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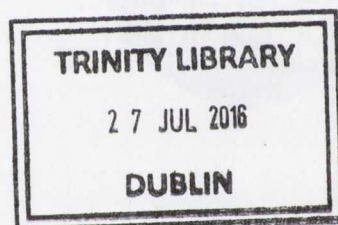
The growth and characterization of Chromium-based p -type transparent conducting oxides



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This dissertation is submitted for the degree of
Doctor of Philosophy



Thesis 11051

Declaration

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Leo Farrell

2016



I would like to dedicate this thesis to my mother and father.

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Abstract

Two Cr-related materials Cr_2O_3 and CuCrO_2 are investigated as *p*-type transparent conducting oxides. They both have Cr in its $3d^3$ electron configuration, a feature that is responsible for the *p*-type conductivity. Epitaxial Cr_2O_3 was grown by electron-beam evaporation in a molecular beam epitaxy system on *c*-plane sapphire. The growth parameters are discussed with an examination of the structural properties. The influence of Mg dopants and the oxygen partial pressure were investigated by thermoelectric and electrical measurements. The conduction mechanism is analysed using the small polaron hopping model, and hopping activation energies have been determined, which vary with doping concentration in the range of $210\text{--}300 \pm 5$ meV. Films with better conductivity were obtained by post-annealing. The effect of post-annealing is discussed in terms of a crystallographic reordering of the Mg dopant. The highest Seebeck mobilities obtained from thermoelectric measurements are of the order of $1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This limits the applicability of the material to devices where the hole mobility is of no concern. The fundamental properties of a Mg dopant in a high crystalline quality epitaxial film of a binary oxide is investigated, helping with the understanding of the role of short range crystallographic order in a *p*-type transparent conducting oxide in detail. This analysis is followed by a discussion of a low temperature ($\approx 345^\circ\text{C}$) growth method for Cu deficient CuCrO_2 performed by spray pyrolysis using metal-organic precursors and a simple air blast nozzle. Smooth films were grown on glass substrates with a highest conductivity of 12 Scm^{-1} . The most conductive samples retain transparencies above 55% resulting in a figure of merit as high as $350 \mu\text{S}$, which is the best performing *p*-type

transparent conducting oxide grown by solution methods to date. No post-annealing of the films is required in contrast to previous reports on crystalline material. The low processing temperature of this method means that the material can be deposited on flexible substrates such as polyimides. As this is a solution based technique, it is more attractive to industry as physical vapour deposition methods are slow and costly in comparison.

Publication list

The following publications and their contents contain material derived from this thesis.

L. Farrell, K. Fleischer, D. Caffrey, D. Mullarkey, E. Norton, and I. V. Shvets, Conducting mechanism in the epitaxial p -type transparent conducting oxide $\text{Cr}_2\text{O}_3\text{:Mg}$, *Physical Review B* **91**, 125202 (2015), PRB.

L. Farrell, E. Norton, B. J. O'Dowd, D. Caffrey, I. V. Shvets, and K. Fleischer, Spray pyrolysis growth of a high figure of merit, nano-crystalline, p -type transparent conducting material at low temperature, *Applied Physics Letters* **107**, 031901 (2015).

K. Fleischer D. Caffrey, **L. Farrell**, E. Norton, D. Mullarkey, E. Arca, and I. V. Shvets, Raman spectra of p -type transparent semiconducting $\text{Cr}_2\text{O}_3\text{:Mg}$, *Thin Solid Films*, (2015).

L. Farrell, E. Norton, C. M. Smith, D. Caffrey, I. V. Shvets, and K. Fleischer, The growth of nanocrystalline Cu deficient CuCrO_2 , *Submitted to Journal of Materials Chemistry C*, September 2015.

E. Norton, **L. Farrell**, I. V. Shvets, K. Fleischer, S. Callaghan, and C. McGuinness, X-ray spectroscopic studies of the electronic structure of p -type transparent conducting oxides, Cu_xCrO_y and $\text{Mg}_x\text{Cr}_{2-x}\text{O}_3$, *Submitted to Physical Review B*, September 2015.

The following publications were published during the thesis but are not directly related to it.

A. Syrlybekov, H.-C. Wu, O. Mauit, Y.-C. Wu and P. Maguire, A. Khalid, C. O’Coileain, **L. Farrell**, C.-L. Heng, M. Abid, H. Liu, L. Yang, H.-Z. Zhang, and I. V. Shvets, Electrical-field-driven metal-insulator transition tuned with self-aligned atomic defects, *Nanoscale*, **7**, 14055 (2015).

K. Fleischer R. Verre, O. Mauit, R. G. S. Sofin, **L. Farrell**, C. Byrne, C. Smith, J. F. McGilp, and I. V. Shvets, Reflectance anisotropy spectroscopy of magnetite (110) surfaces, *Physical Review B* **89**, 195118 (2014), PRB.

R. Ramos, A. Anadón, I. Lucas, **L. Farrell**, M. H. Aguirre, R. G. S. Sofin, I. V. Shvets, P. A. Algarabel, L. Morellón, and M. R. Ibarra, Influence of the substrate on the anomalous Nernst effect of magnetite thin films, *MRS Proceedings*, **1674** (2014).

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Glossary

AC Alternating-Current. 32

acac Acetylacetonate. 50

CCD Charge-coupled Device. 20

CCR Closed-cycle Refrigerant. 14

CF Conflat. 6

CVD Chemical Vapour Deposition. 50

DC Direct-Current. 6, 13

DFT Density Functional Theory. 21, 26, 31

FIB Focused Ion-Beam. 20, 27

FOM Figure of Merit. 12, 13, 45, 46

IR Infrared. 36

LVM Local Vibrational Mode. 34, 35, 46

MBE Molecular Beam Epitaxy. 5, 6, 21, 22, 29, 30, 34, 36, 37, 47

- PID** proportional-integral-derivative. 8, 16
- PLD** Pulsed Laser Deposition. 45, 47, 50
- PPMS** Physical Property Measurement System. 17, 42
- RSF** Relative Sensitivity Factor. 12
- RSM** Reciprocal Space Mapping. 10, 25, 27, 31–33
- RT** Resistance-Temperature. 5
- SAED** Selected Area Electron Diffraction. 27, 28
- SEM** Scanning Electron Microscopy. 19, 20
- SP** Spray Pyrolysis. 2, 5, 7, 36, 45, 46, 49–51
- SPH** Small Polaron Hopping. 4, 30, 31, 37–41, 43, 44, 46, 47
- TCO** Transparent Conducting Oxides. 1–4, 11–13, 21, 30, 31, 42, 45, 47, 49, 50
- TEM** Transmission Electron Microscopy. 20, 27, 28, 30
- UHV** Ultra-high Vacuum. 5–7, 11
- UV** Ultraviolet. 17
- UV-Vis** Ultraviolet-Visible. 5, 12, 30
- VRH** Variable Range Hopping. 31, 39
- XPS** X-ray photoelectron spectroscopy. 5, 11, 39
- XRD** X-ray Diffraction. 5, 9, 10, 23, 24, 30–32
- XRR** X-ray Reflectivity. 6, 10, 11, 25, 32

Chapter 1

Introduction

This chapter will introduce the topic of transparent conducting oxides (TCOs) in general and outline briefly the contents of the thesis. This section also includes an overview of the state-of-the-art *p*-type TCOs.

1.1 Motivation

TCOs are a material class used in transparent heaters, flat screen displays, touch screens, organic light emitting diodes, and thin film solar cells as electrical contacts that are transparent to visible light. In terms of materials for such electronics, the oxides have become leading candidates as they show high transparency, high conductivity and their mobilities have surpassed amorphous and low temperature poly-crystalline silicon for display devices [1]. The industry standard material is indium tin oxide (ITO) due to its high conductivity ($\approx 1000 \text{ Scm}^{-1}$) and transparency ($>80\%$) [2]. The development of indium gallium zinc oxide (IGZO), a ternary oxide retaining mobility in its amorphous state, has allowed for commercial products utilising IGZO as a thin film transistor (TFT) in the backplane of flat panel displays [3]. IGZO has been essential for high dots per inch, low power, and 4 K high resolution displays.

In contrast to the success of n -type oxides there is a limited number of high mobility p -type TCOs [4, 5]. To obtain the full functionality of oxide electronics technically feasible p -type TCOs are required. This lack of clear candidates for p -type transparent semiconductors demands further research. Without suitable n and p -type dopable materials active bi-polar devices using complementary-metal-oxide-semiconductor (CMOS) technology for transparent electronics are not feasible. The noise immunity, low static power consumption and high density of logic functions arising from CMOS technology is therefore lost. Other uses of p -type TCOs include efficient charge injection layers for organic light emitting devices and solar cells with better band matching [6].

The development of such a material is not a trivial task as the very nature of band structures limit the potential of most common oxides. n -type TCOs have rather high mobility typically related to the dispersion of the 4s orbitals that form their conduction bands. Doping can actually improve the transparency of the material close to the band edge, where the bottom of the conduction band is occupied and optical transitions require higher energies, an effect termed the *Burstein-Moss* shift, seen in degenerately doped TCOs. The curvature of the conduction band is close to parabolic and relatively low effective electron masses are obtained. By comparison most p -type TCOs have relatively flat valence bands with high hole effective masses. The discovery of a high mobility p -type TCO will allow for the design of new devices. Thus research into viable p -type TCOs is merited.

Cr-related oxides such as $\text{LaCrO}_3\text{:Sr}$, CuCrO_2 , $\text{MnCr}_2\text{O}_4\text{:Li}$, and $\text{Cr}_2\text{O}_3\text{:Mg}$ are an emerging class of p -type TCOs [7–9]. The Cr $3d^3$ electron configuration is responsible for the p -type conductivity, as the Chromium states compose the top of the valence band [10, 11]. Oxides with filled $3d^{10}$ orbitals such as the Cu delafossites have already been widely investigated. However, it seems that the forbidden d - d^* transitions in non-filled $3d$ orbitals do not significantly limit the transmission in thin film form, opening up a range of

candidate materials. In this thesis both Cr_2O_3 and CuCrO_2 will be investigated as *p*-type TCOs.

1.2 State-of-the-art *p*-type TCOs

The main interest in the field of *p*-type TCOs originated from the potential of the delafossites, with the $\text{A}^{1+}\text{B}^{3+}\text{O}_2$ lattice structure, first highlighted in 1997 when CuAlO_2 was reported to exhibit *p*-type conductivity while maintaining high transparency [12]. These materials retain the *p*-type conductivity of Cu_2O while having a larger bandgap due to the introduction of the metal cation. These materials include, but are not limited to, CuGaO_2 [13], CuScO_2 [14], CuBO_2 [15], and CuCrO_2 [16]. However Cu-delafossites have proven to be hindered by their Small polaron hopping (SPH) mechanism, high deposition temperature, and, in some cases, inter-band transitions limiting their transparency [17]. Nonetheless one of the highest conductivities to date for a *p*-type TCO is for $\text{CuCrO}_2\text{:Mg}$ with reports of 220 Scm^{-1} [16].

Spinel *p*-type TCOs are another class of materials being investigated. ZnRh_2O_4 , despite the advantage of retaining their conductivity as amorphous thin films, has relatively low conductivity (0.1 Scm^{-1}) [18]. In this material the mobility actually increases due to the disorder of the RhO_6 octahedrons in the spinel type lattice. The optical bandgap determined from a Tauc plot is around 2 eV, which negatively affects its optical transmission in the visible range [19]. The distorted delafossite SrCu_2O_2 has better optical properties but has low conductivity (0.053 Scm^{-1}) [20]. ZnCo_2O_4 is another spinel material that has high conductivity, up to 20 Scm^{-1} . The drawback is its low transparency of 25% for a 100 nm thick film [21].

Oxychalcogenides display greater mobility than the Cu-delafossites while maintaining wide bandgaps. This class of material consists of layered $[\text{M}_2\text{O}_2]^{2+}$ and $[\text{Cu}_2\text{Ch}_2]^{2-}$ blocks, where M represents a 3^+ cation, typically La or Ba, and Ch represents one of the chalcogenides such as S, Se, Te. The bandgap has been shown to decrease for the larger atomic

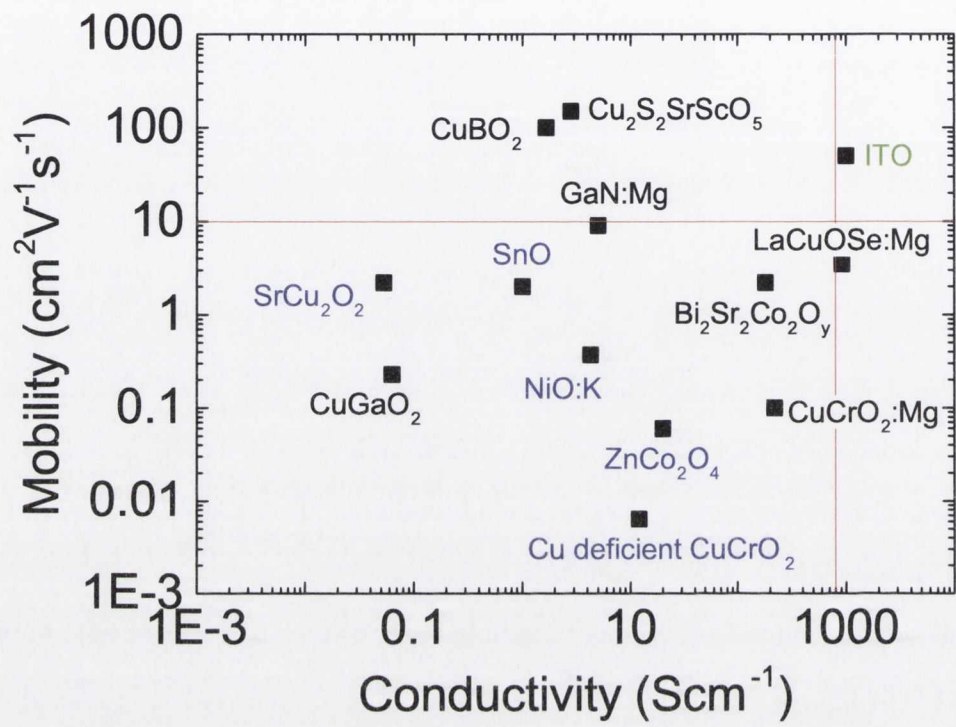


Fig. 1.1 Mobility and conductivity logarithmic plot for high-performing *p*-type TCOs. The top right corner is the optimum region where the current *n*-type TCOs reside such as ITO shown in green. Materials compatible with flexible substrates are highlighted in blue.

radii of Se and Te, with a corresponding increase in conductivity [22]. The Cu-Cu distance is typically an essential feature in the delafossites as this is the nearest-neighbour hopping distance. A larger Cu-Cu bond results in a lower mobility. For the oxychalcogenides, in comparison, the distance only affects the band gap as the conduction mechanism does not proceed by hopping. The most likely defects responsible for the charge carriers are V_{Cu} and divalent substitution on the M^{3+} sites. This can be achieved with K, Mg, Sr, and Ca, but after doping the oxychalcogenides show reduced transparency.

The oxychalcogenide related $[\text{Cu}_2\text{S}_2][\text{SrScO}_5]$ which has a perovskite-like block has been shown to exhibit the highest *p*-type mobility to date of $150 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [23]. This is exceptionally high as most *n*-type TCOs are limited to approx $40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ by ionized impurity scattering. The undoped material has a conductivity of 2.8 Scm^{-1} . However the

carrier concentrations in the undoped oxychalcogenides are too high for field effect transistor devices and can't be controlled as in oxides.

Recently cobalt layer oxides $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Bi}_2\text{Sr}_2\text{Co}_2\text{O}_y$ have attracted attention due to high conductivity values of 137 and 181 Scm^{-1} respectively [24, 25]. This material has a misfit structure with two sub-cells consisting of an alternated stack of the CdI_2 -type CoO_2 conducting layer and a rock salt-type insulating layer along the c -axis consisting of either $\text{Bi}_2\text{Sr}_2\text{O}_4$ or Ca_2CoO_3 . Fig. 1.1 shows a log-log plot of the mobility and conductivity of selected high-performing p -type TCOs. It does not indicate the transparency of the films, which can be quite below the >80% achievable by n -type TCOs.

One of the main drawbacks of the current state-of-the-art materials is the sophistication of the chemical composition and synthesis procedure required to achieve these high-performing films. Typically the performance is only achieved with rare/expensive/toxic elements, with the additional problem of requiring c -axis orientation to maintain their p -type conductivity. From the currently known p -type TCOs there are significantly few that can be deposited below 400°C on amorphous substrates while retaining their p -type properties, which are requirements to be compatible with flexible substrates. These materials are highlighted in blue in Fig. 1.1.

1.3 Thesis Outline

The thesis involves the investigation of two p -type TCOs, $\text{Cr}_2\text{O}_3:\text{Mg}$ and CuCrO_2 . Chapter 2 is an overview of the research methods and experimental details. This thesis will build on previous work on the p -type TCO $\text{Cr}_2\text{O}_3:\text{Mg}$ by spray pyrolysis (SP). Epitaxial growth will be performed in order to investigate the conduction mechanism in these films. Chapter 3 is an overview of the growth parameter of undoped Cr_2O_3 . Chapter 4 is an in depth electrical and thermoelectrical characterisation of Mg doped Cr_2O_3 . The charge transport is discussed. Beyond basic material research there is also a need to obtain lower processing temperatures

and improve the ease of fabrication of current *p*-type TCOs. One of the leading candidate *p*-type TCOs is $\text{CuCrO}_2\text{:Mg}$ due to its high conductivity. Considering this, low temperature SP of CuCrO_2 was investigated in Chapter 5. This material is promising due to its facile synthesis and amorphous nature, lending itself to use with flexible substrates. Finally Chapter 6 concludes the main results of the thesis, with a short section on future work.

Chapter 2

Experimental overview

This thesis is mainly concerned with the growth and characterisation of thin films. This chapter will inform the reader of the experimental techniques used. Both deposition methods; molecular beam epitaxy (MBE) and SP will be discussed in detail. The structural, chemical, optical and electrical characterisation of the thin films was performed by a number of techniques such as resistance-temperature (RT), Hall effect, X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible (UV-Vis) spectrophotometry. The details of these techniques are discussed in the second section entitled 'Material Characterisation'. The theoretical understanding of the methods is also elaborated on.

2.1 Deposition Methods

2.1.1 Molecular Beam Epitaxy

Epitaxial growth is the growth of one material on another (hetero-epitaxy) or on the same material (homo-epitaxy) where the atoms stack in an ordered manner on a crystalline substrate due to the matching of the crystal lattice parameters. MBE is an advanced technique for epitaxial growth. It operates in the ultra-high vacuum (UHV) range (10^{-7} Pa) which allows

a low level of impurity inclusion during growth and precise control over the stoichiometry. Evaporation proceeds at very low rates, if required, which allows good thickness control and hence improves the reproducibility. Low deposition rates also facilitate controlled dopant inclusion [26].

The commercial name for the MBE system used in this thesis is the DCA M600 MBE. The system is depicted in Fig. 2.1. The system consists of two chambers separated by a gate valve. The smaller chamber, operating at a typical pressure of 7×10^{-5} Pa, is used for loading the samples into the main chamber with a 1.3×10^{-7} Pa operating pressure. This is achieved by a transfer arm with a specially designed transfer cup. The samples are held by a custom design sample holder. The temperature of the sample holder is controlled by a EUROTHERM 2408 controller used in conjunction with a direct-current (DC) power supply and a C-type thermocouple (W/Rh). The heater is a pyrolytic boron nitride and pyrolytic graphite (PBN/PG/PBN) cup heater element. The UHV is maintained in the main chamber by a VARIAN 1000 ls^{-1} turbo pump backed by a VARIAN Tri Scroll 800 vacuum pump. The load-lock is pumped down by a HiCube turbo pump from Pfeiffer with a pumping speed of 35 ls^{-1} . All attachable parts to the chambers are fitted with standard conflat (CF) type flanges for use in conjunction with oxygen-free flat copper gaskets. The films are grown by using e-beam evaporation from a Telemark electron beam source. This involves the generation of a molecular beam from a metallic or oxide source which is directed at the target substrate. An INFICON IC/5 deposition rate controller is used in conjunction with crystal monitors to control the growth rate for the e-beam evaporator. There is a four pocket e-beam evaporator (operating at 7 cc each) used to deposit a variety of materials and a single pocket e-beam evaporator (25 cc). There is also a 20 cc Knudsen-cell with a crystal monitor to determine the rate. The crystal monitors are calibrated by cross-checking the actual thickness of the deposited film by X-ray reflectivity (XRR).

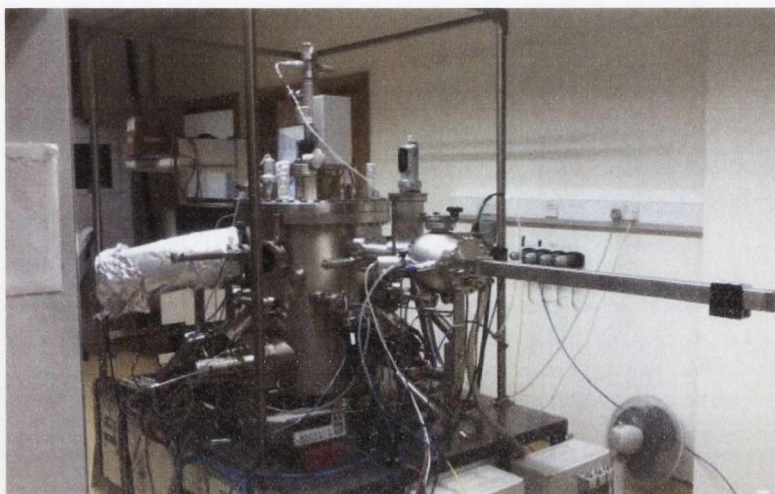


Fig. 2.1 MBE system

During growth of oxides from metal sources it is necessary to introduce an oxygen partial pressure. This is done by using a leak valve attached to the main chamber. To induce greater reactivity during oxide growth an Oxford Scientific OSPrey Plasma Source is used to generate oxygen plasma. This instrument uses the phenomenon of electron cyclotron resonance to create high density plasma. A magnetron generates microwaves of a frequency of 2.45 GHz which are coupled to ions on the 86 mT surface of a quadrupole magnetic array. The spiralling motion extends the electron path length causing the probability of collision with other molecules to increase [27]. The reactivity depends on microwave power, oxygen partial pressure and the ratio of atomic and ionised oxygen molecules.

