34 and 4.35. While the effects of air exposure to Cr$_2$O$_3$ and CuPc are difficult to quantify, the error in the spectroscopy measurements is 0.1 eV.

The two band offset diagrams provide conflicting results; if the HOMO is located 1.5 eV below the Fermi level, then there is no barrier to hole transport, while if the HOMO is located 0.5 eV below the Fermi level, there is a barrier of 0.25 eV for holes
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Figure 4.33: Survey spectrum (a), work function (b), and HOMO (c) of bulk CuPc as determined by UPS and XPS. The UPS was performed with a bias of 7 V applied to the sample to shift the secondary edge of the analyser; this has been subtracted on the scale here. Both HOMO values of 0.6 eV and 1.5 eV were determined by fitting lines to the relevant leading edge and the background, and finding the points of intersection (marked by the thick black lines) between the two.

Figure 4.34: Band Alignment between ITO, Cr$_2$O$_3$ and CuPc, assuming that the bulk HOMO level of CuPc lies 1.5 eV below the Fermi level.
to be transported across the CuPc/Cr$_2$O$_3$ interface. Previously published results show that the HOMO level (relative to the Fermi level) of CuPc can vary from 0.4 eV to 1.0 eV [53, 54].

Without the Cr$_2$O$_3$ ABL, the CuPc LUMO is separated in energy from the ITO CBM by a 0.5 eV step, implying that this side of the cell has little-to-no charge carrier selectivity and will demonstrate poor performance.

The non-ideal characteristics of the IV curves exhibited by cells containing ITO with a Cr$_2$O$_3$ anode suggest that the second band offset diagram is correct, and there exists a barrier to holes at the the CuPc/Cr$_2$O$_3$ interface. This would not be expected to improve much in the case of using a Cr$_2$O$_3$:Mg buffer layer, as the band offset results of Section 4.6.2 show that there is at most an upwards shift of 0.1 eV of the VBM of Cr$_2$O$_3$ towards the Fermi level as it is doped with magnesium, which would act to increase the barrier to hole transport across the interface.

### 4.7 Conclusion

In this chapter, the growth of Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg on FTO was used to determine its suitability as an anode buffer layer in a simple organic solar cell. The increase in resistivity of both ITO and FTO when exposed to high temperatures was quantitatively analysed and the growth process of the Cr$_2$O$_3$ layers modified to avoid this. The variation of magnesium incorporation in epitaxial Cr$_2$O$_3$:Mg films was studied and shown to exhibit a strong temperature dependence. RHEED studies were carried out on Cr$_2$O$_3$/Al$_2$O$_3$ to quantify the in-plane lattice parameter relaxation.

Solar cells were produced with Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg as an ABL; these cells demonstrated a factor of 3 improvement in efficiency when compared to a cell with no ABL. This compares to the state of the art MoO$_3$ ABL where a factor of $\sim$10
efficiency improvement is seen.

The band offset measurements of both Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg on FTO and ITO show that the only difference in the band diagrams of Cr$_2$O$_3$:Mg compared to Cr$_2$O$_3$ is a possible shift of the VBM of Cr$_2$O$_3$:Mg by 0.1 eV closer to the Fermi level. By looking at energy levels alone, both Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg would expect to have similar ABL properties and produce cells with similar characteristics.

For FTO, the band alignment measurements with Cr$_2$O$_3$:Mg indicated that a barrier to hole transport possibly as large as 0.4 eV exists at the interface between these two materials; this barrier could be the source of the S-shaped $IV$ characteristic in cells which use an FTO anode. No such barrier was found via the same technique for the case of ITO.

To understand why ITO/Cr$_2$O$_3$:Mg possesses no hole transport barrier yet cells fabricated produce S-shaped $IV$ curves, the band offsets at the interface with CuPc were measured. This interface was found to demonstrate a barrier of 0.25 eV, which is large enough to impede hole transport across the ITO/CuPc interface. Any solar cell involving CuPc and Cr$_2$O$_3$ as an ABL will show poor hole collection and non-ideal solar cell characteristics.
Bibliography


Chapter 5

p-Type Transparent Conducting Oxides in Silicon Heterojunction Solar Cells

In this chapter, two high performing p-type transparent conducting oxides, $\text{Cu}_x\text{CrO}_2$ and $\text{Cr}_2\text{O}_3$:Mg are deposited on n-Si to form a low cost, facile synthesis silicon heterojunction solar cell. The aim was to produce a high performing solar cell without the need for complex high temperature diffusion steps, TCO layers, surface texturing, etc., that are currently present in the highest efficiency cells produced to date. The growth of $\text{Cu}_x\text{CrO}_2$ by spray pyrolysis is introduced. Thin films of $\text{Cu}_x\text{CrO}_2$ are deposited by spray pyrolysis, while thin films of $\text{Cr}_2\text{O}_3$:Mg are grown by MBE. As the latter are deposited in UHV, spectroscopy measurements can be performed, allowing the effect of the native silicon oxide layer to be quantified. For Si/$\text{Cr}_2\text{O}_3$:Mg cells, band offset measurements are performed on silicon substrates with two different resistivities; these are compared with the theoretical band line up predicted by Anderson’s rule.

5.1 Growth of $\text{Cu}_x\text{CrO}_2$

The $\text{Cu}_x\text{CrO}_2$ films was grown by spray pyrolysis. Before growing on silicon for solar cell fabrication, samples were first grown on glass coverslips at various substrate temperatures. While the ideal growth temperature of $\text{Cu}_x\text{CrO}_2$ has been shown to be $345 \pm 5 \degree C$ [1], microscope glass slides were the substrates used for the optimisation of growth conditions in that previous report. As the silicon substrates to be used in this work have a thickness of 200–280 µm compared to microscope slides which are 1 mm thick, there is a possibility of the substrate having a different surface temperature due to being substantially thinner. This is of particular importance for
this material, as the electrical properties of the Cu$_x$CrO$_2$ vary strongly with a shift as small as 10°C from the optimum substrate surface temperature. Glass coverslips were used as substrates for growth temperature screening, as their thickness of 0.13–0.16 mm is much closer to that of the silicon substrates. The optimum growth temperature was determined through resistivity measurements (a combination of XRR and sheet resistance measurements); the growth temperature that resulted in the minimum resistivity was chosen. The minimum resistivity achieved was typically 0.1–0.2 Ω cm. The substrate temperature was measured with a type K (chromel-alumel) thermocouple welded to the hot plate, near the substrate location. The temperature was controlled to within 10°C of the chosen set point by a PID controller during growth.

The chromium precursor used was chromium (III) acetylacetonate (97% purity, obtained from Sigma Aldrich), also known as Cr(C$_5$H$_7$O$_2$)$_3$ or Cr(acac)$_3$. The copper precursor used was copper (II) acetylacetonate (97% purity, obtained from Sigma Aldrich), also known as Cu(C$_5$H$_7$O$_2$)$_2$ or Cu(acac)$_2$. These precursors consist of the chosen metal cation bonded to multiple bidentate pentane-2,4-dione ligands as seen in Figure 5.1. The chosen precursors contain the metal cation in the desired oxidation state. These chemicals are stable in air, dissolve readily in organic solvents, have low decomposition temperatures, and are non-toxic [2]. Their decomposition products are also highly volatile [3].

The above precursors were dissolved in methanol. The solution was stirred until all precursor was fully dissolved. Methanol was chosen as alcohol solvents typically have a low surface tension, allowing the formation of small liquid droplets, which is particularly important for the low cost air blast nozzle used in this work [4]. The low boiling point of methanol (∼65°C) ensures its evaporation from the substrate.
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Figure 5.2: XRR of a CuₓCrO₂ film on glass. The thickness was measured to be 55 nm. The interface roughness is 0.6 nm and the surface roughness is 2.0 nm. The simulated curve was fit to data in the 2θ range of 0.6 to 1.75.

Surface after spraying, preventing incorporation in the growing film.

The Cr(acac)₃ concentration used was 0.03 mol while the Cu(acac)₂ concentration was 0.013 mol. The growth rate is approximately 6 nm min⁻¹, verified by XRR of samples which were grown with a suitable thickness. An example of an XRR measurement of a CuₓCrO₂ film deposited on a glass coverslip is shown in Figure 5.2. Prior to deposition of all samples, the growth chamber was purged with nitrogen. A mixture of compressed air and nitrogen gas was used as the carrier gas for the spray solution. The total gas flow rate was fixed at 171 min⁻¹, while the separate flow rate of each constituent was controlled with mass flow controllers to keep an oxygen gas concentration in the growth chamber of 5% at all times during spraying. This was measured by an oxygen sensor in the chamber, placed at a distance of 35 cm from the nozzle, similar to the nozzle-substrate distance of 30 cm. A Watson-Marlow 520s peristaltic pump was used to pump the precursor solution to the spray nozzle at a flow rate of 1.66 ml min⁻¹. The liquid lines were cleaned after each growth to ensure that they remained free of precursor and solvent.

A separate precursor solution was made for each growth rather than large batches at a time as it was observed that the precursors would slowly precipitate out of solution over the course of several hours. Combining the growth rate of 6 nm min⁻¹ with the liquid flow rate 1.66 ml min⁻¹ gives a solution volume of 5 ml per 18 nm of desired film thickness. All solutions were made approximately 20 ml larger to account for liquid which would remain in the lines between the peristaltic pump and the spray nozzle.
5.2 n-Si/Cu$_x$CrO$_2$ Heterojunction Solar Cells

Solar cells were prepared on two different silicon substrates. The first, hereinafter called standard resistivity silicon, has a resistivity in the range of 1–10 $\Omega$ cm, a thickness of 275 $\mu$m and is <100> oriented, single side polished and doped with phosphorus. The carrier concentration is estimated as $\sim 10^{15}$–$10^{16}$ cm$^{-3}$ [5]. The second, called low resistivity silicon, has a resistivity in the range of 0.001–0.005 $\Omega$ cm, a thickness of 280 $\mu$m and <100> oriented, single side polished and doped with arsenic. The carrier concentration is estimated as $\sim 10^{19}$–$10^{20}$ cm$^{-3}$.

Two different carrier concentrations were used with the intent of modulating the depletion region width of the device. As the vast majority of photon absorption is expected to take place in the silicon layer due to the much larger transparency and much lower thickness of the Cu$_x$CrO$_2$ layer, it would be ideal to contain the majority of the depletion region within the silicon. Assuming both materials in the junction have the same electrical permittivity $\varepsilon$, the depletion width of a p-n junction $W$, can be shown to be [6]

$$W = \sqrt{\frac{2V_0\varepsilon}{q} \left( \frac{1}{N_A} + \frac{1}{N_D} \right)}$$  \hspace{1cm} (5.1)

where $V_0$ is the built in voltage of the cell, $q$ is the charge of the charge carriers, $N_A$ is the acceptor concentration and $N_D$ is the donor concentration. The total width increases as the carrier concentrations are reduced. It can also be shown that the width in the separate p and n layers is proportional to the carrier concentration in the other layer, i.e., if the n-type side has a much larger carrier concentration then the depletion region will extend much farther into the p-type side. As Cu$_x$CrO$_2$ is predicted to be degenerate and thus have a high carrier concentration [7], the silicon with a lower carrier concentration (and a higher resistivity) would be expected to have a larger depletion width and possibly show improved cell characteristics when compared with cells fabricated with the lower resistivity silicon.

The back contact to the cell was made by depositing 100 nm of aluminium via electron-beam evaporation. Polyimide tape was placed around the edges of the cell in such a way so as to allow the aluminium to deposit over as large an area as possible, but to ensure that it was not deposited on the edges of the cell. Contact tests were performed to ensure that they did not show rectifying behaviour. An example of such a contact IV curve is shown in Figure 5.3. While not perfectly ohmic, the deviation from ideal behaviour is minimal.

The front contact to the cell was 5 nm Ti/45 nm Au and was deposited by electron-beam evaporation in such a way to leave (6×6)mm$^2$ or 0.36 cm$^2$ free of Ti/Au contact. This defined the active area of the cell.

It was briefly mentioned in Section 2.5.2 that the growth of Cu$_x$CrO$_2$ might
potentially proceed when the substrate is not in direct line of sight with the nozzle, i.e., via a chemical vapour deposition-like process. To ensure that no $\text{Cu}_x\text{CrO}_2$ is present on the sides of the cell leading to a possible short circuit, the edges of cells were either ground with a diamond saw or the edges were broken off after scoring with a diamond pen after $\text{Cu}_x\text{CrO}_2$ growth.

Light and dark $IV$ curves were measured using a Keithley 2400 sourcemeter operating in four-wire mode, while the light source used was a 135 W Oriel solar simulator with an AM 1.5 filter. The solar simulator was calibrated against a reference silicon cell regularly.

Cells were fabricated with 30 nm, 60 nm, 120 nm, 240 nm and 360 nm thick $\text{Cu}_x\text{CrO}_2$ layers. The $IV$ curves of all cells fabricated on low resistivity silicon are shown in Figure 5.4 (a), while those fabricated on standard resistivity silicon are shown in Figure 5.4 (b).

All cells deposited on low resistivity silicon demonstrated no power generation, nor did they show an diode characteristics. This can be seen by looking at the semilog plot of the $IV$ curves, in Figure 5.4 (c). The curves are symmetric about the origin, implying that the devices are simply showing non-ohmic rather than rectifying behaviour. Due to the high carrier concentration present in both materials the depletion width is expected to be quite narrow and restricted to the interface between the two materials. As the depletion region is responsible for the separation of charge carriers in the device which leads to power generation maximising its spatial extent is of the utmost importance. If little to no power generation is occurring, the depletion region will act as a highly resistive layer at the interface between the two materials and could lead to the non-ohmic behaviour shown.

All cells which were fabricated on the standard resistivity silicon demonstrated
Figure 5.4: $IV$ curves of all Si/Cu$_x$CrO$_2$ cells fabricated on (a) low resistivity silicon (b) standard resistivity silicon. (c) A semilog plot of the curves in (a). Inset of (b): a zoomed in graph of the power generating region of the $IV$ curves. The dashed lines represent the dark $IV$ curves.

power-generating characteristics. No attempt has been made to model these $IV$ curves in terms of an equivalent cell model due to the extremely low fill factor and far-from-ideal shape of the curves. Neither the short circuit current nor the open circuit voltage show any clear dependence on the thickness of the Cu$_x$CrO$_2$ layer.

One potential reason for the failure to achieve any high performing cells could be the native oxide layer present on the surface of the silicon. This oxide layer has an extremely large band gap of $\sim 9$ eV and could act as a barrier to both electron and hole transport between the n-Si and p-Cu$_x$CrO$_2$ [8]. No attempt was made to remove this layer by the typical procedure of hydrofluoric acid (HF) etching as spray-pyrolysis is not a vacuum deposition method, so the silicon would remain exposed to both ambient conditions during transfer to the spray pyrolysis growth chamber and would be exposed to temperatures of $350^\circ$C in a partial pressure of oxygen before growth commenced. This would be expected to at least partially re-form the native oxide layer on the silicon surface, rendering any effort to remove it useless. It has been observed before, when attempting growth of a material on a silicon surface, that the deposited material can react with the native silicon oxide layer and reduce it to a volatile species. This was observed for the case of growing yttria stabilised zirconia on silicon, where the incident Zr atomic flux reacted with any SiO$_2$ bonds to reduce them to volatile SiO [9]. This has not been seen for Cr or
Determination of the presence of a thin layer in a device is readily performed through XRR measurements. To ensure that the Cu\textsubscript{x}CrO\textsubscript{2} is growing on silicon as a closed layer, XRR was performed on a sample consisting of 28 nm of Cu\textsubscript{x}CrO\textsubscript{2} deposited by spray pyrolysis on a silicon substrate and is shown in Figure 5.5 (a). While the oscillations from the Cu\textsubscript{x}CrO\textsubscript{2} layer are evident, a good fit to the data is only obtained when a thin SiO\textsubscript{x} layer is inserted between the Si and the Cu\textsubscript{x}CrO\textsubscript{2} in the XRR model. The presence of this native oxide layer is expected as no attempt has been made to remove it. The best fit was found when the SiO\textsubscript{x} layer had a thickness of 2.2 nm and density of 2.43 g cm\textsuperscript{-1}. This compares with the density of stoichiometric SiO\textsubscript{2}, which is 2.65 g cm\textsuperscript{-3}. An XRR model is fully determined by the electron density as a function of depth profile of the sample. By varying the thickness and densities of the expected layers in the sample model, a simulation of the data can be produced and fit to the actual data by a least squares algorithm. The two electron density profiles for the models used here are shown in Figure 5.5 (b). The interfaces between the layers are not atomically sharp; the roughness that is present in real materials is modelled by broadening the electron density profile with a Gaussian function at the interfaces. In this case, the fit to data was found to
not be sensitive on the SiO$_x$ thickness, but was found to be highly sensitive on the
density of the SiO$_x$ layer.