2.1.2 Spray Pyrolysis

SP is an in-expensive technique that can achieve large-area deposition. Although it lacks the sophistication of UHV systems it is a versatile system for facile synthesis of a wide range of materials. This is important if rapid screening of compositions and dopants is required. The deposition occurs through a chemical vapour process. Precursors, typically metal salts, are dissolved in a suitable solvent. The solution is then sprayed onto a heated substrate. The

heat from the substrate causes the solvent to evaporate leaving behind the precursors which react in the environment to form compounds on the substrate [28]. The distance between the delivery nozzle and the substrate needs to be optimized to ensure that the solution has enough time to evaporate. Large solvent droplets impinging on the substrate can crack and damage the surface. Additionally if the distance is too large powders will form and conglomerate in the film. Similarly the temperature of the substrate influences the growth of the desired material as the solvent will evaporate more readily at elevated temperatures [29].

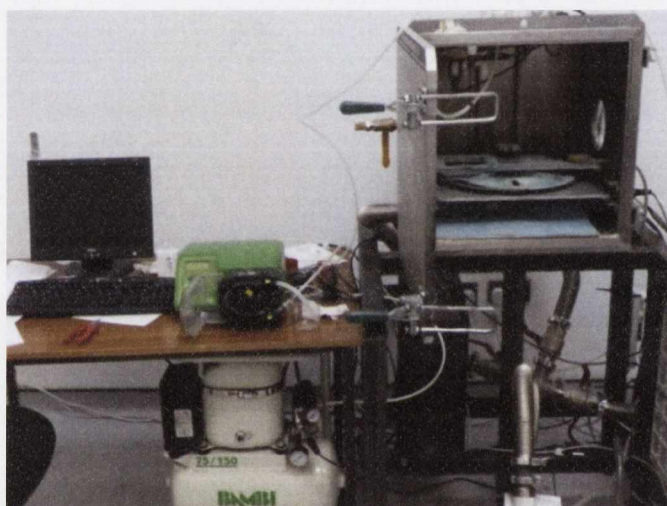


Fig. 2.2 Spray Pyrolysis system

For the nebulization of the solution an air atomizer nozzle (PNR Air assisted ultrasonic atomizer, model MAD 0331 B1BA) was used at a distance of 25 cm from the glass slides acting as substrates (Fisher brand, thickness 0.8-1 mm). Although this nozzle is not the best performing in terms of particle size and distribution it is quite robust, chemical resistant and easy to clean or replace. Other nozzle types used in SP include ultrasonic and electrostatic atomizers. During the deposition, the substrate was kept at a constant temperature through a ceramic heater (Thermo Scientific, Barnstead/Thermolyne Cimarec) controlled by a closed loop proportional-integral-derivative (PID) system, which adjusted to variations in temperature. Heater surface temperature readings during spraying were taken using a type K

thermocouple (chromel vs alumel) welded to the top of the hot plate. The temperature was PID controlled during spray conditions within $\pm 10^{\circ}\text{C}$. Air, nitrogen, oxygen or a mixture of them, were regulated using a mass flow controller (Vögtlin, model red-y). The oxygen concentration inside the chamber was monitored using an oxygen sensor (Sensor technics, model XYA1) placed at a distance of 35 cm away from the nozzle. The delivery of the liquid was achieved using a peristaltic pump (Watson Marlow Pumps Peristaltic 520S) through Marprene pipes. A picture of the system is shown in Fig. 2.2.

2.2 Material Characterisation

2.2.1 Electrical and Thermoelectrical measurements

There are numerous methods to measure the electrical conductivity of a material and how it varies with temperature. Only DC methods are considered here using the linear four point probe and the *Van der Pauw* configuration. The measurement of the Seebeck effect is also discussed. Hall effect measurements are described in the following section.

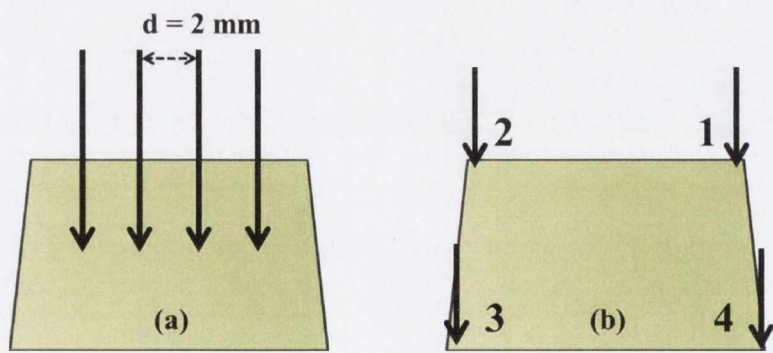


Fig. 2.3 The two contact layouts for the DC measurements. (a) shows the linear probe method and (b) shows the *Van der Pauw* configuration.

To quickly test the sheet resistance of samples a linear four point probe set-up was employed. A Keithley 2400 source-meter was used to apply a current to the outer probes

and record voltage across the inner two probes. The probes were made from gold and were compressible, with spring-loaded tips to ensure reliable contact pressure. See Fig. 2.3(a) for the contact layout.

$$R_s = \frac{\pi}{\ln(2)} R \quad (2.1)$$

The sheet resistance R_s can be calculated from the measured resistance R using Eq. 2.1, which comes from considering the voltage generated by a dipole source in an infinite sheet. This was scripted into the software. However this equation is only accurate above a certain sample width to probe spacing ratio [30]. In our set up the probe spacing, d was 2 mm. For square samples of width 10 mm the sheet resistance is over-estimated and a correction factor of 0.73 can be applied. In general for a sample over 25 mm in width the correction factor is 0.95 or greater. In this set up it was also possible to measure the change of resistance with temperature. The sample was heated by a Watlow ceramic heater from below, which varied the sample temperature from 50-150°C.

For low temperature measurements samples were mounted on a detachable sample holder, which was then attached to the top of a Sumitomo cold head (RDK-101E 4 K). The *Van der Pauw* configuration (Fig. 2.3(b)) was used in this set-up with four gold probes at each corner of the 1 cm² sample. The cold head was held under vacuum using a rotary pump. The cold head was also attached to a closed-cycle refrigerant (CCR) system (Sumitomo cryogenics condenser HC-4E2) which used helium as the refrigerant. A Lakeshore 330 Temperature Controller was used to control the sample temperature. The cooling effect of the CCR system was offset by supplying sufficient current through the heating wire to attain a dynamic equilibrium about the set point. The temperature range attained with this system was from 4 K to 300 K measured using a silicon diode. A Keithley source meter was also used but now current is applied between contact 1 and 2 while the voltage across contact 3 and 4 is measured (see Fig. 2.3(b) for numbering). The measured resistance is denoted $R_{12,34} = V_{34}/I_{12}$. Averaging this resistance with $R_{34,12}$ gives the parallel resistance R_p . This

can also be repeated for the vertical edge $R_{23,41}$ and $R_{41,23}$ to obtain the vertical resistance R_v .

$$R_p = \frac{R_{23,41} + R_{41,23} + R_{32,14} + R_{14,32}}{4}, R_v = \frac{R_{12,34} + R_{34,12} + R_{21,43} + R_{43,21}}{4} \quad (2.2)$$

Repeating this for reversed polarity (to remove unwanted offset voltages) then extends the number of resistances to be averaged to four for both R_p and R_v as shown in Eq. 2.2. Finally to relate these resistances to the sheet resistance Eq. 2.3 is used. To calculate R_s from Eq. 2.3 it is necessary to use iterative methods. This is performed numerically by a stand alone C program. Note this technique can be used for any arbitrary shape. [31]

$$e^{-\pi R_p/R_s} + e^{-\pi R_v/R_s} = 1 \quad (2.3)$$

Thermoelectrical measurements

When a temperature gradient exists in a material a potential difference will occur due to the diffusion of charge carriers. The Seebeck coefficient S measure this effect,

$$S = -\frac{\Delta V}{\Delta T} = -\frac{V_{hot} - V_{cold}}{T_{hot} - T_{cold}} \quad (2.4)$$

where ‘hot’ and ‘cold’ refer to the hotter and colder ends of the sample respectively due to the temperature gradient. Consider the case of a n -type material. Electrons will flow to the cold side of the sample leaving the hot side with a lower density of carriers. A positive potential is developed on the hot side. For a p -type material holes will move to the colder side. The hot side will be at a negative potential. The voltage difference is measured for heating and cooling cycles. The Seebeck coefficient is then the ratio of the voltage difference to the temperature gradient obtained from a linear fit of the data using Eq. 2.4.

The measurements were performed using a home-built system which varied the temperature gradient from 1 to 10 K across the sample while measuring the potential difference. An estimate of the Seebeck coefficient in the 293 to 308 K range was obtained. The sample was clamped between two sets of copper blocks; one at the cold side and the other at the hot side. The set of blocks on the cold side sat on electrically insulating heat exchange foil over a metal block that acted as a heat sink. The other set of blocks (on the hot side) sat on a ceramic heater (Watlow). The supplied heater power was controlled using a PID controller, while the actual temperature at either end of the sample was measured using a Type K thermocouple (chromel vs alumel) thermally connected but electrically isolated from the copper block. The measurements were taken in a vacuum of approximately 200 Pa. The potential difference was measured using an Agilent 34401A Multimeter. The contribution of the Cu connection to the Seebeck coefficient ($1.5 \mu\text{V/K}$) is subtracted from the obtained values. The system

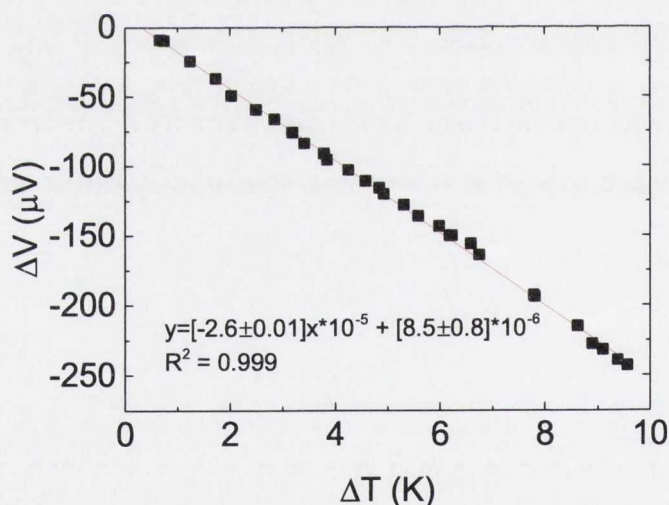


Fig. 2.4 Voltage difference as a function of temperature gradient for a chromel wire.

was tested for accuracy by measuring the Seebeck coefficient of a chromel wire (an alloy of 90% Ni and 10% Cr). A linear fit of Fig. 2.4 gives a Seebeck coefficient of $24.5 \mu\text{V/K}$ after correcting for the Seebeck coefficient of Cu. When compared to a literature value of $22 \mu\text{V/K}$ [32] the difference is small, indicating an error in the system of approximately 10%.

2.2.2 Hall effect measurements

The Hall effect is a useful technique to measure the charge carrier concentration of samples. It is a physical phenomenon that occurs when electrons are moving under a potential gradient in the presence of a magnetic field. An opposing voltage is created perpendicular to both the magnetic field and the direction of current caused by the separation of charge due to the Lorentz force. This voltage can be measured as a function of magnetic field and can be related to the charge carrier concentration n . Eq. 2.5 shows the relation for the Hall coefficient R_H to the Hall electric field E_y , the current density j_x and the magnetic field B . See Fig. 2.5(a).

$$R_H = \frac{E_y}{j_x B} = \frac{1}{qn} \quad (2.5)$$

Where q is the positive or negative electric charge. As the direction of the force felt by electrons is directly opposite to that experienced by a hole the sign of the Hall voltage can be used to distinguish the dominant charge carrier type.

Ultraviolet (UV) lithography was used to fabricate a Hall-bar structure, see Fig. 2.5(b). It is necessary to ensure that the length to width ratio of the Hall bar is greater or equal to 4 to minimize geometrical errors in the calculations. [33] Similarly any contact-size errors can be reduced by placing contacts at the ends of contact arms [34]. Microposit S1813 G2 positive photoresist was used to define the pattern. The sample with the spun-on photoresist (3000 rpm) was exposed using an Optical associates (OAI) mask aligner and then developed using MF319. The sample was then etched to leave only the Hall-bar structure. Although Ar^+ milling can be used to etch the pattern it is a slow technique. A chemical method was tested to speed up the process: Diammonium hexanitratocerate 20-25% and nitric acid 5-10% in water was used to etch the pattern with an etch rate of ≈ 0.5 nm/sec. A lift-off technique was also used to deposit gold contact pads on this structure.

Thin silver wires of 0.05 mm (Advent) and silver paint (Agar scientific, Batch number OW20728440) were used to contact these pads. A Quantum Design Physical property

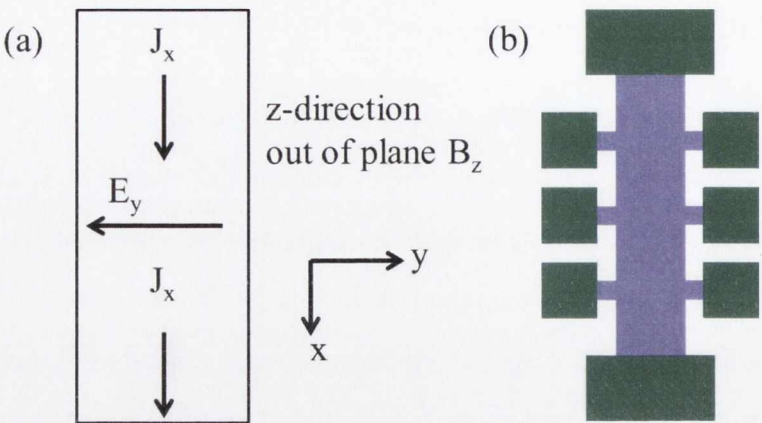


Fig. 2.5 (a) A diagram illustrating the direction of the electric field created by the Lorentz force. (b) The design of the Hall-bar structure. The green areas are the contact pads while the purple areas are the remaining sample after etching.

measurement system (PPMS) was used to measure the Hall effect. This system had a helium-cooled cryostat with a nitrogen-filled jacket which allowed the temperature to be varied between 400 K and 2 K with a typical error of $\pm 0.5\%$. The probe sat inside a dewar of helium and the samples were inserted into the evacuated probe. The system uses a 14 T superconducting magnet which could be operated in a persistent or driven mode.

2.2.3 X-ray Diffraction

X-ray diffraction (XRD) is a useful non-destructive *ex-situ* technique to characterise crystalline thin films. XRD exploits the uniform stacking of atoms in crystals. Constructive interference occurs for specific angles of the incident x-ray corresponding to characteristic diffraction planes of the sample. Structural information such as the lattice parameter, crystallite size, disorder and strain can be obtained from the diffraction patterns. The governing equation is Bragg's Law which describes the condition for constructive interference,

$$n\lambda = 2d \sin \theta \tag{2.6}$$

where n is an integer, θ the Bragg angle, λ the wavelength of the incident beam and d the spacing between diffraction planes. The system used for this study was a Bruker D8

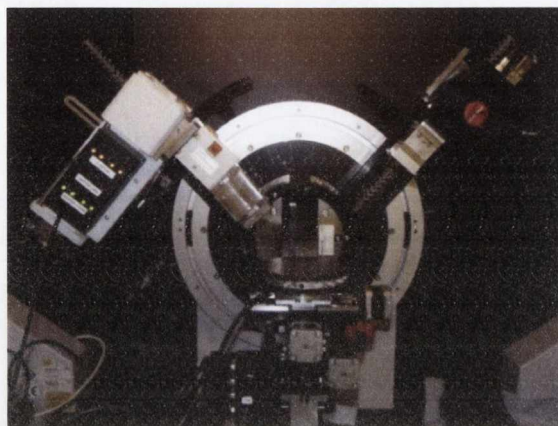


Fig. 2.6 X-ray diffraction system in high-resolution mode

Advance multi-crystal high-resolution x-ray diffractometer equipped with a Cu K- α source ($\lambda = 0.1543$ nm). The system used a Göbel mirror, to induce parallel rays, and a double bounce Germanium channel cut monochromator. The system has an automated x , y , z , χ , and ϕ sample stage in order to align the sample, see Fig. 2.7. In high-resolution XRD mode (Fig. 2.6) the incident and diffracted beam directions are separated by a 2θ value determined by the main substrate peak. The epitaxial film is then detected by scanning around the substrate reflex. The system has approximately a 0.01 degree resolution.

Reciprocal Space Mapping

To determine both the in-plane and out of plane lattice constants of a particular film it is necessary to perform Reciprocal space mapping (RSM) of an asymmetric peak, which involves scanning a two-dimensional region of reciprocal space. This is performed by combining the 2θ - ω scan mode with the ω scan mode (also called a 'rocking curve'). For a given length of the scattering vector, defined as $[q = 4.\pi\sin(\theta)]/\lambda$, an ω scan is performed, then the 2θ - ω scan mode is employed to change the length of the scattering vector by a small

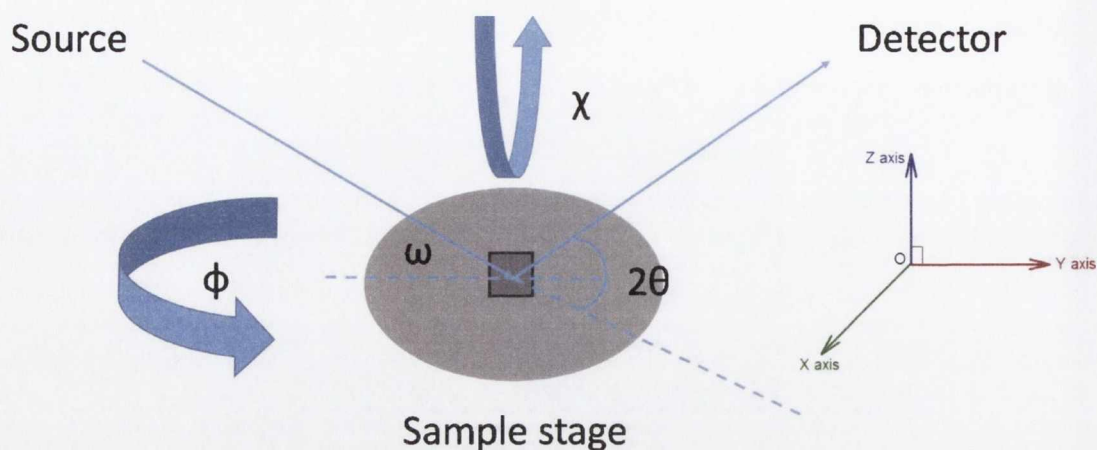


Fig. 2.7 Diagram of the different angles used for alignment of the X-ray diffraction system.

amount δq . This is then repeated to obtain a two-dimensional 'map' of reciprocal space. The degree of relaxation and strain in the film can also be calculated from these measurements.

2.2.4 X-ray Reflectivity

XRR can be used to determine the thickness, density and roughness of thin film layers. The basic principle of XRR is to measure the intensity of a reflected x-ray beam near a glancing incidence configuration. The reflection at the surface and interface of the film is due to the difference in electron densities in different layers which corresponds to different reflectivity indexes. The incident angle (θ_i) is equal to the reflected angle and the scan is performed over a 2θ range less than 6 degrees. Total internal reflection will occur for an angle less than the critical angle θ_c and reflection will occur at the top and bottom of the film. Interference of the reflected beam from the top and the bottom of the film results in interference fringes which are used to model the film. Experimental reflectivity curves are analysed and compared to optical reflection and refraction formula. The thickness, density and roughness of the films can be calculated by comparing the measurement to a simulated pattern. The analysis of the XRR data was performed by using the Leptos software.

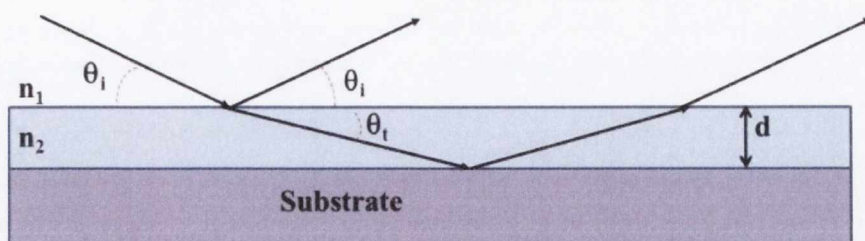


Fig. 2.8 XRR diagram illustrating the incident and reflected beams.

2.2.5 X-ray Photoelectron Spectroscopy

To quantify atomic ratios and assess chemical composition, XPS measurements were performed. This involves the irradiation of a sample in an UHV environment by x-rays. The excitation of the atomic species causes an emission of an energetic photoelectron whose energy is determined by the nature of the irradiated species. The wavelength dependent penetration depth determines how deep into the film the signal is arising from and is typically in the 1-10 nm range. Alternate physical processes such as Auger electrons can occur although they are not discussed here. As the incident x-ray energy ($h\nu$) is known and the kinetic energy of the emitted photoelectrons (E_K) can be measured Eq. 2.7 can be used to calculate the binding energy (E_B) of the particular species for a given detector work function ϕ .

$$E_B = h\nu - (E_K + \phi) \quad (2.7)$$

Experimentally a hemispherical analyser applies electrostatic fields to adjust the pass energy. An XPS spectrum shows the intensity (number of electrons detected) as a function of binding energy. Comparing the set of intensity peaks to known excitations allows the determination of the elemental species as they are characteristic of each element. These peaks correspond to the electronic configuration of the given element arising from core level electrons. Additionally

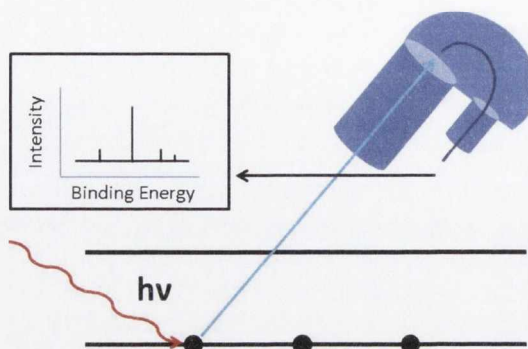


Fig. 2.9 A diagram illustrating the excitation of a core electron and the detection of the photoelectron after passing through the hemispherical analyser.

the comparison of the area of elemental peaks will allow the determination of the atomic percentage taking into account the relative sensitivity factor (RSF).

The measurements presented in this thesis were performed on an Omicron Multiprobe XPS system using Al $K\alpha$ x-rays ($h\nu = 1486.7$ eV) with an EA125 analyser. All samples were chemically cleaned in acetone and isopropanol with an ultrasonic bath and sputter-cleaned using an Ar ion gun operated at 500 V for 10 minutes with a sputter current of 2-3 μA (at low voltage to prevent oxygen sputtering) to remove traces of unreacted precursors precipitating after growth during sample cool down.