While information on the band offsets present at the interface of the Si/SiO$_x$/Cu$_x$CrO$_2$
would help to reveal the reason for the poor cell performance, some Cu(acac)$_2$ pre-
cursor typically remains on the surface of Cu$_x$CrO$_2$ after growth [1], obscuring the
photoemission from the Cu$_x$CrO$_2$ layer. These precursors can be removed by argon
sputtering, but such a method is known to often alter the structure and atomic
concentrations at the surface relative to the bulk of the material. This will lead to
inaccurate measurements of the work function, where extra precaution must be taken
to have a clean surface as the extremely surface sensitive technique of UPS is used to
obtain this value. For these reasons, no band alignment or other spectroscopy was
performed on the Cu$_x$CrO$_2$ films.

As the XRR measurements suggest that there is an SiO$_x$ present in the devices,
and as Cu$_x$CrO$_2$ is not suitable for photoemission experiments, further analysis into
the reason behind the poor performance of the cell is difficult. Instead, it was decided
to fabricate cells with a similarly performing p-type TCO, Cr$_2$O$_3$:Mg. This was
chosen as its growth conditions are well established and it demonstrates a similar
conductivity to Cu$_x$CrO$_2$.

While Cu$_x$CrO$_2$ has the advantage of a quick and inexpensive deposition, the
MBE deposition of Cr$_2$O$_3$:Mg allows for clean surfaces of Cr$_2$O$_3$:Mg to be produced
and measured by XPS without exposure to air. Furthermore, the MBE possesses a
sample heater which can reach temperatures high enough to desorb the oxide layer
from a silicon surface. In principle, this allows the growth of layers directly on a
clean silicon surface.

### 5.3 Deposition conditions for Cr$_2$O$_3$:Mg

Growth of Cr$_2$O$_3$:Mg followed a slightly modified procedure to that presented in
Section 4.3. As the interface of interest is Si/Cr$_2$O$_3$:Mg, the native oxide layer which
is present on all silicon exposed to atmosphere must be removed, and modifications
must be made to the Cr$_2$O$_3$:Mg growth procedure to avoid this layer from re-forming
before Cr$_2$O$_3$:Mg growth has occurred.

### 5.3.1 Silicon Oxide Removal

A clean silicon surface, if exposed to ambient conditions, will develop a native oxide
layer of SiO$_x$ over the course of several hours [10]. The rate of formation and final
thickness of this oxide layer will depend on the temperature and moisture content of
the atmosphere it is exposed to, but in standard conditions the oxide layer will have
Figure 5.6: XPS of the as-received silicon surface and the surface after successive annealing steps. (a) The Si 2p core level region. Any silicon oxides show up at a binding energy above 101 eV. Annealing at 700°C for as little as one minute is seen to drastically reduce the peak intensity of the SiOₓ components, indicating oxide removal. The oxide is seen to be completely removed after 20 minutes of annealing at 700°C. (b) The Si 2s core level region, showing the same oxide removal after annealing. The oxide component appears at approximately 155 eV.

The two standard methods to remove this oxide layer are either removal via diluted HF, which is the method of choice when the wafer is involved with other clean-room processing techniques, or a high temperature UHV anneal, which is more often used when the silicon is to remain in a UHV chamber, for surface studies such as scanning tunneling microscopy or electron diffraction. Despite the facile nature of HF treatment for SiOₓ removal, it has been shown to result in an oxide layer thickness of 2–4 Å remaining/reforming immediately after HF etching [10]. As the MBE main chamber contains a heater which can reach high temperatures, removal of the oxide via thermal annealing was instead explored.

To determine the annealing time necessary for complete removal of the oxide layer, silicon was annealed for various times at different temperatures in the preparation chamber of the XPS system before being transferred in-situ to the analysis chamber where XPS was performed. The XP spectra of the Si 2p and Si 2s core levels regions before and after various annealing treatments are shown in Figure 5.6.

Photoemission signal due to Si-O bonds in the native oxide layer is present in...
Figure 5.7: XP spectra of the O 1s core level of a silicon surface after each annealing treatment. The O 1s peak intensity is seen to reduce drastically upon annealing for 20 minutes at 750°C.

both core level spectra at higher binding energies in the silicon sample which was inserted in the XPS system without any surface treatment. A short anneal at 700°C for 1 minute is seen to already significantly reduce the amount of oxide present on the surface of the sample. Some of this oxide is likely hydroxide species due to atmospheric water vapour. An additional 20 minute anneal at 750°C is seen to remove all traces of the oxide layer. A further 40 minute anneal was performed, but this is seen to have no effect on either core level spectra.

While these spectra indicate that no oxygen remains on the surface, the presence of oxygen is more readily detected by examining the O 1s core level rather than the Si 2p or Si 2s levels due to the difference in relative sensitivity factors between the two core levels (2.93 for O 1s, 0.817 for Si 2p, and 0.955 for Si 2s). By examining the oxygen 1s core level as seen in Figure 5.7, it is seen that a small amount of oxygen remains on the surface even after all annealing treatments. The reduction in the amount of oxide between 20 minutes annealing at 750°C and 40 minutes at this temperature is seen to be negligible. Furthermore, a trace amount of carbon remains on the surface. It is likely that there are trace amounts of both silicon oxide and possibly carbon monoxide on the surface.

As both the XPS sample heater and MBE sample heater are determined to be accurate to only ±50°C, it was decided that any silicon substrates would be annealed

1This implies that for a given amount of Si-O bonds, the intensity will be ∼3 times as great in the O 1s spectrum as it would be in the Si 2s or 2p spectrum.
at 840°C for one hour in the MBE main chamber before growth commenced to ensure complete removal of the native silicon oxide layer.

After one hour at 840°C, the silicon substrate was cooled to room temperature. The power to the MgO and Cr₂O₃ evaporation sources was increased to the desired level. Only after the evaporation rates of each source material was set and growth was ready to begin was oxygen admitted to the chamber and the substrate temperature raised to 600°C.

### 5.3.2 Growth on Cr₂O₃:Mg

In contrast to the epitaxial Cr₂O₃:Mg that grows c-axis oriented on Al₂O₃, when grown on silicon the Cr₂O₃:Mg films were found to exhibit only a single weak (10T4) diffraction peak as seen in Figure 5.8. While the films grown on silicon may not show the same crystalline quality as epitaxial films, they show a comparable roughness as can be seen from the XRR measurements in Figure 5.9. The epitaxial sample has a thickness of 57.8 nm, a surface roughness of 0.6 nm and a negligible interface roughness, while the sample grown on silicon has a thickness of 55.5 nm, a surface roughness of 1.1 nm and an interface roughness of 0.8 nm. The increased interface roughness in the sample grown on silicon results in the oscillations disappearing at a lower 2θ value. Furthermore, these two samples were grown in the same conditions and intended to have a film thickness of 55 nm. The similarity in the thickness serves to establish that Cr₂O₃:Mg grows at the same rate on both Al₂O₃ (0001) and silicon (001).
Following the same procedure as for Cu$_x$CrO$_{2}$, two separate models were made to fit the data, one assuming the presence of a SiO$_x$ layer between the silicon and Cr$_2$O$_3$:Mg and the other assuming no oxide layer. This is shown in Figure 5.10. As in the case of Cu$_x$CrO$_2$, the model with an oxide layer provides a better fit to the data, particularly for 2θ values below 1.5°, where the count rates are highest and the data most accurate. It should be noted that the simulation is not particularly sensitive to the thickness of the SiO$_x$ layer; a good fit was produced with thicknesses ranging between 0.5–2.5 nm. The simulation is however, quite sensitive to the density; a change of 0.1 g cm$^{-3}$ has a noticeable effect on quality of the fit produced. The optimum fit was produced when the oxide layer had a thickness of 1.8 nm and a density of 2.81 g cm$^{-3}$. These measurements indicate that even after having its native oxide removed in the MBE, a thinner yet more dense oxide layer grows in comparison with the native oxide.