2.2.6 UV-Vis Spectroscopy

A Perkin Elmer 650 lambda spectrophotometer, operating from 200 nm to 850 nm, was used to measure the UV-Vis spectrum of thin film samples. The system consists of a deuterium and tungsten-halogen lamp as sources in conjunction with a R6872 photomultiplier as the detector. The system is a double beam and double monochromator (to separate the different wavelengths of light), ratio recording optical system [35]. Integrated transmittance and reflectance are measured using an integrating sphere to include the scattered transmittance and reflectance. This allows the absorption coefficient to be correctly measured. All measurements were performed including the substrate with air as a reference.

For a TCO the optimization of both the optical and electronic properties is equally important. Hence the total transmittance and reflectance of our samples were usually measured in order to calculate the figure of merit (FOM) as given by Eq. 2.8. This is a method to compare results to literature values. Both transmittance and reflectance data are used to minimize the effect of *Fabry-Pérot* oscillations.

$$F = \frac{\sigma}{\alpha} = \frac{-1}{R_{sh} \ln(T + R)} \quad (2.8)$$

Where σ is the conductivity, α is the optical absorption coefficient, R_{sh} is the sheet resistance, T is the average transmittance and R reflectance. The T and R values are the average of 30 points over the 1.5-3 eV range, the optical range of the spectrum. Typically for p -type TCOs FOMs are expressed in $(M\Omega)^{-1}$ or μS , with values ranging anywhere from 1 to 1350 [36, 37], although mostly below 100.

2.2.7 Raman scattering

Normally incident light on a sample undergoes Rayleigh scattering where the energy of the incident photon does not change after the scattering process; an elastic process. However Raman scattering occurs for a small fraction of incident photons. Fig. 2.10 shows a schematic of the Raman scattering process. In this case the energy of the scattered photon ($\hbar\omega_s$) is different than the incident photon ($\hbar\omega_i$) due to inelastic Raman scattering. The incident photon creates an electron-hole pair which either emits (Stokes) or absorbs (anti-Stokes) a phonon and then recombines. The scattered phonon has a lower/higher energy depending on the process. Thus by conservation of energy:

$$\hbar\omega_s = \hbar\omega_i \pm \hbar\Omega_j \quad (2.9)$$

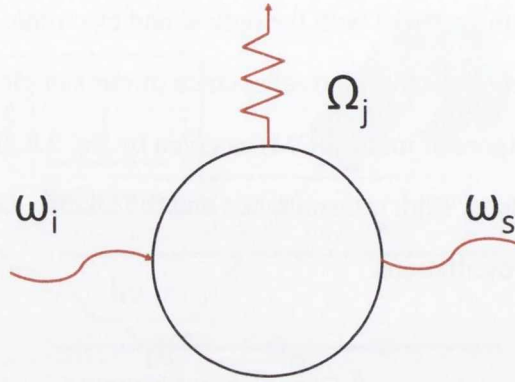


Fig. 2.10 Schematic diagram of the Raman scattering process.

The anti-Stokes effect is a weaker phenomenon as it requires a population of phonons which is more prevalent at higher temperatures. k_s the momentum vector for the scattered phonon is small for a bulk material due to the large momentum difference between an incident photon (k_i) and the bulk material. Due to momentum conservation this means only those phonons with $q_j < 2k_i$ can be excited near the Γ point, see Eq. 2.10. This is because the wavelength of light is much greater than the lattice constant of the material being probed. Broadening of the Raman modes is seen due to defects in the sample and can reveal information about the crystallinity in addition to phase identification.

$$k_s = k_i \pm q_j \quad (2.10)$$

The phonon vibrational modes are characteristic to the bonding structure present in the sample. Therefore Raman scattering can be used as a fingerprinting technique. Typically a laser is used with wavelengths in the visible regions of the spectrum. If the incident photon energy coincides with allowed optical transitions the Raman intensity can be resonantly enhanced.

A Micro-Raman spectrometer in a Renishaw *in-via* system using a 488 nm Ar ion laser in backscattering geometry was used to measure Raman shifts. Typically this is expressed in reciprocal wavenumbers (cm^{-1}).

2.2.8 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to image the surface morphology of samples in this thesis. The theoretical basis for using electrons for imaging is related to their shorter *de Broglie* wavelength. It is possible to image smaller objects than when using visible light with magnifications as high as 10^6 . In a SEM electrons are generated by field emission and are directed down an evacuated column before being focused onto the sample to be imaged. The focused beam is raster-scanned across the surface. Control of the beam is achieved through manipulation of electrostatic and/or magnetic lenses. Electrons are scattered when they interact with the top layer of the material. The secondary electrons emitted from the sample reveal the topography as the plume of secondary electrons emitted are partially exposed for tilted surfaces resulting in a higher number of detected secondary electrons. A Everhart-Thornley detector (a scintillator inside a Faraday cage) is used to collect the secondary electrons. In this study imaging was typically performed at 5 kV on a Carl Zeiss Ultra instrument. Resolution as low as 1 nm can be achieved at this operating voltage.

2.2.9 Transmission electron Microscopy

In this technique electrons are transmitted through an ultra-thin sample. The electrons interact with the sample forming an image which is detected by a charge-coupled device (CCD) camera. The electrons are generated by a field emission gun. Transmission electron microscopy (TEM) can achieve even higher resolution than SEM [38]. Samples need to be electron transparent which requires special preparation. Typically this is performed using a focused Ion-beam (FIB) system.

For selected samples, cross-sectional lamellae for TEM were prepared using a FEI Strata FIB. Final low-kV (2-5 kV) thinning was also made using a Carl Zeiss Auriga FIB. TEM imaging of these lamellae was performed using a FEI Titan operating at 300 kV.

2.2.10 Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is a non-intrusive technique that measures the optical properties of a sample. Typically this involves the measurement of the change in the polarisation of a light wave reflected from a sample. The two main parameters that are measured are the amplitude ratio Ψ and the phase difference Δ between the *s*- and *p*-polarised light waves [39]. These values are measured as a function of the wavelength, most commonly by scanning in the UV-Vis region. They are defined by the fundamental equation of ellipsometry

$$R_p/R_s = \tan[\Psi]e^{i\Delta} \quad (2.11)$$

R_p and R_s are the Fresnel reflection coefficients for light polarised parallel to the incidence plane and light polarised perpendicular to the incidence plane respectively. From these ‘interaction’ parameters the physical parameters are deduced, e.g. the film thickness by computational modelling. If the film thickness is known the refractive index of the material can also be determined.

Chapter 3

The epitaxial growth of Cr_2O_3

In the next two chapters the Cr_2O_3 system is investigated as a potential *p*-type TCO. This material has a number of advantages over current *p*-type TCOs including the potential to fabricate homo-junctions as both *p* and *n*-type doping has been reported [40]. The material also demonstrates excellent stability, even at high temperature in contrast to ZnO:N and SnO_x based *p*-type TCOs [41, 42]. Chromium is relatively abundant, inexpensive and non-toxic making it advantageous in comparison to other *p*-types such as ZnRh_2O_4 and LaCuOSe [43]. Cr_2O_3 is an anti-ferromagnetic wide-bandgap material with the mineral name Eskolaite and has a Néel temperature $T_N = 307\text{ K}$ [44]. Cr_2O_3 is the most stable form of chromium oxides [45]. This oxide has a variety of uses such as a protective layer against corrosion in industrial alloys. [46, 47] Cr_2O_3 and $\text{Cr}_2\text{O}_3\text{:N}$ have also received attention as buffer layers in organic solar cells where the large bandgap (3.4 eV [48]) is advantageous [49, 50]. Additionally Cr_2O_3 has been employed in spintronic devices and as a gas sensor [51–53].

Previously *p*-type conductivity was reported in polycrystalline films and solid solutions. To investigate the conduction mechanism in detail a crystalline material is needed to investigate the effect of disorder. In this chapter undoped epitaxial films of Cr_2O_3 are synthesised by MBE. The growth parameters are discussed, followed by the structural characterisation of the films.

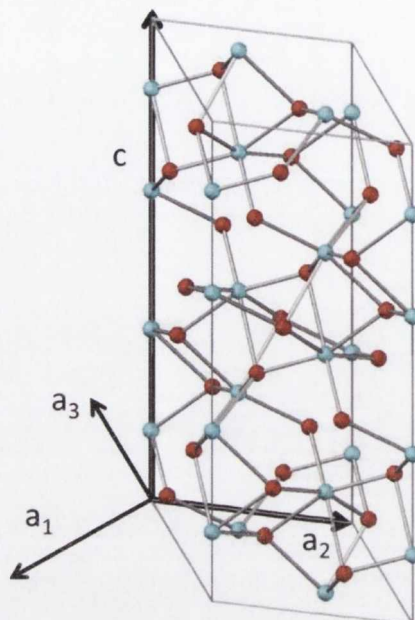


Fig. 3.1 Hexagonal unit cell of Cr_2O_3 with the a and c lattice directions indicated. Red spheres indicate O atoms, while the cyan spheres are Cr atoms.

Cr_2O_3 adopts the corundum structure where oxygen atoms form a hexagonal close-packed structure. The Cr atoms occupy two thirds of the interstitial octahedral sites [54, 55]. The primitive cell is rhombohedral, while the unit cell is hexagonal with lattice parameters of $a = 0.4958 \text{ nm}$ and $c = 1.3594 \text{ nm}$ (PDF number 00-038-1479), see Fig. 3.1.

To study the undoped system thin films of Cr_2O_3 were grown on 1 cm^2 c -plane sapphire substrates by MBE. The effect of changing the oxygen partial pressure was investigated. The substrates were chemically cleaned and then annealed *in-situ* at 600°C , 1.7 mPa oxygen partial pressure, prior to deposition. In order to grow these films, Cr was e-beam evaporated in the presence of an oxygen partial pressure with the substrate temperature set at 500 or 600°C . The initial pressure in the chamber prior to deposition was set to either 2.7 mPa or 5.3 mPa by inserting O_2 via a leak valve for each deposition. During the deposition, Cr consumes part of the oxygen present in the chamber to form Cr_2O_3 . Therefore the pressure during deposition varies in the range from 0.1 to 4 mPa depending on the growth rate (from

0.01 nm/s to 0.05 nm/s). Thus the rate and pressure are dependent on each other and they influence the stoichiometry of the sample.

3.1 Structural analysis by XRD and RSM

A number of thin film samples ranging from 20 to 150 nm in thickness were grown at different oxygen partial pressures. The effect of the oxygen partial pressure on the a and c lattice parameters was examined. All samples were analysed by XRD *ex situ*. As the films grew epitaxially on the c plane of sapphire, only the (006) hexagonal c plane peak of the Cr_2O_3 film and its higher order (0012) reflex were observed in 2θ - ω XRD scans. See Fig. 3.2. From the scans it was possible to calculate the c lattice parameter for the hexagonal unit cell. Gaussian fits of the Cr_2O_3 reflexes are used to obtain an accurate 2θ value. This can then be used with Eq. 2.6 to obtain the d spacing for each sample. To calculate the lattice parameters Eq. 3.1 is used, which relates the reciprocal lattice parameters of a hexagonal crystal lattice (a^* , c^*) to the $d_{h,k,l}$ spacing with miller indices h, k, l .

$$\frac{1}{d_{h,k,l}^2} = \frac{4(h^2 + hk + k^2)}{3a^{*2}} + \frac{l^2}{c^{*2}} \quad (3.1)$$

The reciprocal space lattice parameters are related to the real space parameters by Eq. 3.2.

$$c = \frac{1}{c^*}, a = \frac{2}{\sqrt{3}a^*} \quad (3.2)$$

A dependency of the c lattice parameter on the oxygen partial pressure was noticed. This is shown in Fig. 3.3(a). As the oxygen partial pressure increases the c lattice parameter also increases. To obtain a stoichiometric c lattice parameter an oxygen partial pressure of ≈ 1.3 mPa is required. The oxygen partial pressure and rate are also interlinked as shown by Fig. 3.3(b). As the oxygen pressure is increased the average growth rate decreases. This is

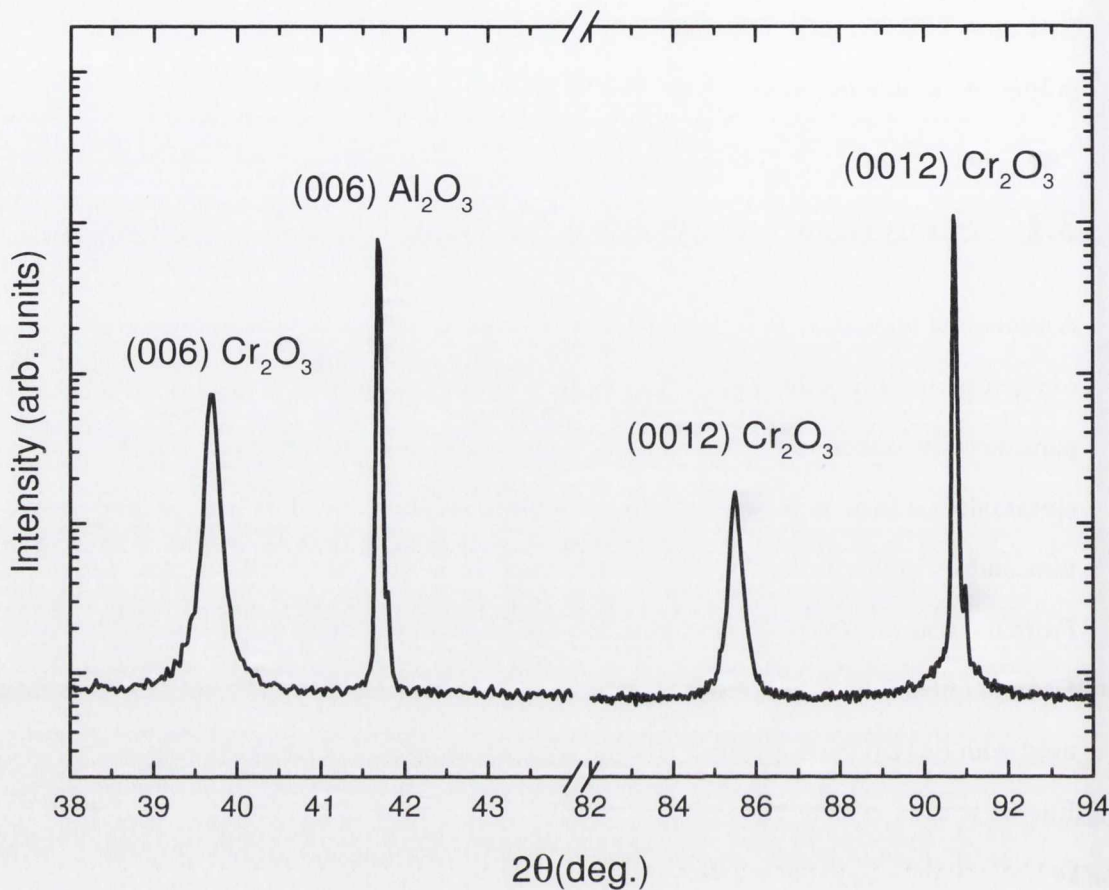


Fig. 3.2 XRD 2θ - ω out of plane scan. The middle angles are cut out to display all of the peaks.

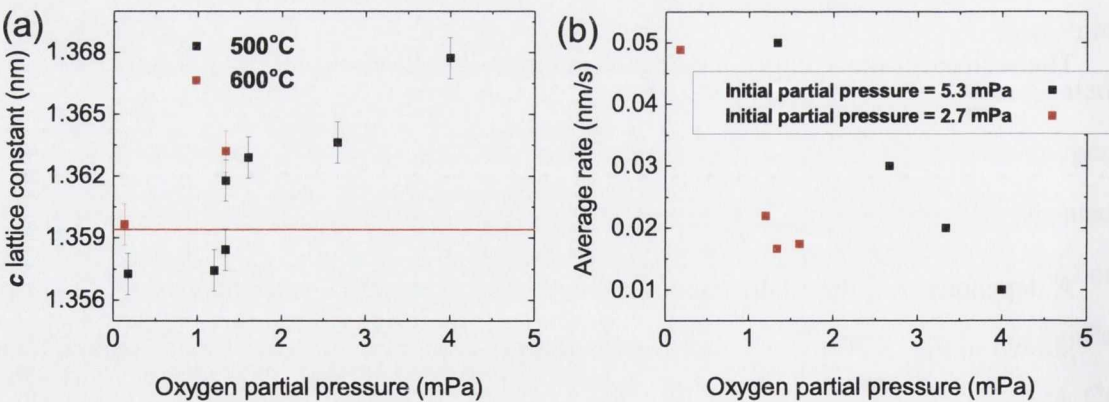


Fig. 3.3 (a) shows the dependence of the c lattice parameter on the oxygen partial pressure. It includes data for both 500°C and 600°C growth temperatures. The red line indicates the value for stoichiometric unstrained Cr_2O_3 . (b) shows the dependency of the average growth rate (nm/s) on the oxygen partial pressure, for two initial oxygen partial pressures.

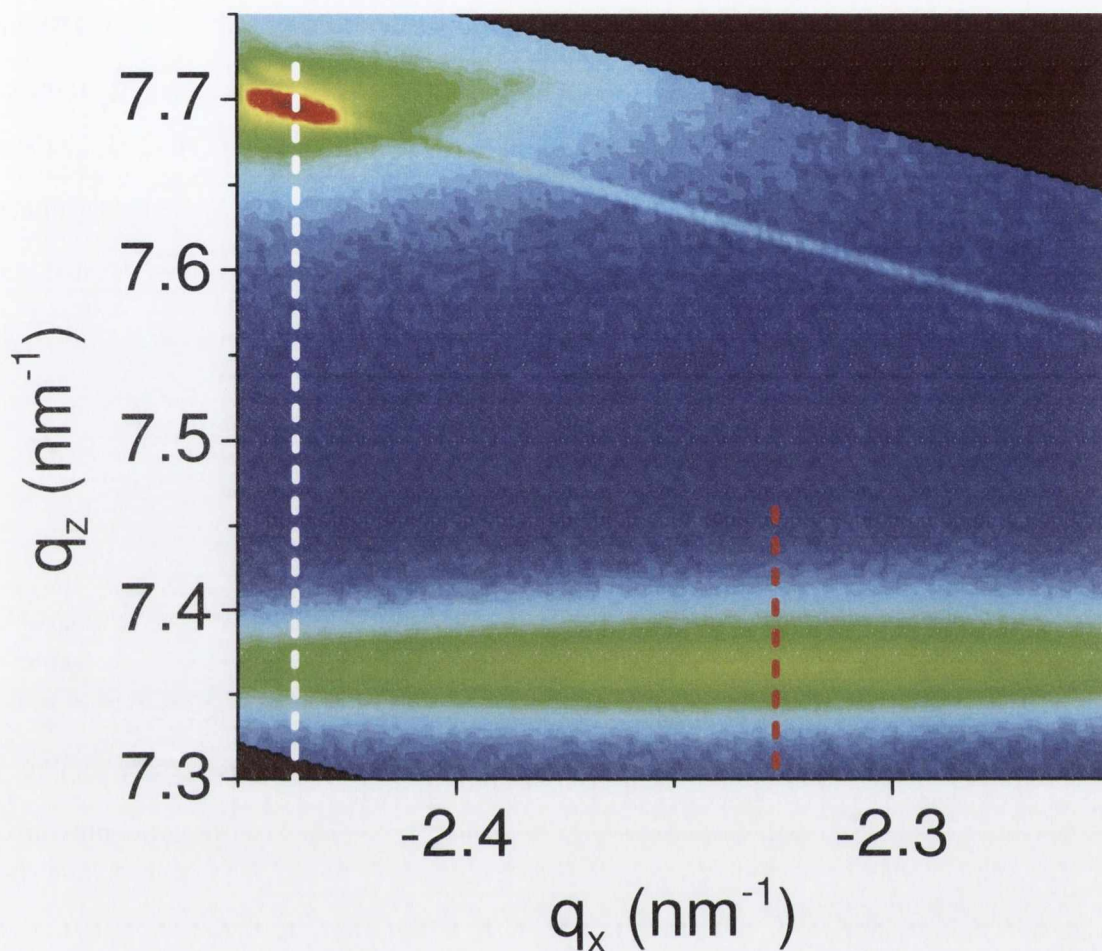


Fig. 3.4 This is a RSM showing the complete relaxation of the films. The dotted lines indicate the stoichiometric q_x positions of Cr_2O_3 and Al_2O_3 in red and white respectively.

because the e-beam evaporation in higher oxygen partial pressure is hampered. As the power is increased more Cr is evaporated which consumes oxygen from the chamber, reducing the overall oxygen partial pressure. The average rate was calculated from measuring the thickness by XRR and taking into account the growth time.

The lattice parameters of Al_2O_3 are $a = 0.4758 \text{ nm}$ and $c = 1.2991 \text{ nm}$ (PDF number 00-010-0173). Due to the in-plane lattice mismatch between the film and the substrate (4.2%), the films grew in a relaxed manner, as previously reported [56]. Despite the large lattice mismatch the films grow in a coherent relaxed manner. Usually one gets either

strained or relaxed rough films. Films as thin as 20 nm are already fully relaxed. There is a thickness difference between films, however the variation in the c and a lattice parameter is not attributed to strain relaxation, as the films are already fully relaxed. This was confirmed from the in-plane lattice parameter measured by RSM (see Fig. 3.4), around the asymmetric (1010) reflex. The RSMs show the reciprocal space lattice parameters. The real space equivalent values can be calculated from Eq. 3.2. The a lattice parameters of the thin film is

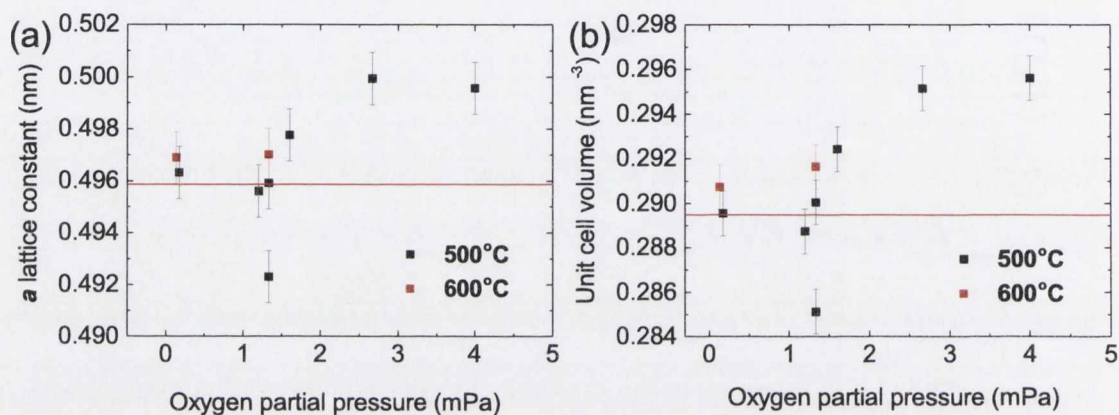


Fig. 3.5 (a) shows the variation of the a lattice constant with the oxygen partial pressure. (b) The unit cell volume is plotted against the oxygen partial pressure. The red lines indicate the position for stoichiometric Cr_2O_3 .

displaced from the substrate and is close to the stoichiometric value for Cr_2O_3 . An epitaxial film is normally confined to the substrates a -axis, while the relaxed pseudomorphic growth enables a different a , while maintaining the overall orientation/symmetry of the substrate. Overall the a lattice parameters had tensile and compressive strain values less than 1%. Note that the width of the thin film peak is exaggerated due to the scaling of the graph. The dependency of the a lattice parameter on the stoichiometry is again a function of oxygen partial pressure as shown in Fig. 3.5(a). As the oxygen partial pressure increases the a lattice parameter increases. This has a significant effect on the overall unit cell volume V (more than the c lattice parameter) which can be calculated from Eq. 3.3 for a hexagonal unit cell.

$$V = \frac{\sqrt{3}}{2} a^2 c \quad (3.3)$$

Density functional theory (DFT) calculations show that oxygen interstitials (O_i) in oxygen rich conditions cause the unit cell to expand. In the under-oxidised condition a smaller expansion is also expected due to the presence of oxygen vacancies (V_O) [57]. This is in line with the experimentally observed expansion of the unit cell volume with oxygen partial pressure shown in Fig. 3.5(b). The unit cell volume at low oxygen partial pressure doesn't change significantly, although there is limited data in this range. The samples grown in this study do not exhibit any measurable conductivity. This is not unexpected as O_i are predicted to be electrically inactive and similarly V_O are predicted to have deep ionisation levels [57].

3.2 TEM analysis

TEM imaging was performed on selected samples. Cross sectional lamellae were prepared by FIB. Uneven milling of the sample is caused by the 'Waterfall' effect [58]. This effect is caused by charging from the non-conductive substrate and is seen in bright field imaging as dark streaks due to thickness contrast in the TEM image. An overview of the cross section of an epitaxial Cr_2O_3 (0001) film is shown in Fig. 3.6 for a ≈ 120 nm film. In Fig. 3.7(a) there is a selected area electron diffraction (SAED) pattern. This is essentially an electron diffraction pattern (in reciprocal space) of a region in the sample made possible by using a selected area aperture. The thin film can be seen slightly displaced from the substrate as expected for a relaxed film. Fig. 3.7(b) displays a higher resolution TEM image of a well-ordered thin film with a few stacking faults at the interface to relieve mismatch induced strain.

3.3 UV-Vis spectroscopy

The transmittance T and reflectance R of the thin undoped samples were measured and plotted as $T + R$ as a function of energy in the inset of Fig. 3.8. Fig. 3.8 itself shows a plot of αE^2 vs E , where α is the absorption coefficient and E is the photon energy. The direct

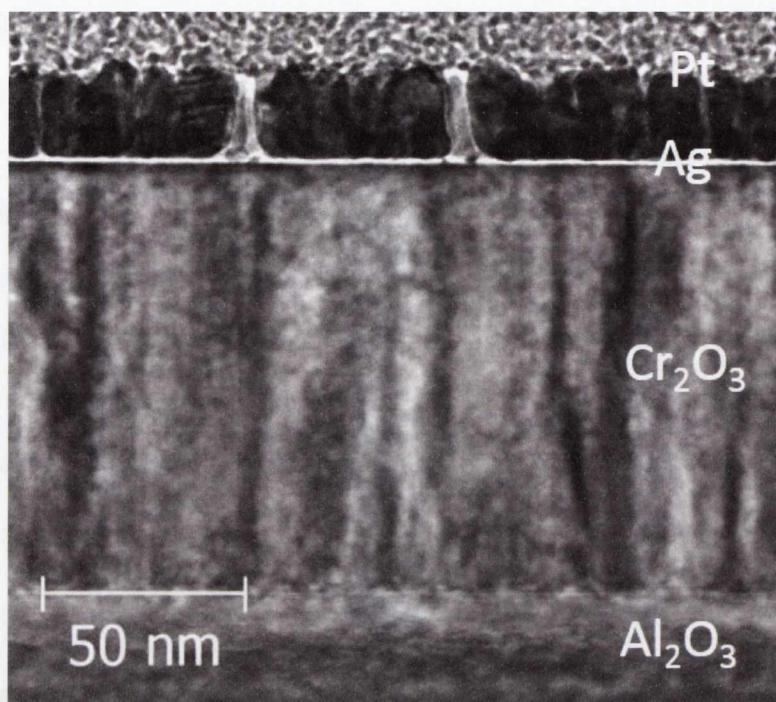


Fig. 3.6 Bright field TEM image of epitaxial Cr_2O_3 (0001) along the $[2\bar{1}\bar{1}10]$ zone axis. After the Al_2O_3 substrate and the Cr_2O_3 film a thin layer of silver is seen (white in image) followed by a capping layer of Platinum.

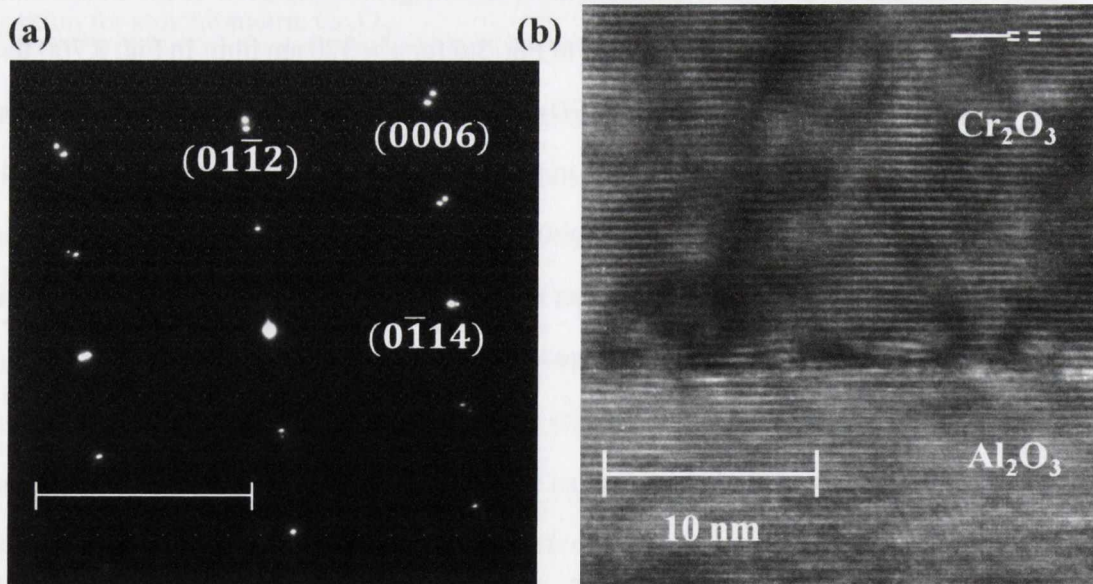


Fig. 3.7 (a) shows a SAED pattern where the orientation of the film can be seen clearly. (b) Bright field TEM image of epitaxial Cr_2O_3 (0001) along the $[2\bar{1}\bar{1}10]$ zone axis. A dislocation is highlighted in the top right corner.

energy gap is estimated by fitting the linear portion of the profile and extrapolating to $\alpha = 0$ (Tauc plot). Due to the presence of weak absorption bands below the optical bandgap and deviation from the ideal square root dependence required for a Tauc plot bandgap estimate, there is a large error in determining the bandgap, as indicated by the two possible Tauc fits of the fundamental absorbance. Tauc plots are well suited for amorphous materials but the structure in ϵ_2 in crystalline material complicates the analysis due to deviations from the simple analytical form. For the films grown in this study the direct bandgaps are in the 3.1-3.4 eV range for undoped films. This compares reasonably with the accepted bulk value of 3.4 eV [44] and previous experimental studies [59]. Optical transitions below the bandgap arise from weak $d-d^*$ transitions of the Cr^{3+} multiplet and are visible at 2 and 2.6 eV in the absorption spectra. The green colour of bulk Cr_2O_3 is attributed to these transitions [60]. These are weak enough to not greatly reduce the transparency of the material in thin film form.

3.4 Conclusion

Epitaxial films of Cr_2O_3 were grown in a MBE system in the 500-600°C temperature range. The change of the lattice parameters with oxygen partial pressure was investigated. The films showed a distinct increase in the unit cell volume with increasing oxygen partial pressure. It is difficult to say conclusively if the unit cell is increasing due to oxygen interstitials, however both the unit cell volume change and lack of conductivity matches theoretical simulations. This would indicate a $\text{O}_i/\text{V}_\text{O}$ defect system. As the films are insulating little can be concluded about their compensating nature. TEM imaging show well ordered epitaxial film complementing the XRD data. UV-Vis data reveals the two absorption peaks at 2 and 2.6 eV characteristic of Cr_2O_3 . This study highlights the growth conditions for high quality crystalline thin films with low defect densities. That the films are insulating, making controlled doping experiments possible, which is discussed in the following section.

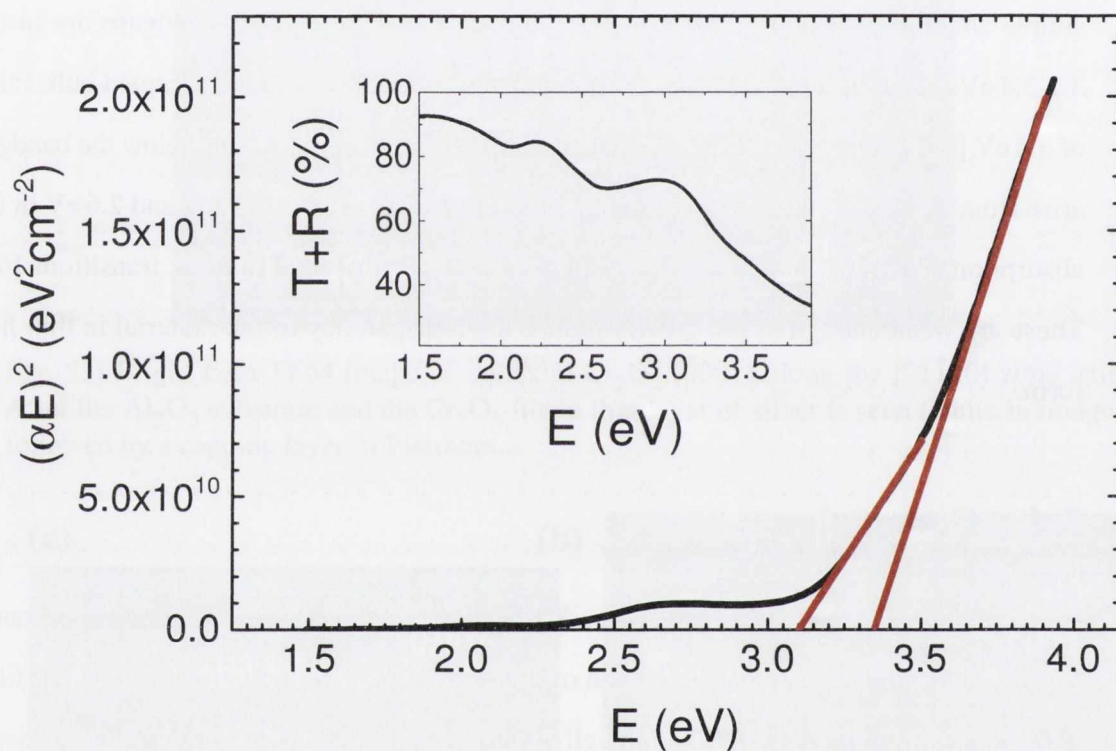


Fig. 3.8 Tauc plot of the undoped Cr_2O_3 films. The two possible band gaps are highlighted. The sum of the transmittance and reflectance as a function of energy is shown in the inset.

Chapter 4

$\text{Cr}_2\text{O}_3\text{:Mg}$ as a *p*-type transparent conducting oxide

In the following section *p*-type Cr_2O_3 is realised by Mg doping. Full electrical and optical characterization of the films is discussed with a particular emphasis on the conduction mechanism.

Undoped Cr_2O_3 is usually regarded as an insulator, although there are reports of very low native *p*-type conductivity [61, 62]. For high quality epitaxial films, no native *p*-type conductivity was present, hence dopants need to be introduced to obtain a conductive material. Doping with Mg [63–67], Ni [64, 67, 68], and Li [67, 68] are known to induce *p*-type conductivity in Cr_2O_3 . In our group co-doping with Mg and N has been already reported [69]. In comparison to the polycrystalline material discussed in these studies, epitaxial films, with band conductor behaviour, are expected to show improved electrical and optical properties due to a significantly reduced number of defects and grain boundaries. In this study, epitaxial *p*-type TCO $\text{Cr}_2\text{O}_3\text{:Mg}$ was grown by electron-beam evaporation in a MBE system on *c*-plane sapphire. The influence of Mg dopants and the oxygen partial pressure were investigated by thermoelectric and electrical measurements. The conduction mechanism is analysed using the SPH model, and hopping activation energies have been

determined, which vary with doping concentration in the range of $210\text{--}300\pm 5$ meV. Films with better conductivity were obtained by post-annealing. The effect of post-annealing is discussed in terms of a crystallographic reordering of the Mg dopant. The highest Seebeck mobilities obtained from thermoelectric measurements are of the order of $10^{-4}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

There is uncertainty in the literature over the exact conduction mechanism in Cr_2O_3 . Band conduction [70], SPH [62], and variable range hopping (VRH) [59] have been suggested. Indeed, it is heavily discussed in the literature what model is applicable for *p*-type TCOs [8]. To fully distinguish whether the SPH model is appropriate, high temperature measurements of conductivity and thermopower are typically analysed to ascertain whether an activated mobility exists [71]. This alone is not enough to distinguish the mechanism definitively without an understanding of the effective density of states [72]. In the absence of DFT such an analysis cannot be performed. Further work is required to exclude the possibility that epitaxial $\text{Cr}_2\text{O}_3\text{:Mg}$ is a band conductor. Here evidence is provided that suggests the SPH mechanism is applicable for epitaxial $\text{Cr}_2\text{O}_3\text{:Mg}$ over the temperature range considered. Unlike the familiar broad-band conduction model where carriers are excited into non-localized energy states, in the SPH model, carriers are localized due to strong electron-phonon interactions and are trapped in potential wells. The carriers move by ‘hopping’ to available sites. Small polaron conduction is unfavourable for a *p*-type TCO as they are usually associated with high carrier concentrations ($>10^{21}\text{ cm}^{-3}$) [18] and correspondingly low mobilities. This work allows us to verify the conduction mechanism in a less complex binary oxide system, to understand the microscopic charge transport mechanism, and to outline paths to increase the mobility in the material. It also provides a basis to understand and improve other related but more complicated ternary *p*-type TCOs such as delafossites and oxychalcogenides.

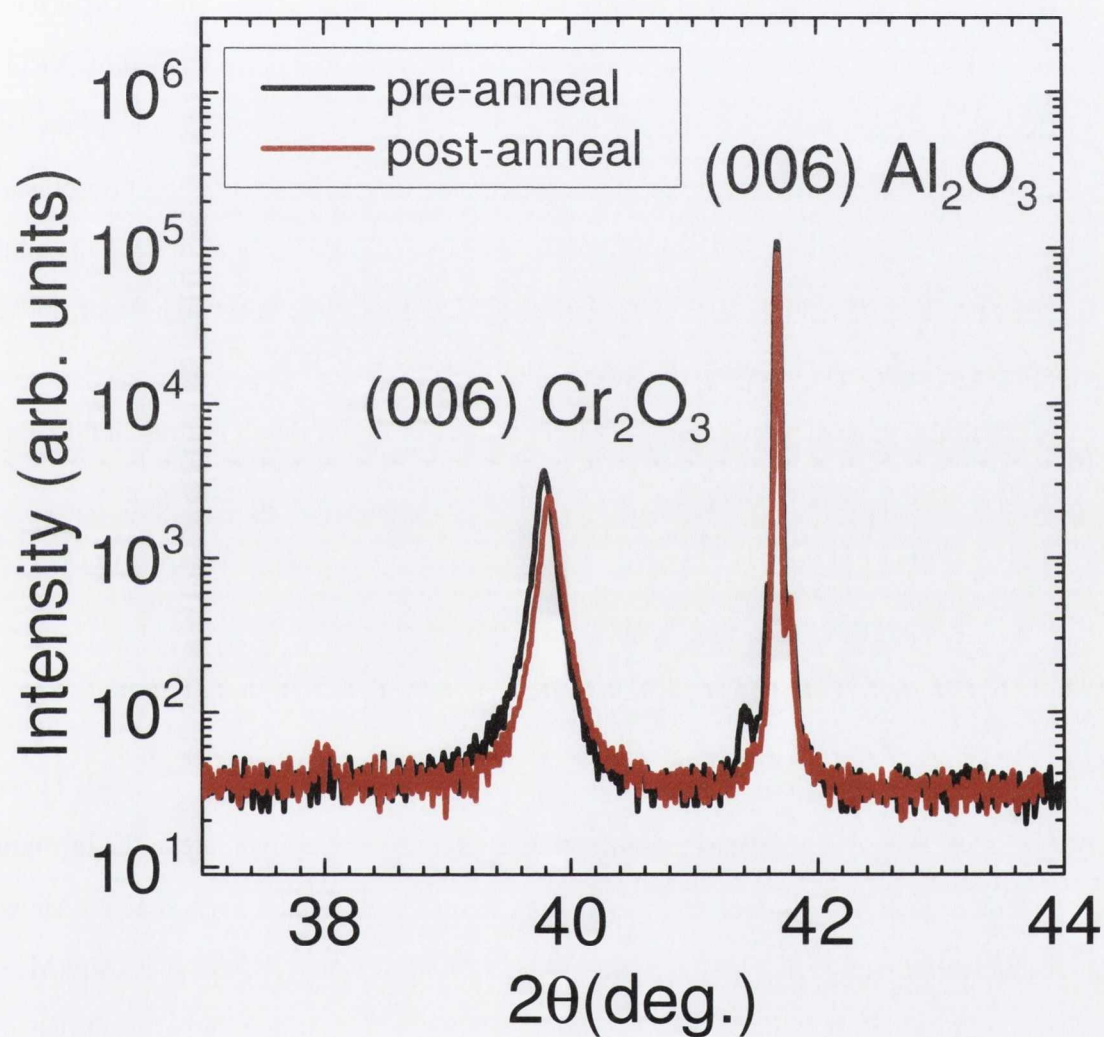


Fig. 4.1 XRD pattern of 120 nm thick $\text{Cr}_2\text{O}_3:\text{Mg}$ film on sapphire. The effect of post-annealing is compared, and only a minor shift in the 2θ reflex of Cr_2O_3 (006) is observed.

4.1 Structural characterization

For highly doped films (>10%), a tetragonal distortion of the crystal structure was observed with resulting larger c lattice parameters, as determined from the 2θ - ω XRD scans. This is possibly a shift to the spinel MgCr_2O_4 phase, as reported before [66]. The effects of post-annealing on the c and a lattice parameter of Cr_2O_3 were investigated by XRD and RSM, to analyse if the post-annealing significantly affects the long-range order of the lattice. A minor shift of the 2θ value in the XRD pattern is visible in Fig. 4.1. This corresponds to a decrease in the c lattice parameter. Similarly a corresponding small increase in the a lattice parameter is observed in the RSM shown in Fig. 4.2. This effect is not significant, and these changes are not responsible for the conductivity increase.

XRR measurements were used to determine the thickness of each individual film in order to calculate the conductivity of the material from the measured sheet resistance.

4.2 Electrical characterization

Previously, Alternating-current (AC) impedance spectroscopy has been used to estimate the contribution of grain boundaries to the bulk electrical conductivity [8, 73, 74]. However, this is not investigated here as the difference is expected to be small due to the low number of such defects in epitaxial samples. Room temperature conductivity data are shown in Fig. 4.3 as a function of the Mg/Cr ratio. Where the Mg/Cr ratio is defined as $(\text{Mg}/(\text{Mg}+\text{Cr}))$ atomic %. Films without Mg doping are insulating, suggesting no significant density of intrinsic, electrically active defects. Once a small amount of Mg is present, the conductivity increases significantly. Most likely the Mg atoms are replacing Cr atoms during growth of the Cr_2O_3 film. As the valency of Cr is in the 3^+ state, Mg substitution (2^+ valency) leads to hole formation. This can be represented using Kröger-Vink notation $\text{Mg}_{\text{Cr}}^\bullet$. Mg concentration in the range 5-10% gives the most conductive films. Higher concentrations

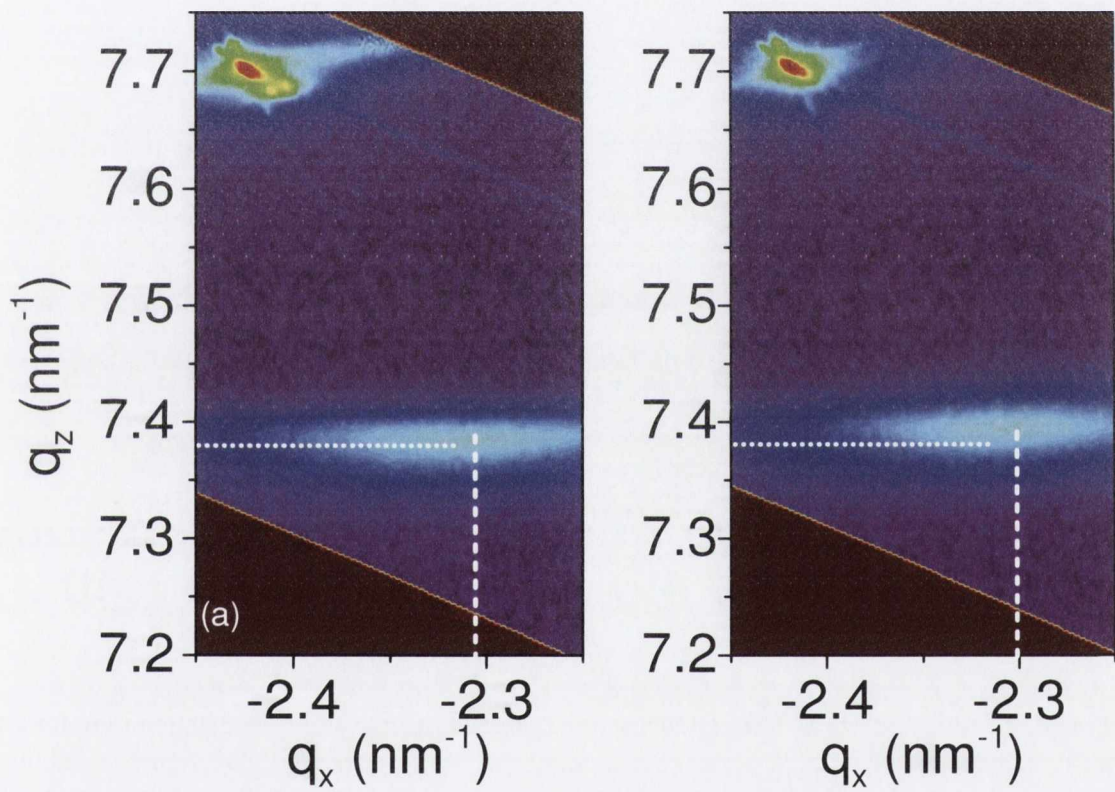


Fig. 4.2 RSM for a pre-(a) and post-annealed (b) sample with 120 nm thickness. No major changes are evident, and the films grow in a relaxed manner, as indicated by the displacement of the substrate and film peaks.