It is possible that this oxide layer does not solely contain Si-O bonds, but also Cr-O bonds. This can easily be determined by XPS, as the various oxidation states of silicon are well separated in binding energy when measuring the Si 2p core level [11]. Figure 5.11 shows this core level region for a sample which has undergone no annealing and is expected to have a native oxide present, and a sample which has had 1 nm of Cr$_2$O$_3$:Mg deposited on top of it. This layer is thin enough that electrons originating from both the silicon substrate and the Cr$_2$O$_3$:Mg layer will easily be detectable.

Before the sample is cleaned, the oxide present on the surface consists solely of
Figure 5.10: XRR measurement and simulations of Cr$_2$O$_3$:Mg on silicon with and without a native oxide (SiO$_x$) layer. (a) The XRR data and simulations assuming no oxide layer is present (—) and an oxide layer is present (—). (b) The density profiles of both simulated samples. Simulations were fit to the data in the range 0.56° ≤ 2θ ≤ 2.38°.

Si$^{4+}$ which corresponds to SiO$_2$. After an annealing cycle to remove the oxide layer followed by growth of 1 nm of Cr$_2$O$_3$:Mg this component disappears and components corresponding to mixed oxidation states appear between the expected energetic position of Si$^{2+}$ and Si$^{3+}$, and Si$^{3+}$ and Si$^{4+}$. The positions of these oxidation states have been known to shift when the oxide layer thickness is below 5 Å, but the XRR results indicate that the oxide layer is nearly four times as thick. It is possible that one of these components arises from a Cr-Si bond which would likely to be present as Cr$_2$O$_3$:Mg is being grown on a clean silicon surface. However, no additional components that could be associated to Cr-Si bonds were seen in any of the Cr core level spectra. This does not necessary mean that the peaks are not present in the Cr core-level spectra; the multiplet spilt core levels of Cr make observing a single extra low intensity component particularly difficult.

Direct growth of Cr$_2$O$_3$ on silicon has been previously attempted but has yet to be demonstrated; efforts have been made to grow highly crystalline Cr$_2$O$_3$ directly on silicon to utilise its antiferromagnetic properties in existing silicon magnetic devices. While this has yet to be achieved, the introduction of various buffer layers between the two materials has allowed silicon to act as a suitable substrate for Cr$_2$O$_3$ growth. These include introducing an yttria-stabilised zirconia (ZrO$_2$:Y$_2$O$_3$) buffer layer upon
Figure 5.11: XP spectra showing the various oxidation states of silicon when (a) a native oxide is present and (b) when 1 nm of Cr₂O₃:Mg is deposited on a surface which has had the native oxide removed. The vertical lines indicate the region where a component with the designated oxidation state would be expected to lie. The 2p₃/₂ components are shown in blue (—) and the 2p₁/₂ in red (—). The energies of the various oxidation states of silicon were taken from [11].

which Cr₂O₃ grows epitaxially in a c axis oriented growth [12], or by introducing a gold buffer layer [13]. Interestingly, the (10T4) texturing of Cr₂O₃:Mg that is seen in this work is also seen when growing on Au/Si (100) substrates.

While an oxide layer is seen to be present in some form, it is thinner than that found when fabricating n-Si/CuₓCrO₂ heterojunction solar cells. Cells with the same structure as previously discussed were fabricated but with Cr₂O₃:Mg as the p-type layer to observe whether a reduced oxide thickness could lead to improved cell characteristics.

5.4 n-Si-/Cr₂O₃:Mg Heterojunction Solar Cells

In this section, the same low and standard resistivity silicon as discussed in Section 5.1 were used as substrates for the growth of Cr₂O₃:Mg layers. The cell contact deposition and testing is also the same as previously mentioned. Cells were fabricated with 2.5 nm, 5 nm, 9 nm, 18 nm, 36 nm and 55 nm thick Cr₂O₃:Mg layers. Thicker layers were not investigated due to the slow growth rate of Cr₂O₃:Mg of ~1 nm min⁻¹. The IV curves of all cells fabricated on low resistivity silicon are shown in Figure 5.12 (a),
Figure 5.12: *IV* curves of all Si/Cr$_2$O$_3$:Mg cells fabricated on (a) low resistivity silicon and (b) standard resistivity silicon. The curves in (a). Inset of (b): a zoomed in graph of the power generating region of the *IV* curves. The dashed lines represent the dark *IV* curves.

While those fabricated on standard resistivity silicon are shown in Figure 5.12 (b).

Perhaps unsurprisingly, the *IV* curves here show a strong similarity to those demonstrated by cells fabricated with Cu$_x$CrO$_2$ p-type layer. Both materials have a predicted large carrier concentration, both have a mobility below $10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ and both are assumed to conduct carriers via a small polaron hopping mechanism. For the cells fabricated on low resistivity silicon no power generation is seen. The reason for this is expected to be the same as for Cu$_x$CrO$_2$; the high carrier concentration in the n-type combined with the extremely high carrier concentration in the p-type leads to a depletion region which is much too narrow to efficiently separate charge carriers and produce power. While no general trend is seen for the short circuit current density with p-type layer thickness, the cell with the thinnest Cr$_2$O$_3$:Mg layer of 2.5 nm has a notably different *IV* curve from all the other cells produced.

For the cells fabricated on standard resistivity silicon, a small amount of power generation is seen. Similar to the Cu$_x$CrO$_2$ case, the *IV* curves are not modelled due to their extremely low fill factors and highly non-ideal *IV* curve shape. The markedly improved short circuit current in such a thin layer suggests that the Cr$_2$O$_3$:Mg is possibly too resistive or has too low a mobility to work well in a silicon heterojunction solar cell, and that sufficient carriers can only be collected when the layer is on the order of several angstroms.

The idea that changing the carrier concentration of the silicon will only affect
the depletion region width is a rather simplified view; the Fermi level of the silicon will change by a large amount as the material is doped to progressively high carrier concentrations; this will produce band offsets at the interface between Cr$_2$O$_3$:Mg and n-Si. The problems that prevented Cu$_x$CrO$_2$ from undergoing accurate photoemission measurements are not present with MBE-grown Cr$_2$O$_3$:Mg, so band offset measurements were able to be performed to examine if a large barrier to carrier transport (which would provide an explanation for the poor cell performance) is present at the p-n interface.

5.5 Band Offsets of Cr$_2$O$_3$:Mg and n-Si

The band offset was measured for Cr$_2$O$_3$:Mg with both standard and low resistivity silicon. The interface sample used consisted of 1 nm of Cr$_2$O$_3$:Mg on the silicon substrate of choice. Such a small thickness was used as the band alignments in Chapter 4 showed that the band bending occurs over a very narrow thickness in Cr$_2$O$_3$:Mg and so a narrow layer thickness must be used to observe this.

The work function and energetic position of the VBM relative to the Fermi level of both standard and low resistivity silicon is shown in Figures 5.13 and 5.14 respectively. For the low resistivity silicon the Fermi level is seen to lie 1.2 eV above the VBM. As the band gap of silicon is $\sim$1.14 eV, this shows that the low resistivity silicon is a degenerate semiconductor. Even though they usually possess a large conductivity, a degenerate semiconductor is not always ideal for devices as the large carrier concentration can act to produce Schottky barriers when placed in contact with a normal semiconductor [6].