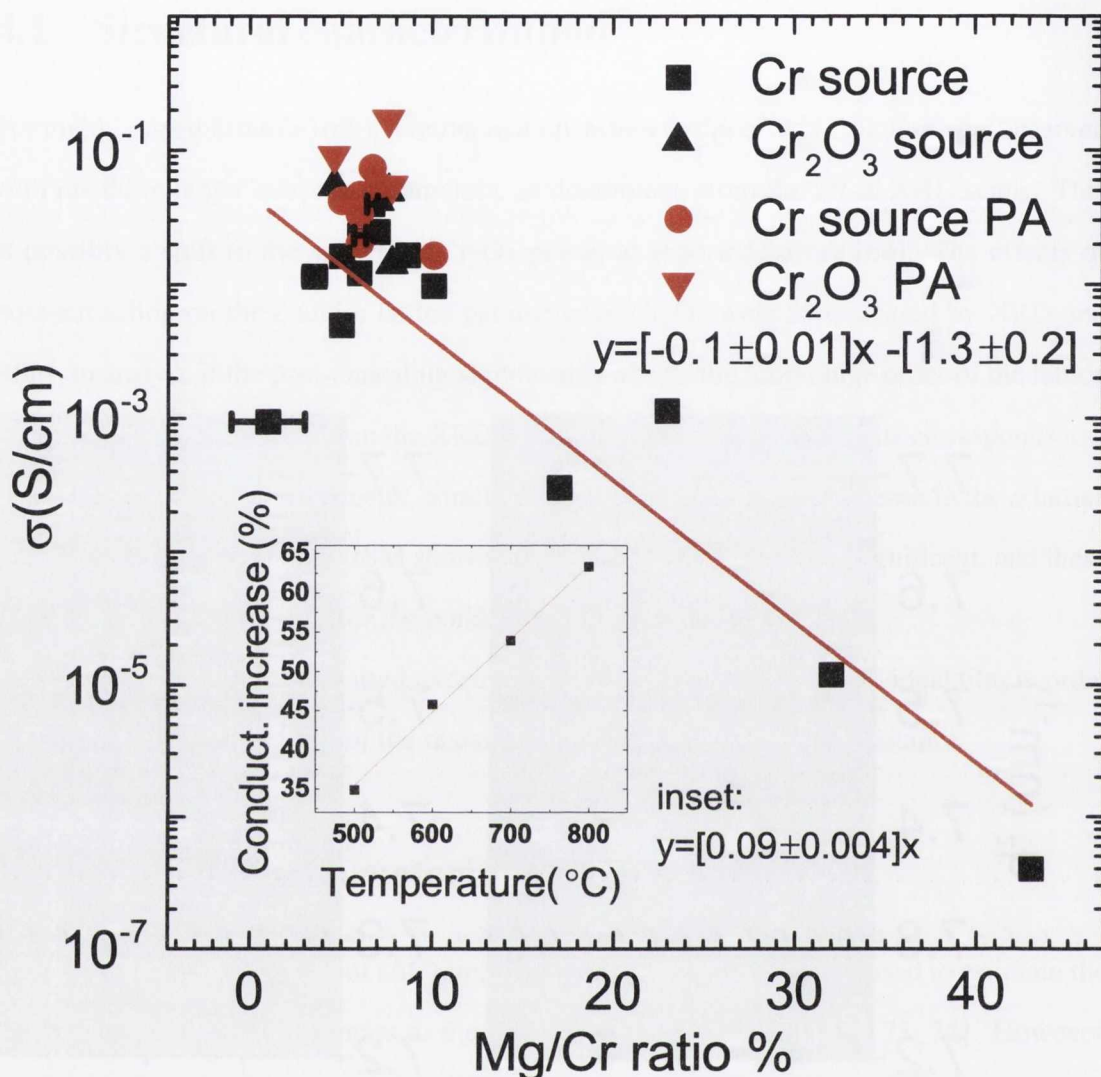


Fig. 4.3 The inset shows the conductivity increase with post-annealing temperature for a two hour anneal in air. The pre-anneal Mg/Cr ratio was 4% for these samples. Square symbols (■) represent samples grown from the Cr metal source, while triangles (▲) indicate those grown from the ceramic Cr_2O_3 source. Circles (●) indicate Cr metal source samples post-annealed, and inverted triangles (▼) are post-annealed samples grown from the ceramic Cr_2O_3 source.

lead to more resistive films. Films grown from a Cr metal source have room temperature conductivity in the 0.017-0.025 S/cm range. When grown from the ceramic Cr_2O_3 source, the film's conductivity is significantly higher, in the 0.03-0.05 S/cm range. This is most likely due to increased oxygen content during growth, as discussed below. Cu delafossites have conductivities that range from 0.025 S/cm for CuYO_2 to 0.36 S/cm for CuAlO_2 and

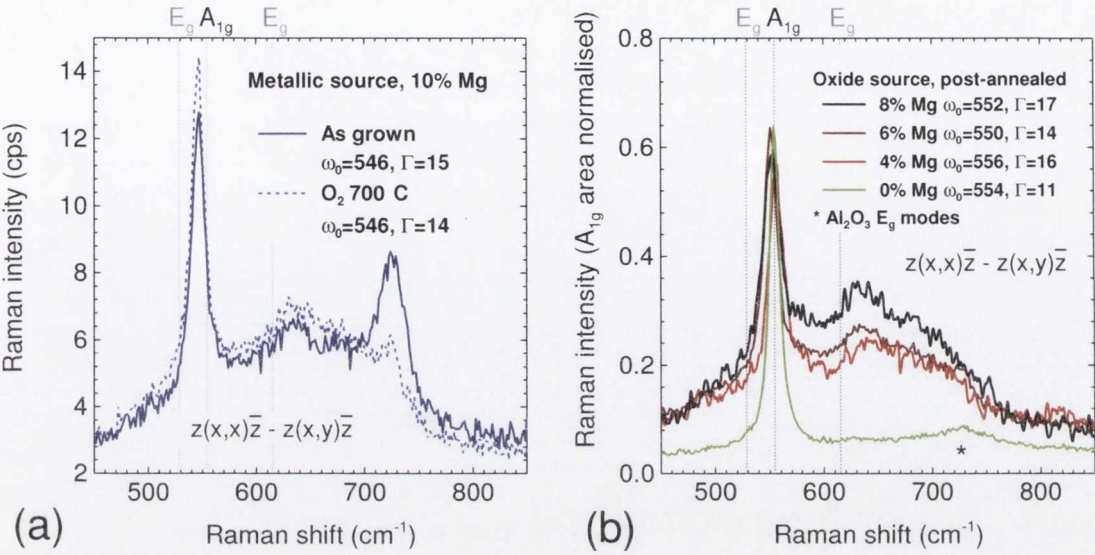


Fig. 4.4 (a) Raman spectra of a sample grown from metallic Cr before and after post-annealing. The reduction in the Mg induced Local vibrational mode (LVM) around 720 cm^{-1} following the anneal is attributed to the redistribution of Mg in the Cr_2O_3 lattice. (b) Raman spectra of post-annealed samples grown from an oxide source with increasing Mg concentration showing the increase in Mg induced broad band defect structures. For better comparison, the signal was normalized to the area of the Cr_2O_3 A_{1g} mode. The dotted lines represent the E_g and A_{1g} Raman modes for stoichiometric bulk Cr_2O_3 .

as high as 220 S/cm for $\text{CuCr}_{0.95}\text{Mg}_{0.05}\text{O}_2$ films [16, 75, 76]. MBE grown $\text{Cr}_2\text{O}_3\text{:Mg}$ films have relatively low conductivity in comparison. The most conductive films ($\approx 0.17\text{ S/cm}$) have conductivities of the same order of magnitude as spray pyrolysis grown samples from a previous report ($\approx 0.33\text{ S/cm}$) [69]. However, this was only achieved after post-annealing in air at 973 K for 2 h. The inset of Fig. 4.3 shows the conductivity increase as a function of the post-annealing process temperature for four samples grown simultaneously. These films have a Mg/Cr ratio of 4% prior to post-annealing. The higher temperatures result in more conductive films. This is attributed to a homogenization of the Mg within the sample. High temperature diffusion of the Mg is an important factor in achieving conductive samples. Raman spectra of as grown samples show a characteristic LVM in A_{1g} symmetry developing at 720 cm^{-1} with increasing Mg concentration (see Fig. 4.4). This phonon mode is consistent with highly pressurized (15 GPa) nanoscale inclusions of MgCr_2O_4 [77]. For

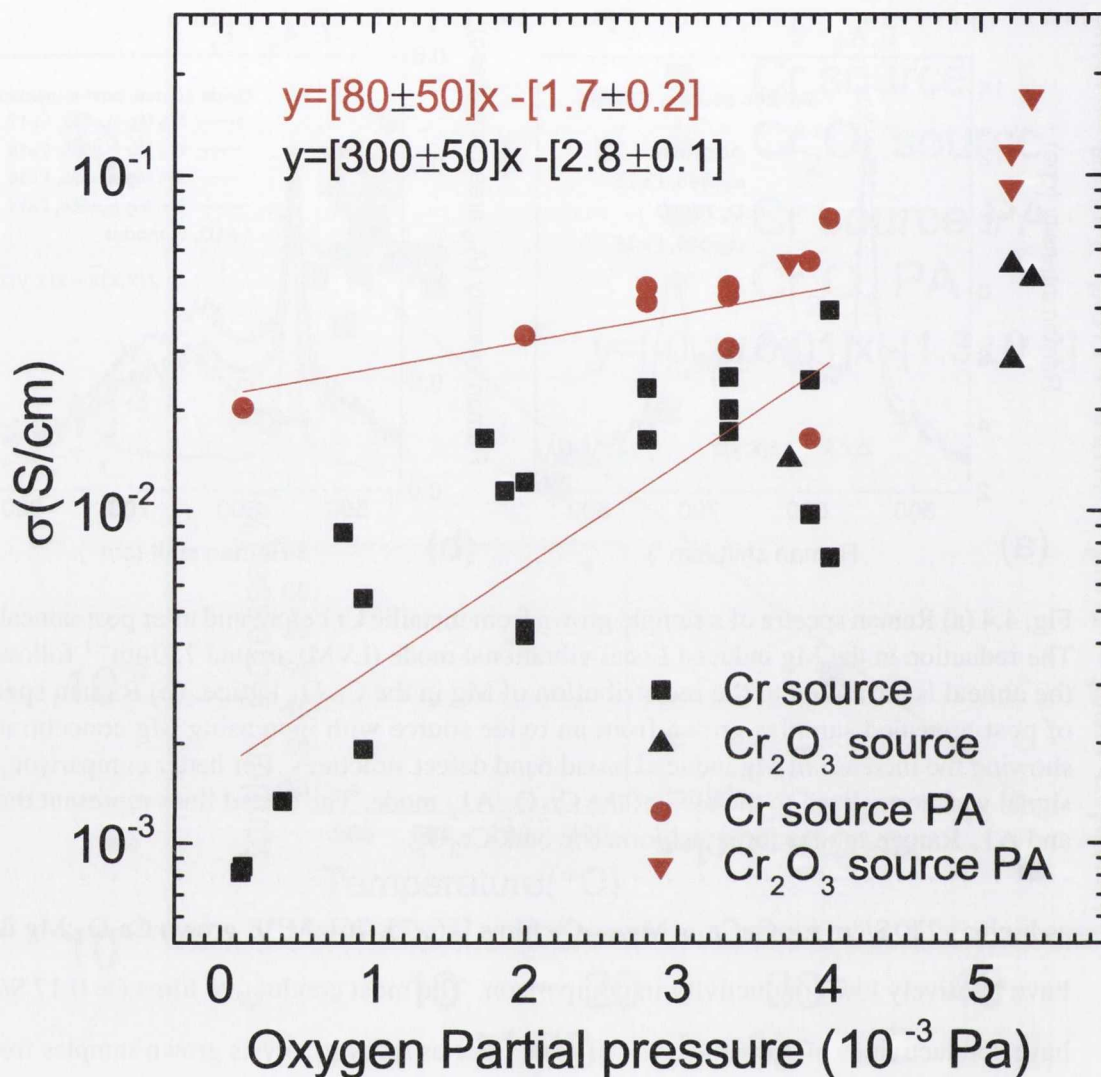


Fig. 4.5 Samples shown are in the optimum doping range of 5–10%. Square symbols (■) represent samples grown from the Cr metal source, while triangles (▲) indicate those grown from the ceramic Cr_2O_3 source. Circles (●) indicate Cr metal source samples post-annealed, and inverted triangles (▼) are post-annealed samples grown from the ceramic Cr_2O_3 source.

such a coherent phonon mode, typically 5-10 adjacent unit cells with similar coordination are required. After post-annealing, the Mg related LVM is dramatically reduced, consistent with a more homogeneous spread of $\text{Mg}_{\text{Cr}}^{\bullet}$ defects throughout the film and a reduction of the number of Mg rich MgCr_2O_4 nano-inclusions. At the same time a broad range defect induced Raman structure remains. The latter is consistent with the appearance of either

more random Mg-O related modes, a defect induced breakdown of Raman selection rules leading to a signal from otherwise Raman forbidden infrared (IR) active Cr_2O_3 modes, or distortions in the oxygen octahedral or Cr atomic positions. The most conductive samples show a particularly strong broad Raman mode with a related reduction in the Cr_2O_3 A_{1g} mode around 545 cm^{-1} . This mode should occur at $553\text{--}555\text{ cm}^{-1}$ for stoichiometric bulk Cr_2O_3 . This peak is always shifted to lower wave numbers, indicative of a Mg induced lattice expansion due to tensile strain and/or disorder [78–80]. This behaviour is again consistent with more equally spread $\text{Mg}_{\text{Cr}}^\bullet$ defects and an increase in the defect induced distortion of the Cr-O octahedral. It was possible to improve the conductivity of the films by growing the films in higher oxygen partial pressure (see Fig. 4.5). This dependency is consistent with many findings for *p*-type oxides, where a suppression of compensating defects such as oxygen vacancies V_O or an increase in hole creating oxygen interstitials O_i leads to improved conductivity [66]. Although Cr_2O_3 is known as an oxygen excess oxide [59, 65], suggesting oxygen interstitial formation, we do not believe that these defects make a significant contribution to the conductivity. The solubility of MgO in Cr_2O_3 is related to the oxygen partial pressure and the growth temperature. [81]. It is likely that the redistribution of Mg dopants is the most dominant effect as oxygen vacancies are not predicted to be readily formed [46] and oxygen interstitials are predicted to be electrically inactive [57]. Thus the oxygen pressure dependence in Fig. 4.5 is representative of greater dopant solubility.

Mixed valency of the Cr ions ($\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$) could also be responsible for charge compensation [64, 82], which would reduce the number of holes. Although, as the oxygen partial pressure in MBE is substantially lower than for atmospheric growth techniques such as SP, no brown discolouration that has been attributed to Cr^{4+} or Cr^{6+} formation is observed [60]. Native *p*- and *n*-type defects such as V_{Cr} and Cr_i could be responsible for charge carriers, as previously theorized [46]; however, no native conductivity was present in undoped samples. Therefore, we expect this effect to be negligible. In many other *p*-type

oxides and nitrides, hydrogen interstitials H_i , have been proven to be detrimental due to their compensating nature [83–85]. But, for MBE-grown Cr_2O_3 , residual hydrogen levels are expected to be low, and the effect of H_i on the conductivity of the films is expected to be insignificant.

4.3 Small Polaron Hopping model

SPH typically occurs in mixed-valence transition metal oxides where the electron-lattice interaction is strong [73, 86, 87]. Unlike in the free electron model, charge is localized to the lattice. This prevents the charge from moving freely through the material. Initial Hall mobility measurements had shown that the mobility is below the experimental limit of our Hall setup ($< 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). If the mobility lies below the *Bosman and van Daal* limit [72] ($< 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), it is likely that electrical transport follows the SPH model. The band conductor model has been previously used to estimate mobility [70]. Single crystal growth was suggested to determine whether a Hall voltage can be extracted as no signal was detected in their measurements. A Hall voltage was also not detected in our measurements and we believe this is at odds with the anticipated mobility a band conductor would exhibit. Considering the Arrhenius activation energy obtained from fitting the electrical data (see Fig. 4.6(a)), we obtain a value of $200 \pm 5 \text{ meV}$ for a sample with 8% Mg doping. The total number of Cr sites are $N = 4.15 \times 10^{22} \text{ cm}^{-3}$, which corresponds to $3.3 \times 10^{21} \text{ cm}^{-3}$ carrier generating Mg sites for this 8% sample. Using the Arrhenius equation to calculate the total number of activated carriers at room temperature results in a concentration of $1.3 \times 10^{18} \text{ cm}^{-3}$. The corresponding mobility is then expected to be $0.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is above the experimental limit of our Hall set-up. Thus the SPH model is used to fit the temperature dependence of conductivity and is used throughout this section.

The question of whether the adiabatic or non-adiabatic SPH model is appropriate can be addressed using the Holstein relation [88]. If the overlap integral J is large (greater than H ,

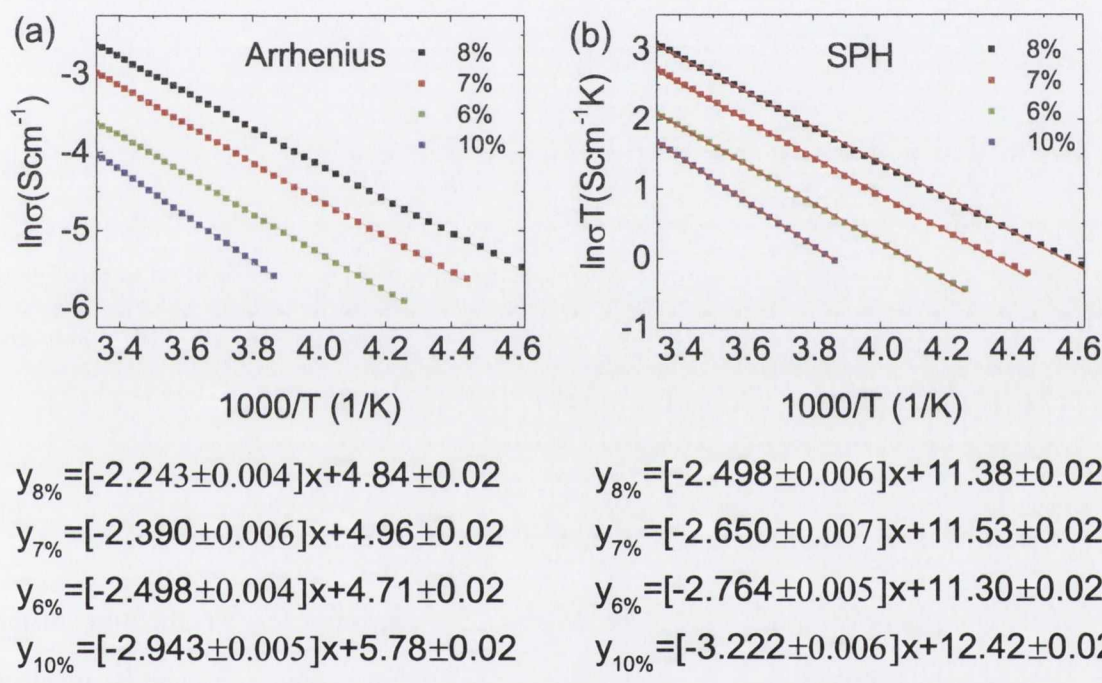


Fig. 4.6 The conductivity was measured as a function of temperature for post-annealed samples with different doping concentration (6–10%) over the 300–200 K temperature range. Both the Arrhenius model (a) and the SPH model (b) are plotted to show their similarity. It is not possible to distinguish the transport mechanism from these fits alone.

defined below) then the tunnelling probability is deemed to be insignificant and therefore the adiabatic case is appropriate. Using Eq. 4.1 H can be calculated to be ≈ 0.012 eV.

$$H = \left[\frac{2k_B T W}{\pi} \right]^{\frac{1}{4}} \left[\frac{h v_{ph}}{\pi} \right]^{\frac{1}{2}} \quad (4.1)$$

Where W is the hopping activation energy, v_{ph} is the phonon frequency, and both are discussed in more detail below. k_B is Boltzmann's constant, and h is Planck's constant. J is estimated as 0.018 eV using the following approximate expression at 300 K [88],

$$J = 0.67 h v_{ph} \left[\frac{T}{\theta_D} \right]^{\frac{1}{4}} \quad (4.2)$$

where θ_D is the Debye temperature. As J is greater than H , there should be negligible tunnelling probability, and in this case the adiabatic model is appropriate. The SPH conductivity (σ) in the adiabatic case can be expressed by

$$\sigma = \frac{g v_{ph} N e^2 a^2 c (1 - c)}{k_B T} \exp \left[\frac{-W}{k_B T} \right] \quad (4.3)$$

where g is a geometric factor, N is the density of conducting sites, a is the jump distance between equivalent sites, c is the fraction of occupied carrier sites, and e and k_B are electric charge and Boltzmann's constant.