The core levels used to calculate the band offsets were the Cr 2$p$ and 3$p$, and the Si 2$s$ and 2$p_{3/2}$. To remove noise from the raw data, the Cr 2$p$ and 3$p$ core levels were first smoothed by using Savitzky-Golay filter using enough points (typically 10) to ensure a smooth curve at the maximum in intensity at each core level. The comparatively less complex Si 2$s$ and 2$p_{3/2}$ core levels could be accurately fit using peaks formed by a linear combination of a Gaussian and a Lorentzian profile which are commonly used in XPS peak fitting.

The band offset calculated for standard resistivity silicon and Cr$_2$O$_3$:Mg is shown in Figure 5.15 (a) while the band alignment predicted by Anderson’s rule is shown in Figure 5.15 (b). For the Anderson’s rule calculation, the bending was assumed to occur only in the n-Si, as it has a carrier concentration that is orders of magnitude lower than Cr$_2$O$_3$:Mg.

Standard resistivity n-Si and Cr$_2$O$_3$:Mg are seen to form a straddling gap heterojunction. There is seen to be a valence band offset of 0.45 eV between the two materials. This barrier is not large enough to completely prevent any holes from
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Figure 5.13: Work function and valence band maximum of standard resistivity n-Si as determined by UPS and XPS respectively. The UPS was performed with a bias of 5 V applied to the sample to shift the secondary edge of the analyser; this has been subtracted on the scale here. Both values were determined by fitting lines to the relevant leading edge and the background, and finding the point of intersection between the two.

reaching the Cr$_2$O$_3$:Mg, but is large enough to hinder transport of photogenerated holes from the silicon to the hole conducting Cr$_2$O$_3$:Mg. This offset explains the very low values short circuit current obtained from the solar cells fabricated with these materials. Meanwhile, a large conduction band offset exists at the interface, preventing electrons from being transported through the Cr$_2$O$_3$:Mg. Anderson’s rule is seen to predict a completely different situation, a valence band offset twice as large, with hole accumulation present on the silicon side of the interface. While this alignment would also prevent electrons from reaching the Cr$_2$O$_3$:Mg layer, it would be just as likely that no holes would transport across the interface, rendering this completely ineffective as a solar cell.

The band offset calculated for low resistivity silicon and Cr$_2$O$_3$:Mg is shown in Figure 5.16 (a), while the band alignment predicted by Anderson’s rule is shown in Figure 5.16 (b). For the Anderson’s rule calculation, the bending was assumed to occur equally in both materials. The carrier concentration of Cr$_2$O$_3$:Mg is most likely larger than that of the low resistivity silicon by an order of magnitude, but Anderson’s rule provides no method to quantitatively estimate how the band bending is shared between two materials. As the offsets present are quite large in energy, modifying the band bending by a small amount won’t change the transport characteristics of
the interface so equal band bending in both materials was assumed.

Immediately noticeable in the band offset diagram of Cr$_2$O$_3$:Mg and low resistivity n-silicon is the lack of a valence band offset, allowing holes to travel without impediment between the two materials. While this might initially appear as an advantage, a solar cell relies on the spatial separation of carriers in order to produce a voltage and generate power. If, as discussed in the previous section, there is a very narrow depletion region at the interface then there will be a significant amount of hole diffusion across the depletion region back into the n-type which will act to reduce the available current to be drawn from the cell. Anderson’s rule, similar to

**Figure 5.14:** Work function and valence band maximum of low resistivity n-Si as determined by UPS and XPS respectively. The UPS was performed with a bias of 5 V applied to the sample to shift the secondary edge of the analyser; this has been subtracted on the scale here. Both values were determined by fitting lines to the relevant leading edge and the background, and finding the point of intersection between the two.

**Figure 5.15:** (a) The band offset calculated for standard resistivity silicon and Cr$_2$O$_3$:Mg compared with (b) the band alignment predicted by Anderson’s rule.
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Figure 5.16: (a) The band offset calculated for low resistivity silicon and Cr\textsubscript{2}O\textsubscript{3}:Mg compared with (b) the band alignment predicted by Anderson’s rule.

the standard resistivity silicon case, predicts a large valence band offset with hole accumulation at the silicon side of the interface. The band bending present in the Cr\textsubscript{2}O\textsubscript{3}:Mg layer also induces a hole depletion region close to the interface, rendering hole transport across this interface extremely unlikely.

In the above two scenarios, the effect of the oxide layer present at the interface has been ignored. Si\textsubscript{2}O\textsubscript{2} is an extremely wide band gap oxide with a band gap of 9 eV and a CBM positioned 3.5 eV above that of silicon. This leads to it acting as a barrier to carrier transport for both holes and electrons for the vast majority of materials. When present at the interface between silicon and either Cu\textsubscript{x}CrO\textsubscript{2} or Cr\textsubscript{2}O\textsubscript{3}:Mg it is found to have a thickness between 1.8 nm and 2.2 nm. While there is at these small thicknesses some probability for carriers to simply tunnel through the Si\textsubscript{2}O\textsubscript{2} layer, the presence of the large band gap native oxide would have a negative effect on the properties of the solar cell as tunneling will be less efficient than direct transport between the valence bands of the Cr\textsubscript{2}O\textsubscript{3}:Mg and the n-Si.

5.6 Conclusion

Thin films of p-type transparent conducting oxide Cu\textsubscript{x}CrO\textsubscript{2} were grown on the surface of n-type silicon substrates to demonstrate a silicon heterojunction solar cell through facile fabrication methods. The poor performance exhibited by these was attributed to either a narrow depletion layer in the case of highly doped silicon substrates, or the native Si\textsubscript{2}O\textsubscript{2} layer present at the interface between Cu\textsubscript{x}CrO\textsubscript{2} and silicon acting as a barrier to charge carriers.

As materials grown by spray pyrolysis typically have a surface that is contaminated with organic precursor and thus accurate photoemission experiments cannot be performed, an alternate p-type transparent conducting oxide ,Cr\textsubscript{2}O\textsubscript{3}:Mg, which exhibits similar properties to Cu\textsubscript{x}CrO\textsubscript{2} was grown on silicon via MBE. The optimum annealing time and temperature was found for removing the native oxide present on the surface of silicon substrates. The growth procedure of Cr\textsubscript{2}O\textsubscript{3}:Mg was modified in
such a way to keep the silicon surface free from oxide before growth began, to prevent the re-formation of an SiO$_2$ layer. Despite these efforts, an oxide layer (potentially containing Cr-Si bonds) was found to form during the growth of Cr$_2$O$_3$:Mg. XRR was used to quantify the thickness of the SiO$_2$ layer present at the silicon interface with both Cr$_2$O$_3$:Mg and Cu$_x$CrO$_2$.

Solar cells produced with Cr$_2$O$_3$:Mg as the p-type layer were found to exhibit similar IV characteristics as those produced with Cu$_x$CrO$_2$. A combination of XPS and UPS was used to measure the band offsets between Cr$_2$O$_3$:Mg and silicon. These band offsets suggested that a barrier for hole transport, which would explain the low quality IV curves, from silicon to Cr$_2$O$_3$:Mg exists when using a standard resistivity silicon substrate, yet no barrier exists when using a low resistivity substrates. As solar cells fabricated on these substrates were shown to generate no power, either the presence of the SiO$_2$ layer or a depletion layer of insufficient width is responsible for the poor cell performance. Finally, the band offset measurements were compared to the simple theoretical alignment suggested by Anderson’s rule to highlight the importance of experimental determination of interfacial band alignment over a simple model.
Bibliography


Chapter 6

Conclusion and Future Work

This thesis has focused on the growth of high-performance p-type transparent conducting oxides $\text{Cr}_2\text{O}_3$, $\text{Cr}_2\text{O}_3$:Mg, and $\text{Cu}_x\text{CrO}_2$ and incorporating these materials into photovoltaic devices. The first of the two applications for these p-type oxides were as an anode buffer layer in organic solar cells. While n-type TCOs, with their much higher performance in terms of conductivity and transparency are suitable for the majority of applications requiring transparent conductors, an anode buffer layer typically requires a p-type material. Furthermore, the lower conductivity and carrier mobility of p-types are not of vital importance when performing this function.