The SPH conductivity is plotted as a function of temperature in Fig. 4.6 (b). There is a small deviation from linearity at low temperature (< 220 K) which is attributed to VRH. The conductivity varies as $T^{-1/4}$ in this model. This is expected for localised charge-carriers and has been observed before in delafossites [89]. However it is not further investigated here as the high sheet resistance of our samples at low temperatures (> 250 M Ω) prevented reliable measurements. Using Eq. 4.3, the conductivity data can be fitted to obtain the hopping activation energy (see Fig. 4.7). In our measurements the temperature was varied

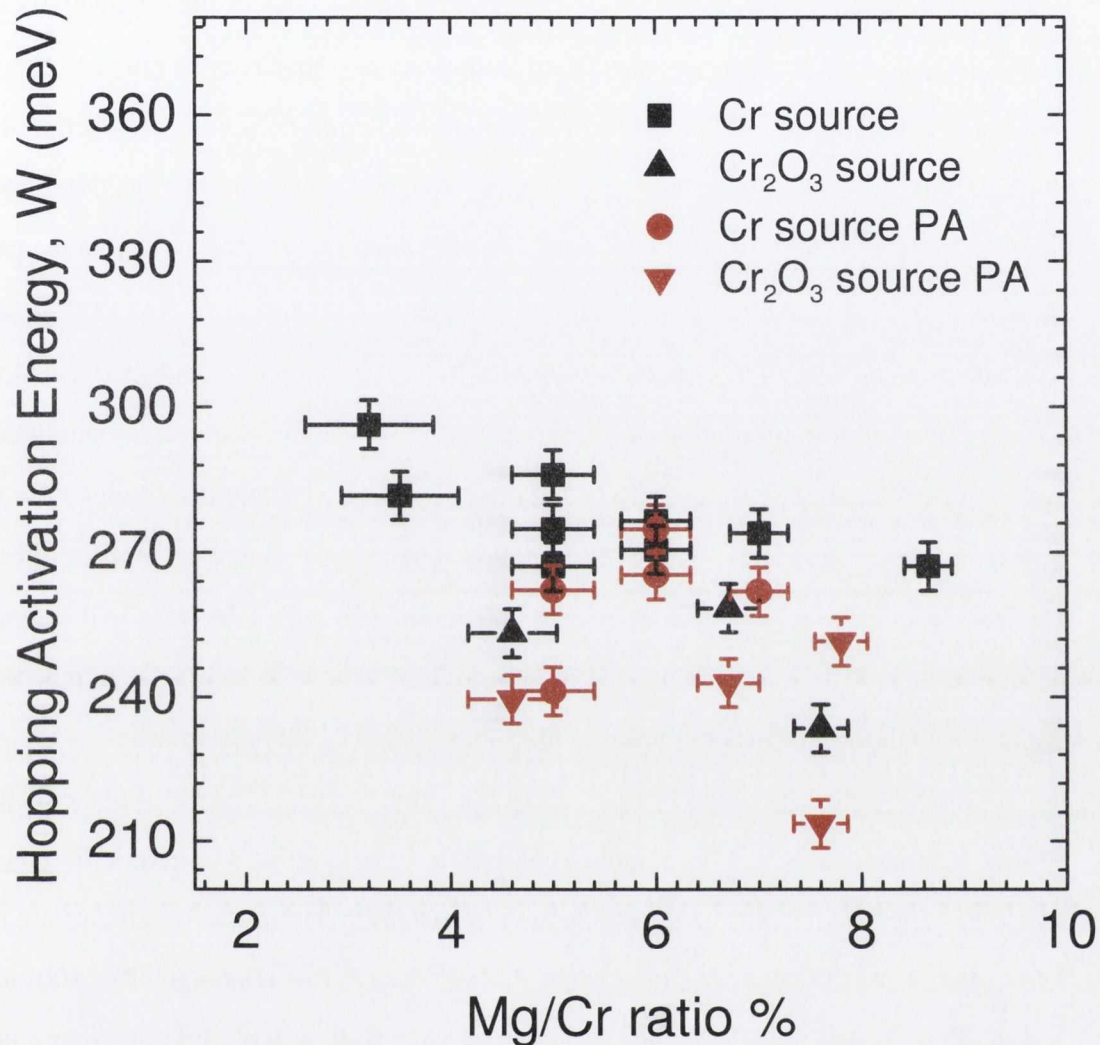


Fig. 4.7 The decrease in W with increasing Mg concentration as determined by XPS. Square symbols (■) represent samples grown from the Cr metal source, while triangles (▲) indicate those grown from the ceramic Cr_2O_3 source. Circles (●) indicate Cr metal source samples post-annealed, and inverted triangles (▼) are post-annealed samples grown from the ceramic Cr_2O_3 source.

from 300 to 450 K. Obtained W values range from $210\text{--}300\pm 5$ meV, in line with previous reports of ≈ 250 meV for non-stoichiometric Cr_2O_3 [59, 62]. Eq. 4.3 is valid once the hopping activation energy is the dominant, limiting term in the conduction. Due to a lack of *ab initio* calculations, the energy level of the Mg dopant is not known yet. To assess whether the measured carrier activation is limited by the acceptor activation energy E_a

or the hopping activation energy W , the temperature dependence of the conductivity (see Fig. 4.6(b)) for different Mg concentration samples over a lower temperature range was analysed. No significant deviation from a single exponential behaviour was found in the latter, and the measured activation energy begins to decrease even for low Mg concentration. This suggests that there is only one dominant activation mechanism. A previous paper for undoped Cr_2O_3 also found no significant dependence of the Seebeck coefficient on temperature up to 450 K [59], which is supported by Seebeck measurements performed with a higher temperature differential (see Fig. 4.8 inset). This suggests that E_a is significantly smaller than W , and the conductivity is dominated by SPH. The conductivity increase with increasing Mg concentration is then likely a combination of an increase in the number of Cr sites occupied by a polaron due to the doping, combined with a decrease in the hopping activation energy W . The latter is expected due to the increased spatial overlap of polarons at an increased number of occupied sites [82].

An additional indication of SPH is to assess the value for ν_{ph} . The basal plane distance of Cr-Cr atoms is used for the hopping distance $a = 2.94 \text{ \AA}$ [90], the geometric factor is taken as $g = 2/6$, and N and c values obtained from thermoelectric measurements are used. Calculated values for ν_{ph} are found in the 2×10^{12} to $3 \times 10^{12} \text{ Hz}$ range ($70 - 100 \text{ cm}^{-1}$), which is reasonable for oxide materials and compares well with the first maximum in the expected phonon density of states for Cr_2O_3 of $6 \times 10^{12} \text{ Hz}$ ($\approx 200 \text{ cm}^{-1}$) [47]. This value can be used to estimate the optical Debye temperature $\theta_D = \hbar\omega/k$, resulting in a value of approximately 120 K. SPH should dominate for $\theta_D > 60 \text{ K}$. All these considerations are consistent with the SPH mechanism.

4.4 Thermoelectrical analysis

In the case of Mg^{2+} acceptor doping, the conductivity is arising from hole creation when Mg atoms replace Cr sites. To a first approximation, the ratio of occupied to available hopping

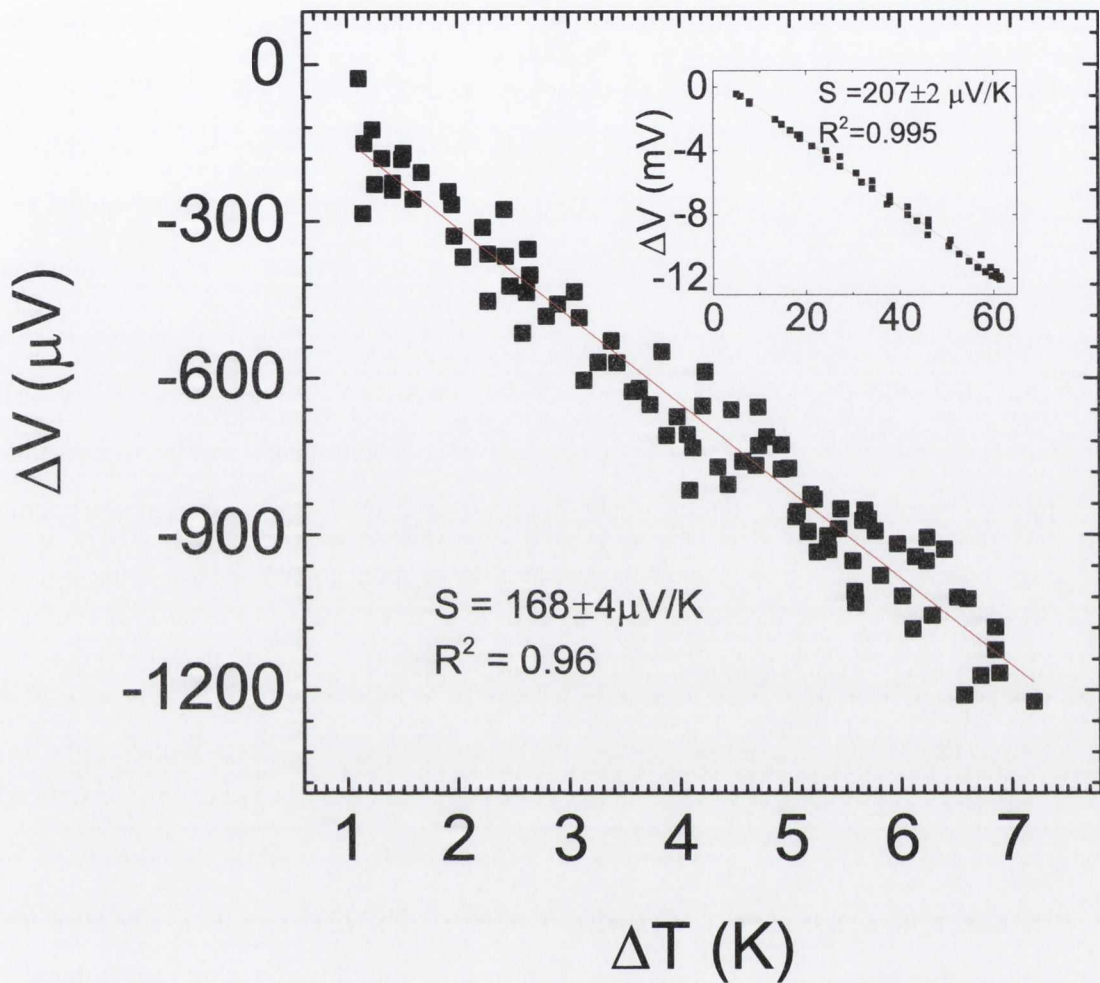


Fig. 4.8 Representative data of the Seebeck voltage as a function of temperature gradient ΔT . The negative slope indicates a positive Seebeck coefficient. Inset shows a Seebeck voltage over a larger ΔT range.

sites c can be expressed as the ratio shown in Eq. 4.4.

$$c = \frac{[Mg^{2+}]}{[Mg^{2+}] + [Cr^{3+}]} \tag{4.4}$$

This implies that every Cr site is a potential hopping site and that every Mg substitution creates one hole, and therefore an occupied hopping site. For a SPH material, the ratio c given by Eq. 4.4 is closely linked to the thermoelectric properties of the material. Fig. 4.8 shows demonstrative thermoelectric data using a temperature gradient ΔT (1 to 10 K) across

the sample of size 10 mm. The temperature gradient induces a hot side and a cold side of the sample. The voltage difference ($\Delta V = V_{Hot} - V_{Cold}$) is measured for heating and cooling cycles. The Seebeck coefficient S is then the ratio of the voltage difference to the temperature gradient obtained from a linear fit of the data using Eq. 2.4. This avoids any unwanted voltage offset effects [91]. We expect the Seebeck coefficient to be independent of temperature as this is typical for small polaron behaviour [75] and has been previously seen in undoped Cr_2O_3 [59]. The sample temperature during measurement is in the range 293 to 308 K. Typical Seebeck coefficients are positive, indicating p -type conduction, and for the most conductive films are $150 \pm 10 \mu\text{VK}^{-1}$. This is similar to Mg doped CuCrO_2 [16]. The Seebeck coefficient can be used as a direct measure of the fraction of occupied carrier sites, c , using Eq. 4.5.

$$S = \pm \frac{k_B}{e} \left[\ln \left[\frac{2(1-c)}{c} \right] + A \right] \quad (4.5)$$

where k_B , e , and c have the same definitions as above. A is the transport constant and is usually zero for the small polaron system. It is possible to compare the expected c values from the Mg/Cr ratios with those experimentally determined via the Seebeck coefficient. Measured c values range from 0.05-0.3 and were around two to three times larger than expected for the nominal Mg/Cr ratio. This is unusual as substitutional Mg^{2+} should only generate one charge carrier per substitution. However, the expected values are based on a very simple assumption of the number of potential available hopping sites and also assuming that a homogeneous Mg distribution does not affect the Cr coordination. This assessment implies doping is caused by the Mg_{Cr} point defect. As highly defective spray samples are more conductive than epitaxial films it is likely that defect complexes such as $\text{Mg}_{\text{Cr}} - \text{V}_\text{O}$ or $\text{Mg}_{\text{Cr}} - \text{O}_i$ will be responsible for the carrier generation. Formation energies and charge states of these are as yet unknown. For highly doped material, de-phasing or the presence of compensating defects reduces the total number of available hopping sites, and a larger c is possible. A similar unusually high c has been reported for other p -type TCOs such as Mg

doped CuCrO_2 [16]. In general we found that during post-annealing, where we homogenize the Mg distribution and reduce the number of oxygen vacancies, c values were shown to be reduced compared to the as grown case.

4.4.1 Seebeck Mobility

To assess the suitability of a p -type TCO for different electronic devices, the carrier mobility is an important parameter. Hall measurements were performed in a PPMS with field sweeps up to 14 T. However, it was not possible to extract a meaningful value for the Hall coefficient. Using the thermoelectric measurements, it is possible to estimate the Seebeck mobility of thin films [18, 71, 75, 82, 92]. Within the SPH model, c is related to the carrier concentration p by $p = Nc$, where the density of conducting sites N can be calculated using the unit cell volume of the Cr_2O_3 crystal and the number of Cr atoms per unit cell. For the hexagonal representation, there are 12 Cr atoms in a unit cell volume of $2.89 \times 10^{22} \text{ cm}^3$, which corresponds to $N = 4.15 \times 10^{22} \text{ cm}^3$. Using the measured conductivity and c values, the Seebeck mobility can be expressed as:

$$\mu = \frac{\sigma}{pe} = \frac{\sigma}{Nce} \quad (4.6)$$

This assumes a negligible concentration of n -type charge carriers. Fig. 4.9 shows the Seebeck mobility calculated from the Seebeck coefficient as a function of Mg concentration. Only the highest conductivity samples were measured. There is a peak in mobility for the Cr source samples around 8%. The samples grown from the Cr_2O_3 source indicated in red also show a peak at this Mg/Cr ratio and generally exhibited higher mobilities. These mobility values are taken as an order of magnitude indication for room temperature. However, our Seebeck mobilities appear to be at best $1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is understandable for SPH but

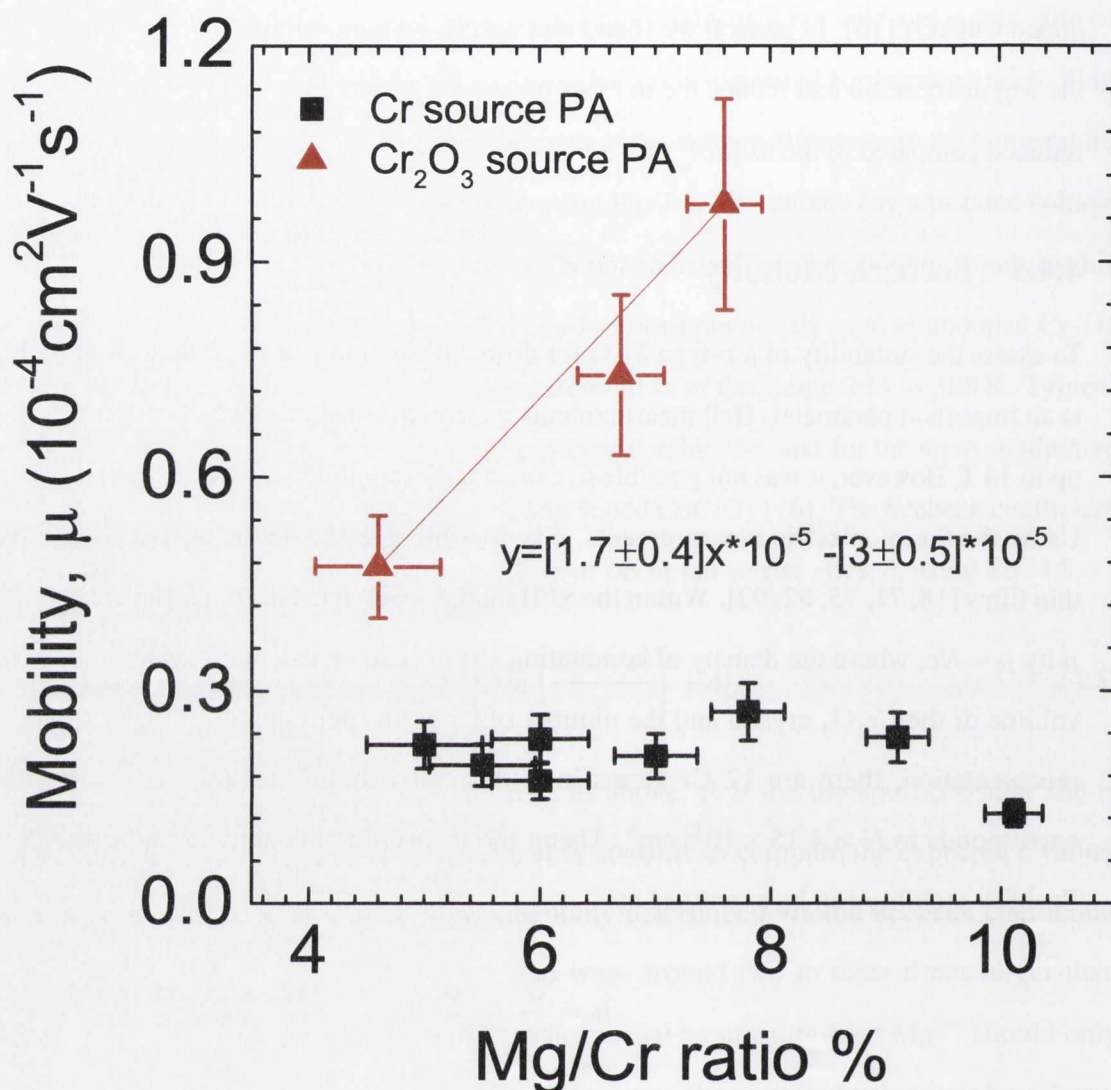


Fig. 4.9 Seebeck mobility as a function of Mg/Cr ratio. Square symbols (■) represent samples grown from the Cr metal source post-annealed, while triangles (▲) are post-annealed samples grown from the ceramic Cr_2O_3 source. Higher mobility was observed for the Cr_2O_3 samples.

rather small for application purposes. In the case that N is overestimated, as not every Cr site is an available hopping site, then the model is underestimating the mobility.

It is possible to obtain an upper limit on the mobility in materials exhibiting the SPH mechanism [93]. Using the Einstein relation and a diffusion coefficient of $D = a^2/2\tau$, the

mobility μ_d is given by Eq. 4.7.

$$\mu = \frac{ed}{k_B T} = \frac{ea^2}{2\tau k_B T} \quad (4.7)$$

Where τ is the time taken for a charge carrier to hop from one site to the next and the other symbols have their usual meaning or are defined previously. For the case of self-trapping the time for phonon induced transitions of the localized charged carrier from ion to ion τ takes considerably longer than the time period of a lattice vibration ν_{ph} . In this condition, the mobility can be expressed as:

$$\mu < \frac{ea^2}{2\tau_0 k_B T} = \frac{ea^2 \nu_{ph}}{2k_B T} \quad (4.8)$$

Where ν_{ph} is the phonon frequency corresponding to a lattice vibration. Specifically for Cr_2O_3 , the room temperature mobility can be estimated as much less than $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, using $\nu_{ph} = 2.5 \times 10^{12} \text{ Hz}$ and $a=0.294 \text{ nm}$ for the basal plane Cr to Cr distance. This fits reasonably with our results. A theoretical study of the charge transport in Cr_2O_3 used the adiabatic SPH model for both hole and electron transfer. Iordanova *et al* [90] obtained an estimate of the mobility using the Einstein relation, and in the case of hole mobility in the basal plane direction they obtained a mobility of 8.4×10^{-5} to $9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This, again, is in good agreement with our results. This does not rule out the possibility of higher mobilities in doped Cr_2O_3 , as the model used in Ref. [90] addresses only a Cr_2O_3 lattice where hole transfer occurs. A more disperse valence band could be achieved by introducing acceptor defects. Changing the crystal structure by doping, either by different cations introducing larger internal strain fields that can reduce the Cr-Cr hopping distance or by anionic doping directly distorting the oxygen octahedral, may positively affect the mobility. For the Cu(I)-based delafossite TCOs, the a lattice parameter (and therefore the Cu-

Cu distances) influences the conductivity of the material [22]. This is related to the hopping mechanisms involved; therefore, a similar dependence should be expected for Cr_2O_3 .

4.5 Optical characterization

For a TCO, the optimization of both the optical and electronic properties are equally important. Hence the transmittance and reflectance of our samples were measured. The transmittance of our films in the visible range were all high with little variance with Mg doping. The sum of the transmittance and reflectance were in the range 70-90% for films of thickness 50-150 nm. In order to compare our films to the literature the FOM, F was calculated.

$$F = \frac{\sigma}{\alpha} = \frac{-1}{R_{sh} \ln(T + R)} \quad (4.9)$$

where R_{sh} is the sheet resistance, T is the average transmittance, and R is reflectance. The T and R values are the average of 30 points over the 1.5-3 eV range. The best FOM of $6.7 (\text{M}\Omega)^{-1}$ was comparable to films previously grown by SP [69], $7.2 (\text{M}\Omega)^{-1}$. This is the same order of magnitude as pulsed laser deposition (PLD) grown CuAlO_2 [94]. Typical films grown from the Cr source without post-annealing have relatively low conductivity and therefore low F ($1 (\text{M}\Omega)^{-1}$). The absorption coefficient α is plotted as function of energy in Fig. 4.10. It compares well to $\text{CuCrO}_2\text{:Mg}$ indicated by red dotted lines [95].

Although epitaxial films should reduce the density of structural defects and grain boundaries in comparison to SP grown samples, it does not improve the conductivity as expected. Partly this is caused by the limitations in the oxygen partial pressure, but, more importantly, it is shown that the conduction is most likely limited by the SPH mechanism. This implies that further improvements of the material require growth modes using oxygen rich environments and dopants aimed to improve the polaron hopping by strain engineering rather than improving the epitaxial quality of the films.

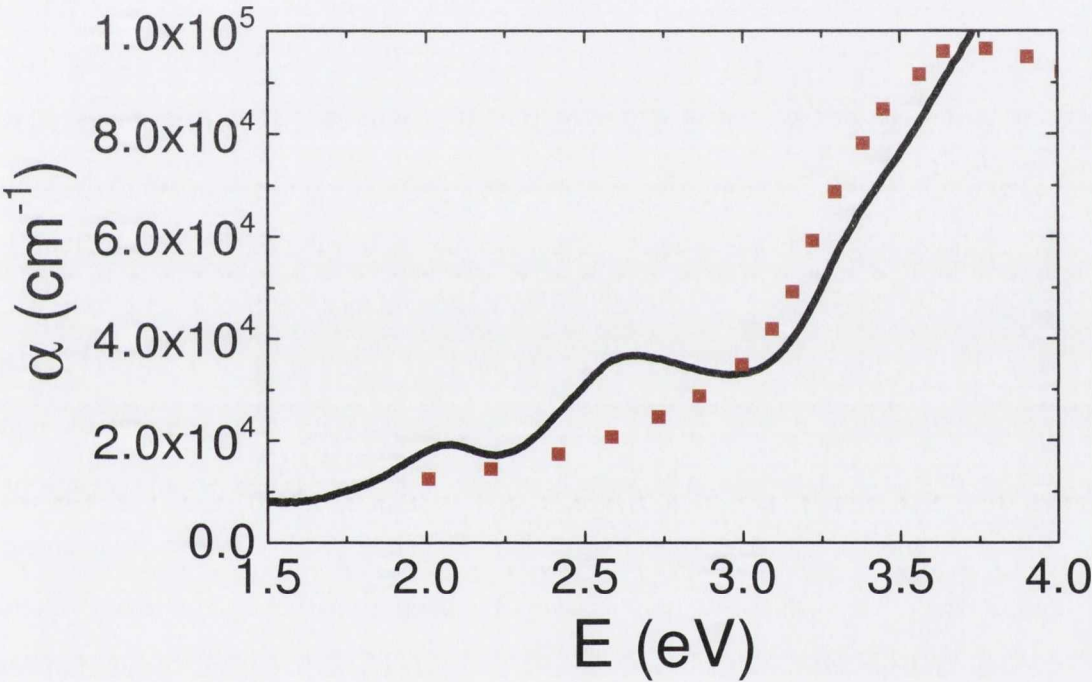


Fig. 4.10 A comparison of the absorption coefficient of $\text{Cr}_2\text{O}_3:\text{Mg}$ to $\text{CuCrO}_2:\text{Mg}$ (dotted red line) [95].

4.6 Conclusion

Epitaxial Mg doped Cr_2O_3 has been characterized using electrical, thermoelectrical, and optical measurements. The deleterious effect of low oxygen pressure during deposition was shown, and the optimum doping range of 5-10% for the Mg/Cr ratio was identified. In poorly conductive material, a MgCr_2O_4 -related LVM was identified at 720 cm^{-1} , which can be suppressed by post-annealing, suggesting a homogenization of the Mg content. As the experimental results are consistent with SPH, the use of the model is the most applicable. However, further work is ongoing to rule out the possibility of a band conductor. The best FOM of $6.7\text{ (M}\Omega)^{-1}$ for our films does not surpass previous work despite the epitaxial nature of the films, which is explained in terms of SPH being the limiting factor in the epitaxial materials conductivity. Thermoelectric measurements showing Seebeck coefficients in the $100\text{-}200\text{ }\mu\text{VK}^{-1}$ range indicate that the mobility of the films are at best $1 \times 10^{-4}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Such low mobilities are expected for the SPH mechanism, while an ideal p -type TCO should be a band conductor. This chapter provides a clear path on how to improve the material mobility by using other growth techniques capable of higher oxygen partial pressure such as PLD or magnetron sputtering. Without further modulation of the valence band to change the conduction mechanism, or without reducing the hopping barrier by employing alternative cationic and anionic dopants, MBE grown $\text{Cr}_2\text{O}_3\text{:Mg}$ could likely only be used in devices where carrier mobility is of no concern.

Chapter 5

Spray pyrolysis of Cu deficient CuCrO_2

CuCrO_2 is well known as one of the most conductive *p*-type TCOs. In this chapter a low temperature ($\approx 345^\circ\text{C}$) growth method for Cu deficient CuCrO_2 is described performed by SP using metal-organic precursors and a simple air blast nozzle. Smooth films were grown on glass substrates by SP with conductivities in the range of 1-12 S/cm, depending on the growth conditions. The most conductive samples retain transparencies above 55% resulting in a figure of merit as high as $350\ \mu\text{S}$, which is the best performing *p*-type TCO by solution methods to date. Remarkably, despite the nano-crystallinity of the films, properties comparable with crystalline CuCrO_2 are observed. No postannealing of the films is required in contrast to previous reports on crystalline material. The low processing temperature of this method means the material can be deposited on flexible substrates. As this is a solution based technique it is more attractive to industry as physical vapour deposition (PVD) methods are slow and costly in comparison.

The first section will introduce CuCrO_2 . The screening of the growth parameters is then described, followed by an in depth characterization of the films. The optical properties are investigated using ellipsometry and UV-VIS spectroscopy, while the electrical and thermo-electrical properties are investigated using conductivity versus temperature measurements and the Seebeck effect.

5.1 Introduction to CuCrO₂

CuCrO₂ has attracted attention in areas other than *p*-type TCOs. Research has focused on the multiferroic nature of the material. Crystalline CuCrO₂ is a triangular lattice antiferromagnet, exhibiting the magnetoelectric effect [96, 97]. The material has also been investigated for its photocatalytic properties [98, 99]. However this thesis is mainly concerned with the *p*-type properties of CuCrO₂. *p*-type conductive films are obtained through intentional doping of the trivalent metal site (Ca, Mg, Ni) [16, 100, 101], as crystalline stoichiometric CuCrO₂ is typically highly resistive [100, 102]. High conductivity can be achieved with one claim of 220 Scm⁻¹ [16], although this seems to be an outlier. The highest conductivities after this value are for Mg doped samples on sapphire substrates synthesized by pulsed laser deposition (PLD) with conductivities in the 30-70 Scm⁻¹ range [102–104]. In contrast (excluding the report by Nagarajan *et al.*) most papers using amorphous substrates report conductivities in the 1-10 Scm⁻¹ range [105, 106]. The transparency of these films is degraded by the doping; reduced to 40% for a 250 nm thick film. CuCrO₂ has also been grown by other methods such as chemical vapour deposition (CVD) using the metal-organic acetylacetonate (acac) precursors Cr(acac)₃ and Cu(acac)₂ at 550°C, resulting in polycrystalline films with conductivity of 0.86 Scm⁻¹ (figure of merit (FOM) $\approx 45 \mu\text{S}$) [107]. Mg-doped films of CuCrO₂ have successfully been synthesized by SP using the same acac precursors with the addition of the Mg(acac)₂ precursor for doping. Only after postannealing at 700°C did they achieve conductivities of 0.6-1 Scm⁻¹ [95, 108]. CuCrO₂:Zn grown by sol-gel processing show conductivities of around 0.47 Scm⁻¹ after two postannealing steps [109]. The performance of these films is significantly reduced in comparison to PVD methods [95, 107–109]. The high temperature required by these methods is a major drawback for using the material in practical devices.

In this chapter SP was used to grow thin (50-100 nm) Cu deficient CuCrO₂ films. The details of the best performing films has been reported in the literature [110]. This was a single

σ (Scm ⁻¹)	S (μVK ⁻¹)	Dopant	Method	Reference
220	150	Mg	PLD	[16]
1	90	Mg	Spray	[95]
0.47	113	Zn	Sol-Gel	[109]
67	-	Mg	PLD	[102]
0.86	-	-	CVD	[107]

Table 5.1 Summary of selected CuCrO₂ properties from different deposition methods.

step method without the need for post-annealing or extrinsic doping, unlike previous reports. Due to the relatively low temperatures ($\approx 345^{\circ}\text{C}$) the Cu deficient material is compatible with flexible substrates (typically $<400^{\circ}\text{C}$ process temperatures [111]). The low growth temperature is in contrast to earlier reports of the dependency of the conductivity on higher growth temperatures ($>500^{\circ}\text{C}$) [112], and the requirement of crystallinity to retain *p*-type properties [113]. Additionally this is a cost effective method as the growth is performed by spray pyrolysis, an inexpensive technique that can achieve large area deposition, and uses the relatively abundant elements Cr and Cu. The films exhibit conductivities in the 1-12 Scm⁻¹ range depending on the growth conditions, with optical transparencies of 55%. This Cu deficient CuCrO₂ material is the best performing *p*-type TCO grown by solution methods to date (excluding reports on single-crystal substrates[114]), surpassing the previous value of 151 μS [6]. The material is promising as it does not require single-crystal substrates, which is typical for high-performing *p*-type TCOs [37, 115]. Most importantly it is the facile synthesis, using inexpensive components, that makes this method exceptional.

In this chapter the growth parameters to obtain these films and the chemistry involved are discussed. To obtain the best performing films, screening of the Cu precursor concentration, temperature, and oxygen partial pressure was performed. A Cu deficient CuCrO₂ phase is obtained with a conductivity in the 1-5 Scm⁻¹ for a Cu/(Cu+Cr) precursor ratio of $\approx 30\%$ at

345°C. This can be further improved by reducing the oxygen partial pressure during growth resulting in films with conductivities as high as 12 Scm^{-1} .

5.2 Experimental

Due to their stability in air and their relatively low toxicity the acetylacetonates are suitable precursors for SP [107]. These precursors are somewhat soluble in alcohol solvents like isopropanol and methanol. Alcohol solvents are advantageous in SP if low cost air blast nozzles are employed, as they create droplets of smaller size than water-based solvents due to their lower density and surface tension. They also have lower boiling points which means they vaporize easily resulting in better pyrolytic decomposition [29]. $\text{Cu}(\text{acac})_2$ and $\text{Cr}(\text{acac})_3$ precursors were dissolved in 100 ml of methanol solvent and sprayed with an air blast nozzle (PNR, model 0331) at a rate of 1.7 ml/min using a mixture of compressed air and nitrogen with an air pressure of 17 l/min onto heated glass microscope slides. The $\text{Cr}(\text{acac})_3$ concentration was typically kept constant at 0.025 M while the $\text{Cu}(\text{acac})_2$ concentration was varied up to 0.025 M. The thickness of the films was determined from XRR measurements. However for films $>90 \text{ nm}$ the films are too rough ($>6 \text{ nm}$) to display X-ray interference fringes. In this case the thickness is determined from modeling UV-VIS reflectance measurements. To determine the optical constants of the Cu deficient CuCrO_2 material, a separate film has been grown on a silicon substrate to minimize the inter-facial roughness of the substrate. The thickness and roughness of the film was measured by XRR prior the optical analysis. Ellipsometric measurements were taken on a Sopra GESP5 at three angles close to the samples pseudo Brewster angle (66, 69, 72°). The measured $\tan \Psi$ and $\cos \Delta$ data have been modeled using the sample geometry as determined by XRR as an input parameter. The dielectric function was described by one 1D bulk critical point and two harmonic oscillators.

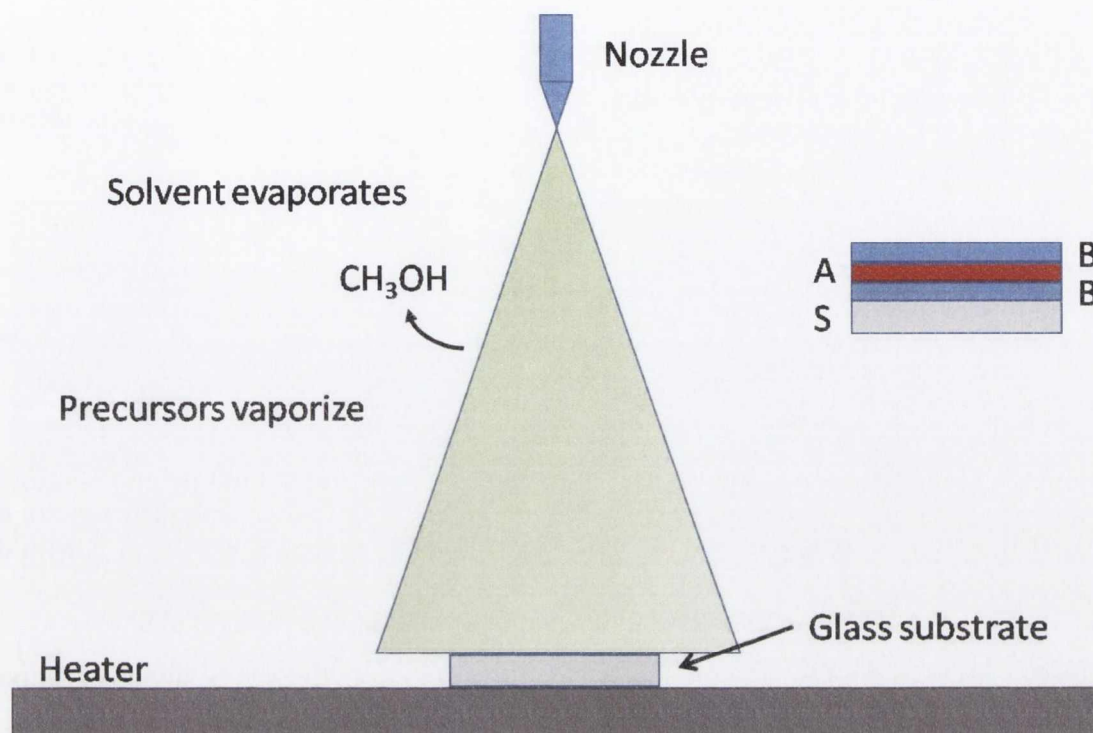


Fig. 5.1 Growth diagram showing the spray configuration.

5.3 Growth of Cu deficient CuCrO_2

During SP there are a number of processes occurring during film formation such as precursor solution atomization, solvent evaporation, drying and decomposition of the precursor salt, making it a complex system to model. Each precursor was initially tested separately to understand better the chemistry involved. Films grown with only the Cu precursor (0.01 M) result in predominately Cu_2O films. XRD diffraction spectra of the Cu_2O films show the expected reflexes for cuprous oxide, although it is difficult to discern the (200) peak from the background noise, see Fig. 5.2(a). The XRD pattern confirms that the films do not show the reflexes for CuO (35.5° and 39°). As the Cu_2O phase is formed in these conditions it is likely that the formation of the delafossite structure, which needs Cu in its 1^+ oxidation state, is more probable. If the growth temperature was higher, CuO is more likely to form [116] and therefore result in the unwanted CuCr_2O_4 spinel phase (Cu in 2^+ oxidation state) once

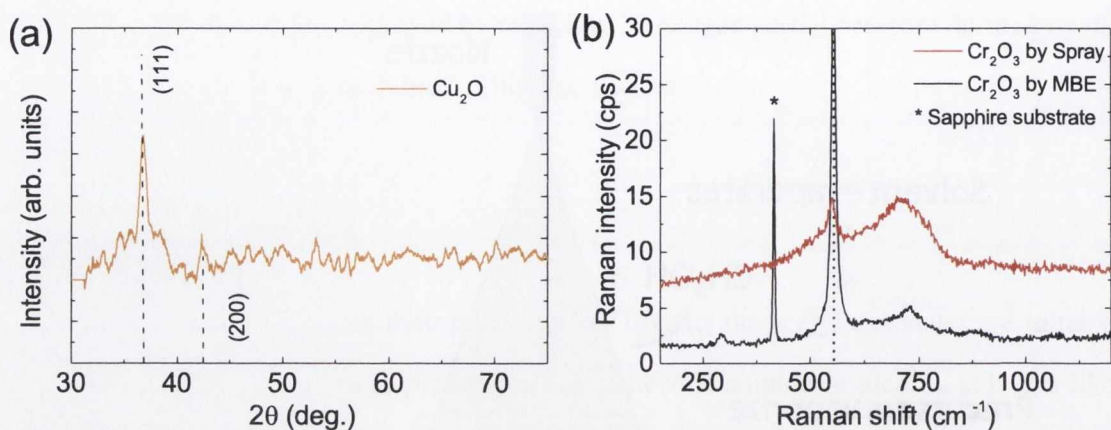


Fig. 5.2 (a) XRD pattern of the Cu_2O films showing the expected reflexes for Cu_2O . (b) Raman signal of Cr_2O_3 films grown by SP and by MBE for comparison. The spectra are offset by 5 cps. The strong A_{1g} Cr_2O_3 vibrational mode is shown at 550 cm^{-1} with the dashed line.

the Cr precursor is added to the solution. Typically this phase needs to be dissolved by post-annealing at higher temperatures [95]. However that can be directly avoided by inhibiting the formation of CuO and CuCr_2O_4 parasitic phases by using lower growth temperatures as demonstrated here.

Films grown using just the Cr precursor (0.025 M) result in smooth insulating amorphous Cr_2O_3 . These films show no XRD reflexes but the Cr_2O_3 vibrational modes were confirmed by Raman spectroscopy, see Fig. 5.2(b). For comparison epitaxial films of Cr_2O_3 grown by MBE on sapphire is shown. The strong A_{1g} vibrational mode of Cr_2O_3 at $\approx 550\text{ cm}^{-1}$ is weaker in the SP films as expected as there is no observable crystallinity in the XRD spectra. The broad mode at 710 cm^{-1} is also related to the amorphous nature of the films and is caused by an increase in edge-sharing octahedral vibrations, also observed in other amorphous materials. [117] Significantly higher temperatures ($>450^\circ\text{C}$) are required to grow these Cr_2O_3 films. The heat stability of $\text{Cr}(\text{acac})_3$ is known to be greater than $\text{Cu}(\text{acac})_2$ and this may explain the higher temperatures required [118].

When the two precursors are mixed the resulting films are conductive Cu deficient CuCrO_2 . Fig. 5.3 shows SEM images of the morphology of the CuCrO_2 samples, confirming

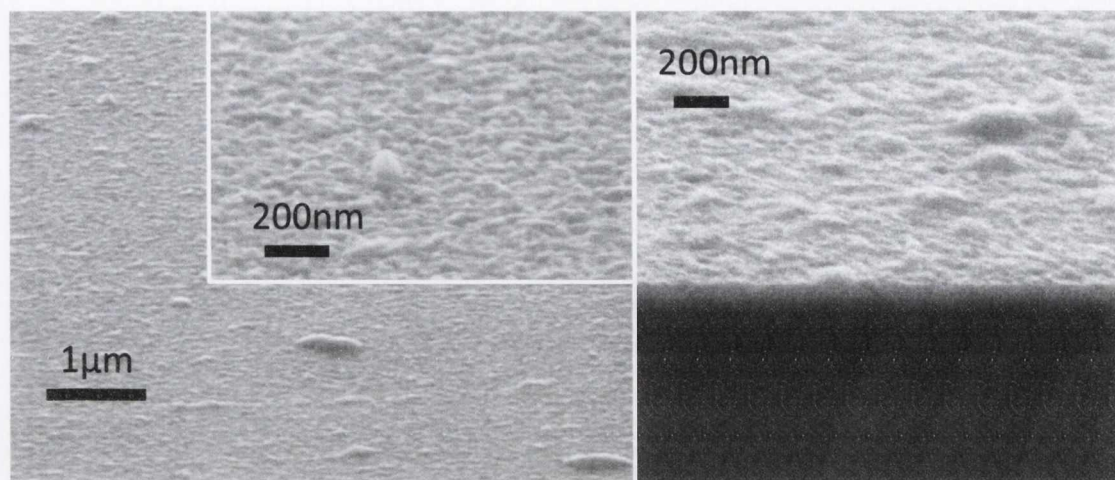


Fig. 5.3 Scanning electron microscopy (SEM, Carl Zeiss Ultra) showing the morphology of the films at a tilt angle of 11°. The imaging was performed at 5 kV.