Fundamental studies on the epitaxial growth of $\text{Cr}_2\text{O}_3$ using RHEED demonstrated that $\text{Cr}_2\text{O}_3$ does not exhibit a full in-plane relaxation at moderate thicknesses when grown on $\text{Al}_2\text{O}_3$. There was found to be a strong dependence of the rate of magnesium incorporation within the $\text{Cr}_2\text{O}_3$:Mg films; as the growth temperature was decreased from 600$^\circ$C to 400$^\circ$C the magnesium evaporation rate needed to be reduced by 18% to result in films with the same magnesium doping level as those grown at higher temperatures. The explanation for this given was the likely formation and desorption of high-vapour pressure elemental Mg which would be expected to occur more at higher temperatures.

The results gained from the temperature study on the doping levels of $\text{Cr}_2\text{O}_3$:Mg were used to grow $\text{Cr}_2\text{O}_3$:Mg at lower temperatures on FTO and ITO, typical organic solar cell anodes. This lower deposition had to be performed as it was found that the resistivity of both materials increased at high temperatures. Solar cells were produced with $\text{Cr}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3$:Mg as an ABL; these cells demonstrated a factor of 3 improvement in efficiency when compared to a cell with no ABL. This compares to the state of the art $\text{MoO}_3$ ABL where a factor of $\sim$10 efficiency improvement is seen. Despite this improvement, the fabricated cells exhibited an “S”-shaped IV curve, which is indicative of a barrier to charge collection for either holes or electrons existing in the cell. A previous publication had showed that for the cell architecture
used here, this barrier must lie on the hole collecting side of the cell [1].

The band offset measurements of both Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg on both FTO and ITO show that the only difference in the band diagrams of Cr$_2$O$_3$:Mg compared to Cr$_2$O$_3$ is a possible shift of the VBM of Cr$_2$O$_3$:Mg by 0.1 eV closer to the Fermi level. By looking at energy levels alone, both Cr$_2$O$_3$ and Cr$_2$O$_3$:Mg would expect to have similar ABL properties and produce cells with similar characteristics. These measurements also demonstrated their importance; the results provided by the often-used Anderson’s rule were found not to agree with experimentally obtained band offset diagrams.

For FTO, the band alignment measurements with Cr$_2$O$_3$:Mg indicated that a barrier to hole transport possibly as large as 0.4 eV exists at the interface between these two materials; this barrier could be the source of the S-shaped IV characteristic in cells which use an FTO anode. No such barrier was found via the same technique for the case of ITO.

To understand why ITO/Cr$_2$O$_3$:Mg possesses no hole transport barrier yet cells fabricated produce S-shaped IV curves, the band offsets at the interface with CuPc were measured. This interface was found to demonstrate a barrier of 0.25 eV, which is large enough to impede hole transport across the ITO/CuPc interface. Any solar cell involving CuPc and Cr$_2$O$_3$ as an ABL will show poor hole collection and non-ideal solar cell characteristics. It is possible that this barrier also exists for FTO/Cr$_2$O$_3$ anodes.

Future work will involve the growth of the FTO/Cr$_2$O$_3$/CuPc structure to perform band offset measurements, to examin whether the same hole barrier exists at the Cr$_2$O$_3$/CuPc interface. While the presence of a hole transport barrier limits the application of Cr$_2$O$_3$/Cr$_2$O$_3$:Mg in cells containing CuPc, there exist a large amount of cells which utilise different organic organic electron donors. When grown on ITO, Cr$_2$O$_3$ would be an effective buffer layer for any organic electron donor material that possesses an ionisation potential that is at least approximately 0.3 eV larger than that of CuPc. In this case, no hole collection barrier would be expected to form, and a high-performance solar cell would result. Fabrication of solar cells which include organic materials possessing this characteristic will be examined in future.

For the second application in photovoltaic devices, thin films of p-type transparent conducting oxide Cu$_x$CrO$_2$ were grown on the surface of n-type silicon substrates to demonstrate a silicon heterojunction solar cell through facile fabrication methods. The poor performance exhibited by these solar cells was attributed to either a narrow depletion layer in the case of highly doped silicon substrates, or the native SiO$_2$ layer present at the interface between Cu$_x$CrO$_2$ and silicon acting as a barrier to charge carriers.

The same cell structure, but by replacing Cu$_x$CrO$_2$ with Cr$_2$O$_3$:Mg was grown,
as the MBE growth of this material better lends itself towards in-situ photoemission experiments which could determine the cause of the poor performance. The growth procedure of \( \text{Cr}_2\text{O}_3:\text{Mg} \) was modified in such a way to keep the silicon surface free from oxide before growth began, to prevent the re-formation of an SiO\(_2\) layer, but despite these efforts an oxide layer was found to form during the growth of \( \text{Cr}_2\text{O}_3:\text{Mg} \). XRR was used to quantify the thickness of the SiO\(_2\) layer present at the silicon interface with both \( \text{Cr}_2\text{O}_3:\text{Mg} \) and Cu\(_x\)CrO\(_2\).

The solar cells produced with \( \text{Cr}_2\text{O}_3:\text{Mg} \) as the p-type layer were found to exhibit similar IV characteristics as those produced with Cu\(_x\)CrO\(_2\). A combination of XPS and UPS was used to measure the band offsets between \( \text{Cr}_2\text{O}_3:\text{Mg} \) and silicon. These band offsets suggested that a barrier for hole transport, which would explain the low quality IV curves, from silicon to \( \text{Cr}_2\text{O}_3:\text{Mg} \) exists when using a high resistivity silicon substrate, yet no barrier exists when using a low resistivity substrates. As solar cells fabricated on these substrates were shown to generate no power, either the presence of the SiO\(_2\) layer or a depletion layer of insufficient width is responsible for the poor cell performance.

While previous work has demonstrated the difficulty of growing \( \text{Cr}_2\text{O}_3 \) on silicon without the native silicon oxide layer present [2], a potential solution to this problem to be explored in the future is to first use the annealing procedure shown here to produce a clean, oxide-free silicon surface, followed by the deposition of a thin layer of chromium metal. As the temperature and oxygen pressure in the MBE are raised in preparation for the growth of \( \text{Cr}_2\text{O}_3:\text{Mg} \), the chromium metal layer would likely oxidise to \( \text{Cr}_2\text{O}_3 \), and a heterojunction solar cell could be grown. As the initial idea is to produce a low-cost, facile synthesis heterojunction, further attempts will be made to produce an efficient Cu\(_x\)CrO\(_2\)/Si cell. These include treating the silicon surface, such as HF etching to remove the oxide layer, surface hydrogen termination, or if the previously mentioned work is succesful, using ultra-thin \( \text{Cr}_2\text{O}_3:\text{Mg} \) as a buffer layer to protect the silicon surface from oxidising.

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Bibliography


Appendices
Appendix A

Electrical Measurements

Electrical measurements in this work were used to measure the sheet resistance of various anode materials and p-type TCOs which would be used as a buffer layer in solar cells. For the growth of Cu$_x$CrO$_2$ the optimum deposition conditions are found by observing at which growth temperature the maximum conductivity is achieved. The method for measuring the carrier mobility of materials is also shown here, even though the p-type TCOs used demonstrate a mobility which is too low to be measured.

A.1 The Hall Effect

The Hall effect (discovered by Edwin Hall in 1879 [1]) is a phenomena that occurs when a metal or semiconductor is simultaneously placed in a magnetic field ($\mathbf{B}$) and has a current (with current density $\mathbf{J}$) passed through it. Suppose that charge carriers with charge $q$ flow through a material with drift velocity $\mathbf{v}_d$. They will then experience the Lorentz force, which is given as the cross product of the drift velocity and the magnetic field:

$$\mathbf{F} = q\mathbf{v}_d \times \mathbf{B} \quad \text{(A.1)}$$

which will deflect them in a direction perpendicular to their drift velocity. This leads to a build up of charge on one side of the material, and thus a transverse electric field $\mathbf{E}_H$; the Hall field. It is seen from figure A.1 that the Hall field changes direction depending on whether the charge carriers are electrons or holes.

This field ($\mathbf{E}_H = \mathbf{F}/q$) will quickly reach a value so that it cancels the Lorentz force, and so steady state will be reached, i.e.,

$$q\mathbf{E}_H + q\mathbf{v}_d \times \mathbf{B} = 0$$

$$q\mathbf{E}_H = -q\mathbf{v}_d \times \mathbf{B} \quad \text{(A.2)}$$
Electrons

Holes

(a) Electrons

(b) Holes

Figure A.1: The effect of the Lorentz force on charge carriers within a material. It is seen that the Hall field direction is opposite for cases where the charge carriers are (a) electrons or (b) holes. The dashed arrow indicates the exaggerated deflection that the indicated charge carrier will undergo while flowing through a material.

\[ \mathbf{E}_H = \mathbf{B} \times v_d \]  

Equations A.2 and A.3 are independent of carrier type, for example, if the carriers are electrons, \( q \) and \( v_d \) both become negative, returning the original equations. As the current density is given by \( \mathbf{J} = nqv_d \) where \( n \) is the carrier density (per unit volume), it can be combined with equation A.3 to obtain

\[ \mathbf{E}_H = \frac{1}{nq} \mathbf{B} \times \mathbf{J} \]  

Equation A.4 indicates that if either there is no magnetic field present, or no current flowing, the Hall voltage should equal zero. Typically, there is a finite zero field offset voltage, which can be larger than the Hall voltage. This can be caused by a variety of factors, including a geometric misalignment in voltage contacts, inhomogeneity of the sample, and temperature gradients [2]. To ensure that the measured data is reliable, the Hall voltage is measured at zero field in order to estimate the zero field offset.

If \( \mathbf{B} \) and \( \mathbf{J} \) are perpendicular to each other, equation A.5 reduces to

\[ E_H = R_H B J \]  

where

\[ R_H = \frac{1}{nq} \]  

is known as the Hall coefficient. As \( R_H \) is inversely proportional to \( q \), and \( n \) is a positive number, the sign of \( R_H \) thus determines the sign of \( q \), i.e., the type of charge carrier.
Appendix A. Electrical Measurements

Figure A.2: The physical dimensions of a sample for Hall measurements. This is shown here for the case where electrons are the charge carriers. The current flows parallel to the length of the sample, \( L \). The hall field acts over the distance \( w \) with the remaining dimension of the sample indicated by \( d \). The direction of electron deflection due to the Lorentz force is shown as a dashed line.

where \( B = |\mathbf{B}| \) and \( J = |\mathbf{J}| \). Since the Hall voltage is given by \( V_H = E_H w \), where \( w \) is the width of the sample (see figure A.2), and the current is given by \( I = J w d \), where \( d \) is the thickness of the sample, then equation A.7 can be rearranged to give

\[
R_H = \frac{1}{nq} = \frac{V_H d}{B I}
\]

which allows the carrier concentration to be calculated in terms of measurable quantities. If conduction is due to electrons and holes, the total conductivity (\( \sigma \)) is given by

\[
\sigma = e(n_e \mu_e + n_h \mu_h)
\]

where \( n_e \) and \( n_h \) are the electron and hole densities respectively, and \( \mu_e \) and \( \mu_h \) are their mobilities. If a single carrier of charge \( q \) dominates (i.e., \( n_e \gg n_h \) or \( n_h \gg n_e \)) then the conductivity is

\[
\sigma = q n \mu
\]

with the carrier mobility then given by

\[
\mu = \frac{1}{nq \rho}
\]

as \( \rho = \sigma^{-1} \). If a Hall measurement is performed in conjunction with a measurement of the resistivity of a sample, then the carrier mobility can be determined. One way of performing both of these measurements simultaneously is known as the Van der Pauw Method.

A.2 Van der Pauw Method

In 1958, Leo van der Pauw discovered a method of measuring the resistivity and Hall coefficient of any arbitrarily shaped sample; the only constraints being that the sample is flat (approximately two-dimensional), and that the contacts (which must
be sufficiently small) be located at the sample’s perimeter [3, 4]. The contacts, all of which should be made from the same material to ensure accurate measurements, are numbered anticlockwise by convention, as seen in figure A.3.

A clover shaped sample helps to lessen the influence of the contacts, reducing the error that is caused by the contacts having a non-zero diameter [5]. The square sample geometry is the most commonly used shape due to its ease of preparation.

### A.2.1 Sheet Resistance

A three-dimensional material with a current flowing along the side of a sample with length $L$, such as between contacts 2 and 3 in Figure A.3, and with cross sectional area $A$ has a resistance given by

$$R = \rho \frac{L}{A} \quad (A.12)$$

If the cross sectional area is rectangular, i.e., $A = wd$, then equation A.12 can be written as

$$R = \rho \frac{L}{wd} = \frac{\rho L}{d} = R_s \frac{L}{w} \quad (A.13)$$

where $R_s$ is the sheet resistance. As $L/w$ is dimensionless, $R_s$ must have the same units as resistance; ohms ($\Omega$). To prevent confusion between measurements of resistance and sheet resistance, the units ‘ohms per square’ or $\Omega/\square$ is used exclusively for sheet resistance.

For sheet resistance measurements, a current must be passed from one contact to an adjacent contact, while the voltage difference is measured over the remaining two contacts. If a current is passed from contact 1 to contact 2 ($I_{12}$), and a voltage is simultaneously measured between contact 4 and contact 3 ($V_{43}$), a resistance can be calculated:

$$R_{12,43} = \frac{V_{43}}{I_{12}} \quad (A.14)$$

If the polarity of the current and voltage measurement is reversed, the resistance $R_{21,34}$ can also be calculated. If these measurements are repeated for all four sides of a sample, eight values of resistance are obtained:
Appendix A. Electrical Measurements

\[ R_{12,43} = \frac{V_{43}}{I_{12}} \quad R_{23,14} = \frac{V_{14}}{I_{23}} \quad R_{34,21} = \frac{V_{21}}{I_{34}} \quad R_{41,32} = \frac{V_{32}}{I_{41}} \]
\[ R_{21,34} = \frac{V_{34}}{I_{21}} \quad R_{32,41} = \frac{V_{14}}{I_{32}} \quad R_{43,12} = \frac{V_{12}}{I_{43}} \quad R_{14,23} = \frac{V_{23}}{I_{14}} \]

Figure A.4: Van der Pauw method of measuring sheet resistance. Each column shows two measurements of opposite polarity. Red contacts indicate that current is passed between them, blue contacts indicate that voltage is measured across them.

In the above, red contacts indicate that current is passed between the two contacts and blue contacts indicate that voltage is measured between them. The opposite polarity measurements (the measurements within each of the four columns in figure A.4) can be averaged to reduce the effects of offsets due to thermal voltages. From the reciprocity theorem:

\[ R_{ab,cd} = R_{cd,ab} \quad \text{(A.15)} \]

Combining this with the measurements of opposite polarity gives two averaged resistances:

\[ R_A = \frac{R_{12,43} + R_{21,34} + R_{43,12} + R_{34,21}}{4} \quad \text{(A.16)} \]
\[ R_B = \frac{R_{32,41} + R_{23,14} + R_{14,23} + R_{41,32}}{4} \]

which can then be used to calculate the sheet resistance, \( R_s \) via the van der Pauw equation

\[ \exp\left(-\frac{\pi R_A}{R_s}\right) + \exp\left(-\frac{\pi R_B}{R_s}\right) = 1 \quad \text{(A.17)} \]

which is derived in his original paper [3]. In general, equation A.17 has to be solved numerically. The special case when it can be solved analytically is when \( R_A = R_B = R \), i.e., the sample is square and homogeneous. The sheet resistance is then given by

\[ R_s = \frac{\pi R}{\ln 2} \quad \text{(A.18)} \]

and the resistivity of the sample

\[ \rho = R_s d \quad \text{(A.19)} \]

can be calculated once a value for the sheet resistance has been obtained along with \( d \), the sample thickness.
A.2.2 Hall Coefficient

The main strength of the Van der Pauw method is that Hall measurements can be carried out using the same sample geometry and with the same contacts that are required for sheet resistance measurements. The differences compared to the sheet resistance measurements are that the current is applied between diagonally opposed rather than adjacent contacts (and the voltage is measured between the remaining diagonally opposed contacts), and that the sample must be placed in a magnetic field to induce a Hall voltage.

The measurements are carried out by first applying a magnetic field $B$ perpendicular to the plane of the sample. The two opposite directions perpendicular to the plane of the sample are given the arbitrary labels of ‘positive’ and ‘negative’. Voltages measured in a positive field are indicated with a subscript $P$, those measured in a negative field are given a subscript $N$.

With the magnetic field applied, a current is passed between two diagonally opposed contacts, while the corresponding voltage is measured between the remaining two contacts. This is shown in figure A.5. As with the sheet resistance measurements, the polarity of the current is reversed and the measurements repeated. The measurements must also be carried out with the magnetic field direction reversed to remove the effects of offset voltages caused by nonsymmetric sample contacts, a non-uniform sample shape or a non-uniform sample temperature. This gives a set of eight voltages: four measured with the field in the positive direction and four with the field in the negative direction. The difference of the voltages for positive and negative fields are taken to remove the effect of the previously mentioned offset voltages:\footnote{The voltages taken in positive and negative fields will have opposite sign (unless there is a particularly large voltage offset present in the experimental set up). An alternate way to write the equations in figure A.5 would be $V_x = |V_{xP}| + |V_{xN}|$.}

\[
\begin{align*}
V_{13} &= V_{13P} - V_{13N} \\
V_{31} &= V_{31P} - V_{31N} \\
V_{24} &= V_{24P} - V_{24N} \\
V_{42} &= V_{42P} - V_{42N}
\end{align*}
\]

Figure A.5: Van der Pauw method of measuring the Hall voltage. Each column shows two measurements of opposite polarity. Red contacts indicate current is passed between them, blue contacts indicate that voltage is measured across them.
these are then combined to give the Hall voltage:

\[ V_H = \frac{V_{13} + V_{31} + V_{24} + V_{42}}{8} \]  \hspace{1cm} (A.20)

where the sign of \( V_H \) determines the sample type; if it is positive the sample is p-type, if negative the sample is n-type. If equation A.8 is rearranged, it is seen that the sheet carrier density \( n_s \), can be obtained from the Hall voltage

\[ n_s = \frac{IB}{qV_H} \]  \hspace{1cm} (A.21)

where \( n_s = nd \). By making use of the relations

\[ \rho = R_s d \quad \text{and} \quad n = n_s/d \]  \hspace{1cm} (A.22)

equation A.11 can be modified to

\[ \mu = \frac{1}{qn_s R_s} \]  \hspace{1cm} (A.23)

which can be combined with equation A.21, allowing the carrier mobility

\[ \mu = \frac{V_H}{R_s IB} \]  \hspace{1cm} (A.24)

to be calculated. This is commonly referred to as the Hall mobility, to distinguish it from the field-effect mobility, which is the carrier mobility measured by incorporating the material into a field-effect transistor. An example of a Hall voltage measurement of a p-type TCO, \( \text{Cr}_2\text{O}_3:\text{Ni} \), is shown in Figure A.6. Despite the large magnetic fields used, the Hall voltage remains in the noise limit of the system. Further information about this material can be found in [6].

All electrical measurements were taken with a Keithley 2400 sourcemeter. Samples were connected to the measurement apparatus via silver wire, which was secured to the corners of the samples with silver paint.
Figure A.6: Hall voltage measurement of Cr$_2$O$_3$:Ni performed at 250 K. The measurement was averaged over a positive and negative sweep of the magnetic field to remove the effects of any magnetoresistance of the material.
Appendix B

Microscopy

Two forms of microscopy were used for physical characterisation of the grown thin layers: scanning electron microscopy to measure the thickness of select films, and atomic force microscopy to gain insight into the surface morphology.

B.1 Scanning Electron Microscopy

For viewing features of a sample in the micrometre to nanometre range, Scanning Electron Microscopy (SEM) is the technique of choice. Electrons are accelerated to an energy of 0.5–20 keV and focused onto the sample of interest which is inserted into a high vacuum chamber. The electron beam is then rastered across the sample through the means of magnetic lenses. At each point of the raster scan, the primary electron beam strikes the sample producing secondary electrons, x-rays, back scattered electrons and more. While much information can be gained from samples by detecting these various electrons/characteristic radiation, the low-energy secondary electrons emitted provide information on the surface topography. As the low-energy electrons originate from within a few nanometres of the surface, the amount produced and thus detected will be sensitive to the topography of the surface, as local changes in the interaction volume of the primary beam and the sample will be caused by features on the surface such as steps, pitholes etc. The signal produced is proportional to the number of the secondary electrons detected. This allows a two dimensional image to be built up as the raster scan proceeds.

The thickness of a thin film can be measured by cleaving the film/substrate and performing a cross sectional scan by SEM. While films with a much larger thickness can be measured when compared with XRR, SEM provides a local thickness measurement, rather than a whole-sample average. To determine the thickness of a non-uniform film, the thickness must be measured at many points and an average taken. Furthermore, only materials which are conductive can be measured using...
SEM, as non-conductive materials will quickly charge as the electron beam is turned on, causing distortion in any images. While a thin metal coating can be applied to some non-conductive materials, this will alter the morphology on a nanometre length scale. All SEM images presented here were taken with a Carl Zeiss Ultra, which has a resolution of less than 2 nm. Cross sections were prepared by scribing the backside of the sample with a diamond tipped pen, cleaving the sample along this line, and securing it to an SEM sample holder with silver paint.

B.2 Atomic Force Microscopy & Profilometry

Atomic Force Microscopy (AFM) is a complementary technique to SEM for imaging surfaces. While the strength of SEM lies in its fast, up to 30 frames per second imaging, AFM is used to provide much higher resolution quantitative images. AFM has height resolution on the order of Ångströms, and can even achieve atomic resolution in the lateral directions. While AFM also benefits from being performed in a high vacuum environment, high resolution can be achieved in ambient conditions.

There are two types of AFM measurements; both involve bringing a sharp tip (with a radius of 10–30 nm) on the end of a cantilever to within a few nanometres of a surface. In the first mode of measurement, known as contact mode, the tip is brought into contact with the surface and rastered across, line by line, until an image is formed. Typical scan areas are on the order of square micrometres. The rastering is performed by applying voltages to piezoelectric materials which are attached to the scan head. As the tip is moved across the sample surface, its deflection is measured by reflecting a laser spot off the cantilever and into a photodiode. By measuring this deflection, a quantitative image of the surface topology is formed.

In tapping mode, the tip is oscillated at its resonance frequency (on the order of hundreds of kilohertz). The interaction between tip and sample surface modifies the oscillation amplitude of the tip with this interaction depending on the tip-surface distance. A feedback loop is used to keep this amplitude constant; by measuring the feedback signal a topographic image can be built up. While higher scan speeds can be performed in contact mode, tapping mode typically results in less damage to both tip and sample, and so is a more common choice for general imaging purposes.

The AFM images presented here were taken with an NT-MDT Solver Pro, operating in tapping mode. Images were taken with aluminium-coated silicon tips, with a typical frequency of 325 kHz and a force constant of 40 N m$^{-1}$. Surface roughness values were obtained from 512 $\times$ 512 pixel (10 $\times$ 10)$\mu$m$^2$ images that were recorded at a scanning speed of 2 lines per second (2 Hz). AFM images obtained were analysed using Gwyddion [7]. Any post-processing of images will be noted in figure captions.
Appendix B. Microscopy

A Profilometer can be considered as a rudimentary atomic force microscope. In the technique of profilometry, a tip, typically made from diamond, is moved laterally across a surface to gain a one-dimensional line scan of the surface topography. The scan speed is much faster and the scan area much larger than AFM. Profilometry is typically used to measure the thickness of films where a well defined boundary between film and substrate is present on the surface. As a much larger tip is used, the lateral resolution is only on the order of tens of nanometres, while a typical height resolution of the instrument is on the order of a few nanometres. Profilometry scans presented here were taken with a Dektak 6M profilometer.