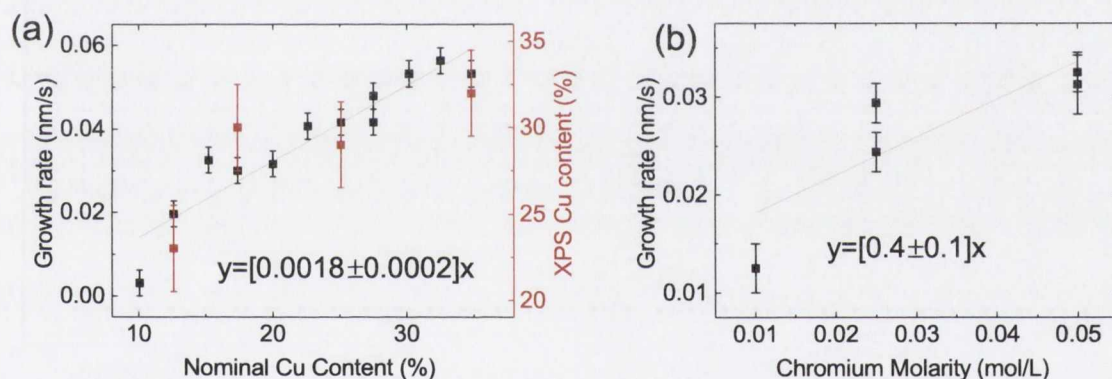


Fig. 5.4 (a) The dependence of the growth rate on the nominal Cu content in the initial solution. The growth is limited by the presence of the Cu precursor. (b) The growth rate also increases for an increased molarity of solution.

the homogeneity of the films. There is a dependency of the growth rate on the Cu content in the films. This is shown in Fig. 5.4, where the growth rate is plotted as a function of the nominal Cu content. The growth rate is calculated by measuring the thickness *ex-situ* using XRR and recording the growth time. The nominal Cu content refers to the precursor ratio in the solution prior to deposition while the actual atomic Cu/(Cu+Cr) ratio was determined by using XPS. Without the presence of Cu no film growth is observed for the Cr precursor up to temperatures of 450°C. However once a small amount of Cu is included the growth

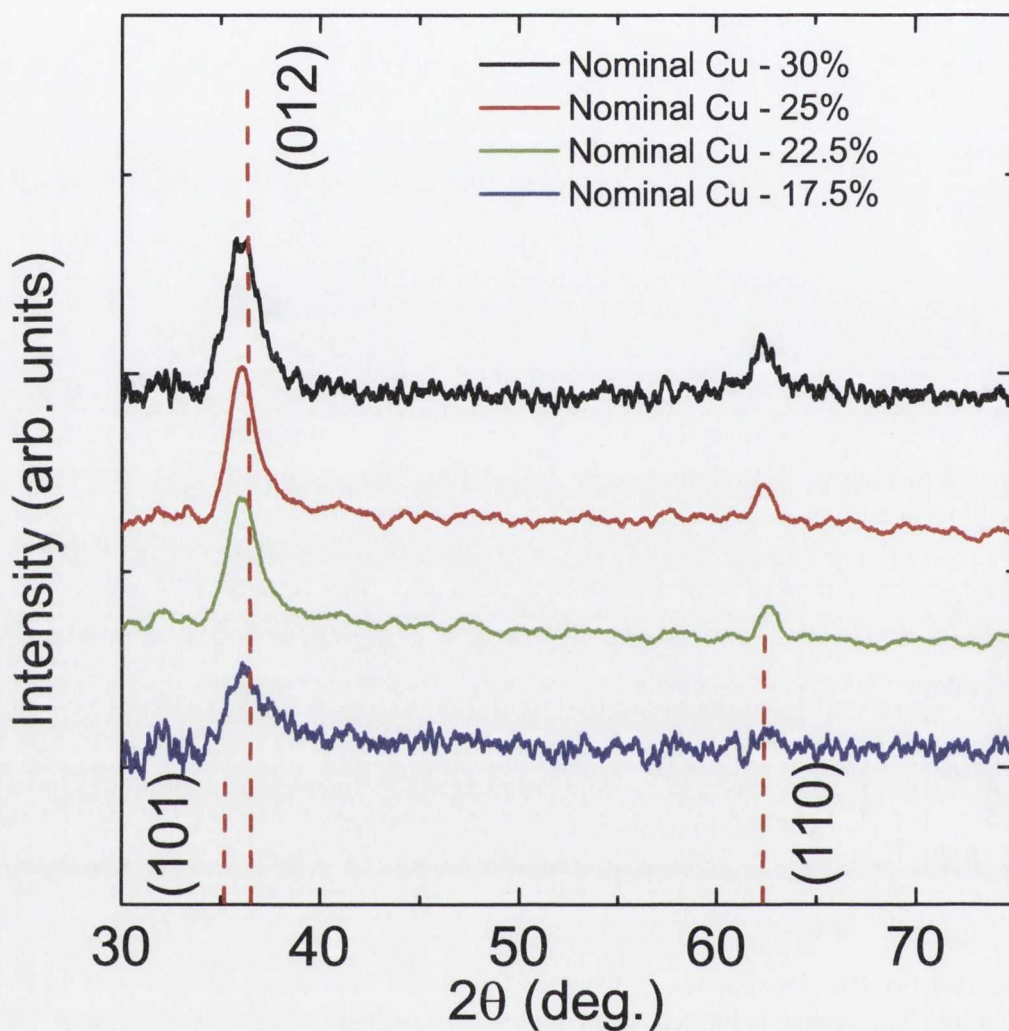


Fig. 5.5 XRD pattern of films for different nominal Cu content. XRD reflexes are indexed for CuCrO_2 (PDF-00-039-0247).

rate increases and the delafossite phase is formed. See Fig. 5.5 for the development of the CuCrO_2 XRD reflexes. Above 22% of nominal Cu content, both XRD peaks at 36.3° and 62.2° are consistent with the (012) and (110) XRD diffraction peaks of delafossite CuCrO_2 , which is a rhombohedral crystal cell with space group $R\bar{3}\text{-mh}$. The (101) diffraction line may also be present hidden in the broad peak of the (012) line. Mixed phases during the synthesis of delafossites have been reported before, and alternative phases are shown in Fig. 5.6(a)

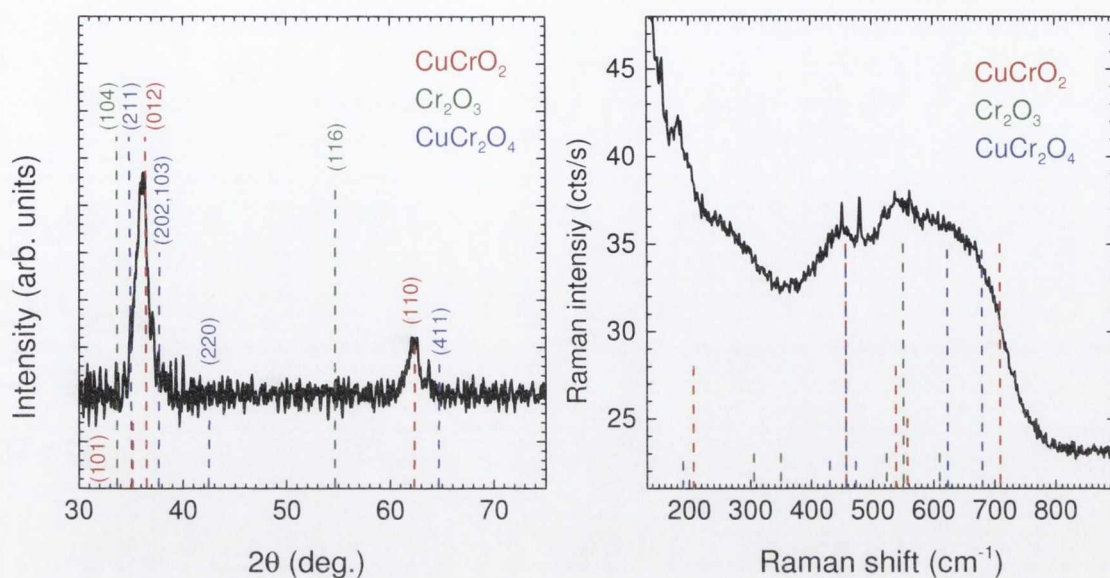


Fig. 5.6 (a) XRD pattern of the Cu-deficient CuCrO_2 films, with the XRD diffraction lines indexed for CuCrO_2 , Cr_2O_3 and CuCr_2O_4 . (b) Raman spectra with the vibrational modes of CuCrO_2 , Cr_2O_3 and CuCr_2O_4 highlighted.

[119]. However, in this case, the presence of both diffraction lines is only consistent with the CuCrO_2 crystallographic phase. Using the MAUD software package and the CuCrO_2 cif file (PDF number 01-089-6744), the a and c lattice parameters were calculated to be 2.98 ± 0.05 Å and 17.16 ± 0.05 Å respectively. The delafossite structure consists of edge-sharing octahedral layers (CrO_6 - A layer), stacked between linearly coordinated Cu atoms in an O-Cu-O dumbbell shape (B layer). This stacking is along the c -axis of the crystal lattice as shown in Fig. 5.7 [120]. However as the thickness is limited by the Cu content the AB stacking only occurs when there is enough Cu being decomposed to fill the lattice structure. The growth rate is also influenced by the molarity of the solution as shown in Fig. 5.4(b). For an increased Chromium concentration and a fixed nominal $\text{Cu}/(\text{Cu}+\text{Cr})$ ratio the growth rate also increases as there is a greater number of Cu atoms present in the solution. The Chromium concentration was typically kept at 0.025 M to be consistent.

Fig. 5.6(b) shows that the Raman modes for crystalline CuCrO_2 at 207, 454 cm^{-1} and 703 cm^{-1} are present, but are very broad and shifted to lower wave numbers. [121, 122]

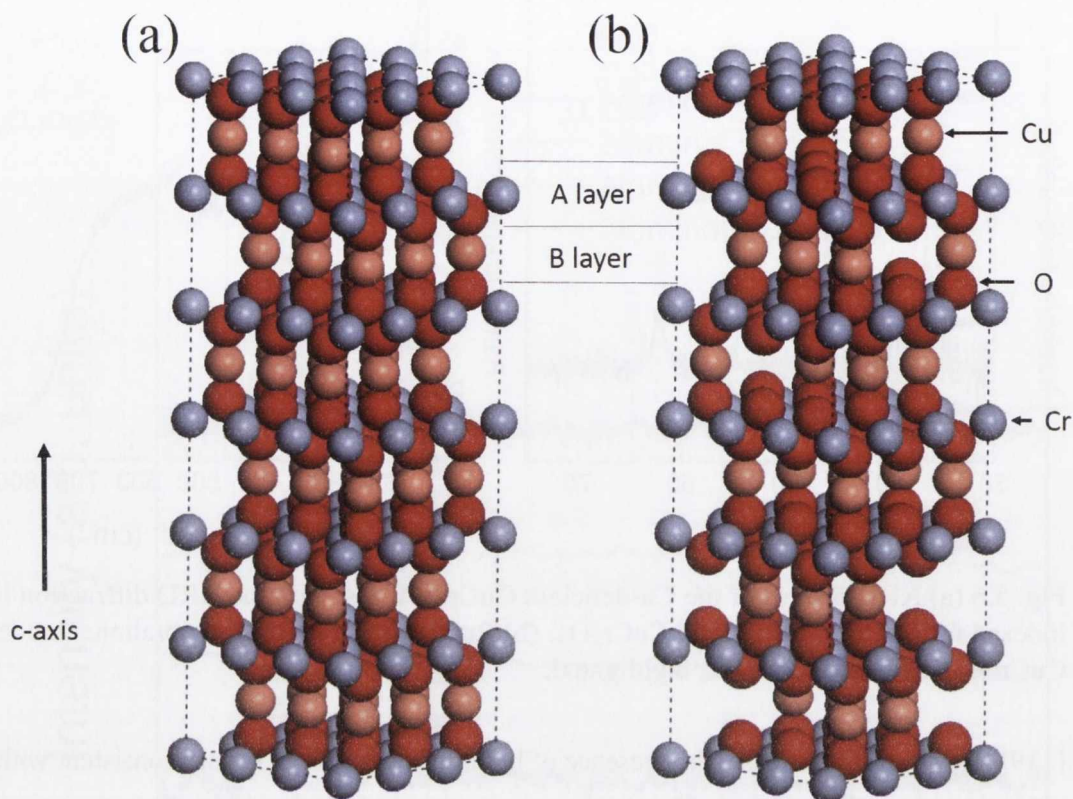


Fig. 5.7 Schematic CuCrO_2 lattice structure showing (a) the stoichiometric unit cell with the A and B layers highlighted. (b) is the same structure with a 1/3 Cu deficiency.

The Raman modes for Cr_2O_3 and CuCr_2O_4 [123] are also highlighted, but it is difficult to determine their contribution due to the broad nature of the spectra. This confirms the poor crystallinity suggested by the XRD data. The weaker, defect induced CuCrO_2 modes around 550 cm^{-1} are quite pronounced in our sample, illustrating a larger number of Cr-O octahedra in the Cu deficient samples compared to crystalline CuCrO_2 . A similar enhancement of these defect modes has been previously reported for stressed $\text{CuCrO}_2\text{:Mg}$ [122, 124].

Fig. 5.8(a) shows the XPS spectra of the Cu-precursor itself, which matches previously published data on $\text{Cu}(\text{acac})_2$ [125]. The Copper region of the CuCrO_2 films shows Cu in a 1^+ oxidation state with a mixture of the unreacted Cu precursor present (Fig. 5.8(b)). All samples were chemically cleaned in acetone and isopropanol with an ultrasonic bath

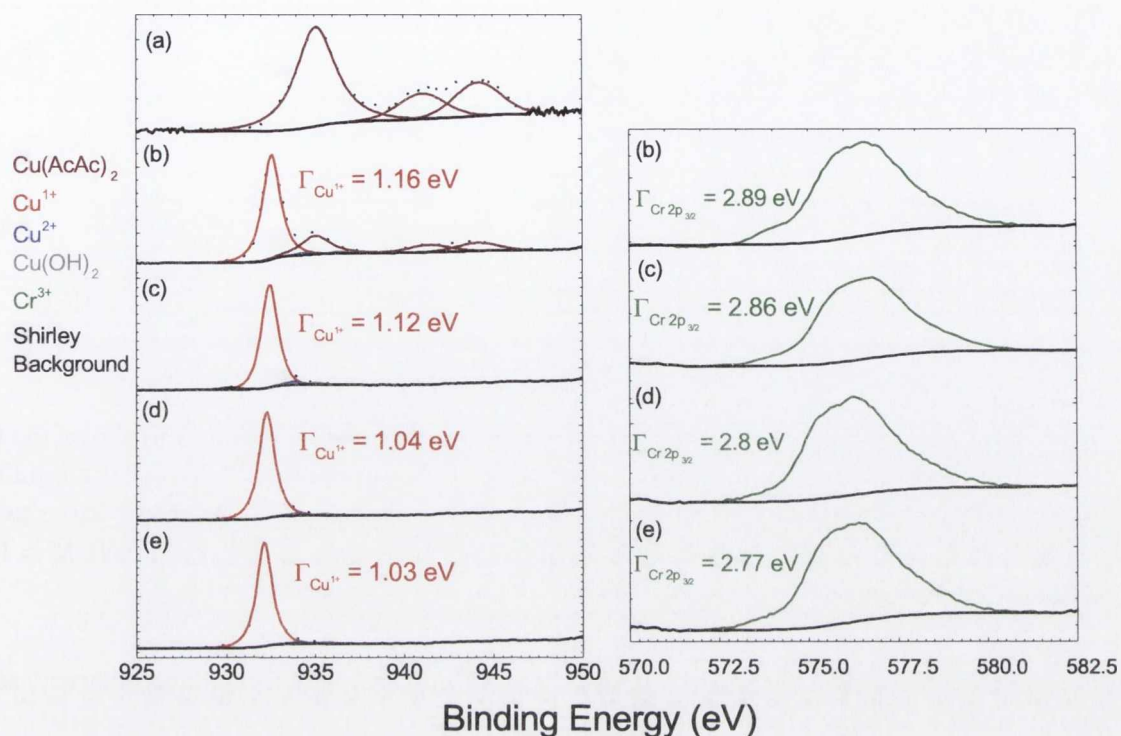


Fig. 5.8 XPS spectra of (a) the unreacted Cu(acac)₂ precursor. (b) shows the XPS spectra of both the Cu and Cr regions of the as received Cu deficient CuCrO₂ sample. (c) is after typical cleaning conditions cleaned using an Ar ion gun operated at 500 V for 10 minutes with a sputter current of 2-3 μA . (d) is after 33 minutes of depth profiling. (e) Depth profiling after 60 minutes. There is no evidence of the shake-up satellite peaks expected between 940-945 eV for Cu in its 2⁺ oxidation state after the unreacted precursor is removed.

and sputter-cleaned using an Ar ion gun operated at 500 V for 10 minutes with a sputter current of 2-3 μA (at low voltage to prevent oxygen sputtering) to remove traces of unreacted precursors precipitating after growth during sample cool down. After the initial cleaning step the precursor traces are removed, while the Cu¹⁺ signature of the oxide material remains unchanged (Fig. 5.8(c)). The XPS Cu content shows that the films typically are Cu deficient with a Cu/(Cu+Cr) ratio of $\approx 33\%$, even if the nominal Cu content is lower. Therefore the Cu deficient phase forms and further growth is limited by the lack of Cu. The growth most likely proceeds by a stacking of the A (CrO₆) and B (O-Cu-O) layers as show in Fig. 5.1. Insufficient Cu would prevent the formation of the dumbbell linkages in the B layer. Growth occurs even when the direct line of sight of the nozzle to the substrate is blocked, which

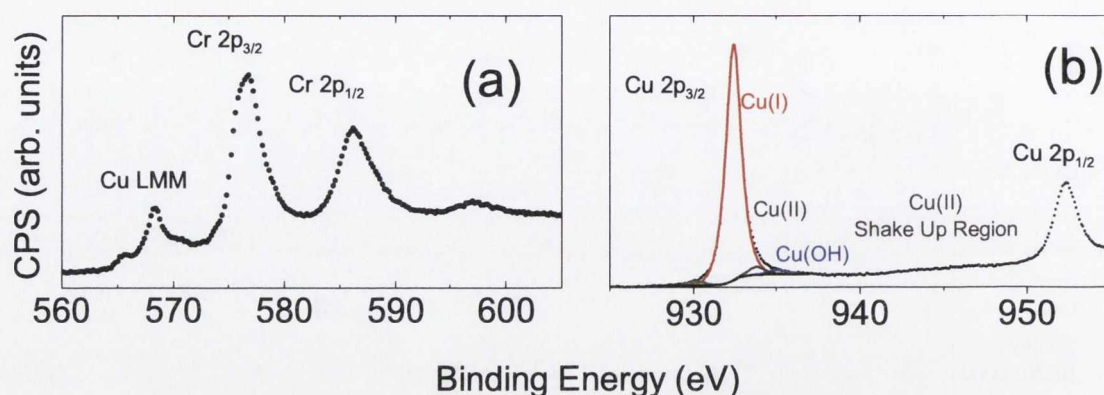


Fig. 5.9 XPS spectra of the Cr 2p and Cu 2p regions of CuCrO_2 . Figure 3(a) shows the Cr 2p peak region is complicated by an Auger peak of copper but the Cr 2p_{3/2} has a binding energy of 576.6 eV which matches reports for CuCrO_2 . Figure 3(b) shows the Cu 2p_{3/2} peak is consistent with a Cu^{+1} oxidation state with a binding energy of 932.4 eV, FWHM = 1.1. The Cu satellite peaks between 940-945 eV for Cu^{2+} is notably absent.

suggests that the growth proceeds by a CVD-like process. The films have relatively low roughness and are homogeneous, as expected for a CVD-like growth. In this case the solvent evaporates, followed by the vaporization of the precursors (the acac precursors are reasonably volatile [107]) and the diffusion of the vapor to the substrate where an oxide is formed, see Fig. 5.1. Previous studies have discussed the SP growth in terms of decomposition of the precursors followed by a chemical reaction between the Cu and Cr oxides on the surface of the substrate [95, 108]. As this was at the higher temperature of 550°C the growth processes discussed here are likely to be different.

Interestingly the films do not tend towards a $\text{Cu}/(\text{Cu}+\text{Cr})$ ratio of 50% as would be expected for a stoichiometric CuCrO_2 phase. Fig. 5.7(b) shows the possible lattice structure for 1/3 Cu deficiency ($\text{Cu}/(\text{Cu}+\text{Cr})$ ratio of 33%). The image is only illustrative and does not account for a possible relaxation of the atomic lattice positions. The Cr:Cu:O atomic ratio from XPS is approximately 1:2:4 which would indicate that the atomic ratio is close to the spinel phase of copper chromite (CuCr_2O_4). However as shown in Fig. 5.9 the expected shake-up satellite peaks between 940-945 eV for the Cu^{2+} oxidation state is absent, which is the oxidation state of Cu in the spinel phase. 93.5% of the Cu 2p_{3/2} peak area is consistent

with a Cu^{+1} oxidation state at a binding energy of 932.4 eV. Smaller components of Cu^{+2} at 933.8 eV and hydroxide at 935 eV are present but account for only a few percent of the peak area. Similarly the binding energy of the Cr $2p_{3/2}$ is 576.6 eV, indicating a 3^{+} oxidation state, which is consistent with previous reports for CuCrO_2 [2, 126].

5.4 Temperature dependence

The substrate temperature is a crucial parameter in SP as it contributes to the solvent evaporation and precursor decomposition [28]. There is a particular optimum temperature range for a given $\text{Cu}/(\text{Cu}+\text{Cr})$ precursor ratio which is related to the vaporization of the precursors followed by oxide formation on the substrate induced by the temperature of the heater. Fig. 5.10 shows the dependence of the FOM for a fixed nominal Cu content of 30%. The FOM used is the same as defined in Chapter 4, Eq. 4.9. Fig. 5.10 shows that there is narrow temperature range of $\pm 3^\circ\text{C}$ where the best performing films are obtained. This is related to the temperature dependent decomposition rate of the precursors which results in an optimum temperature window. Similarly the decomposition of the precursors is influenced by the presence of oxygen.

5.5 Oxygen partial pressure dependence

The conductivity of the films was influenced by the oxygen partial pressure in the chamber during growth. A reduced oxygen partial pressure is essential for the most conductive films. Pre-evacuation of the growth chamber is required to remove residual oxygen by purging with nitrogen gas. If there is an oxygen rich environment present during the start of the growth then the formation of Cr_2O_3 is favoured, as it is more stable. To understand better the phase purity of the material and the dependence on oxygen partial pressure, depth profiling was performed. This was done using an Ar^{1+} ion gun operated at a higher voltage of 750 V with a

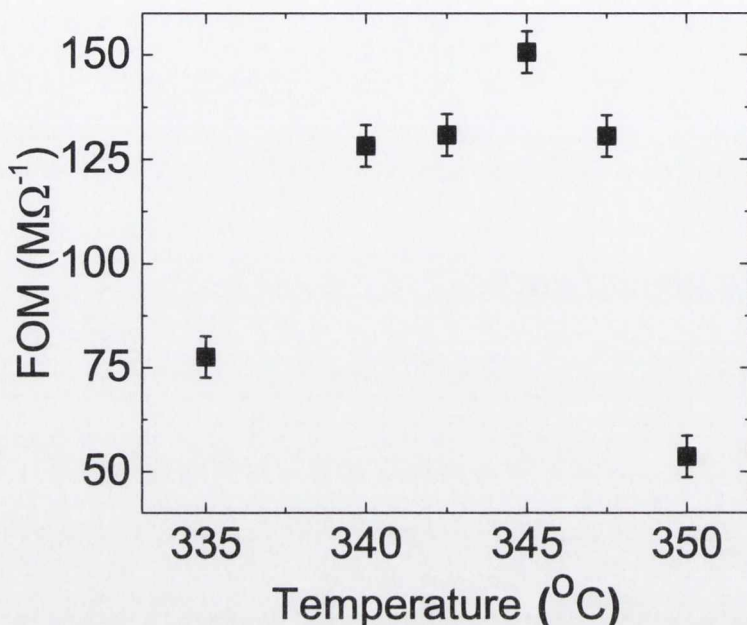


Fig. 5.10 The dependence of the FOM on the growth temperature for a fixed nominal Cu content of 30%.

sputter current of 8.5 μA . The atomic ratio was taken at each interval. After sputtering for 10, 33 and 60 minutes the Cu^{1+} and Cr^{3+} line-shapes do not change significantly, as shown in Fig. 5.8(c)-(e). With XRR thickness measurements before and after sputtering the effective sputter rate was estimated to be 0.35 nm/min, while the initial cleaning step at lower voltage does not lead to a significant oxide removal. Fig. 5.11 shows the oxygen partial pressure in the chamber with no pre-evacuation (a) and after evacuation (b). The corresponding XPS determined ratios as a function of etch time are shown in Fig. 5.11 (c) and (d) corresponding to (a) and (b) respectively. The ratios indicate that in the reduced oxygen environment Cu deficient CuCrO_2 ($\approx 33\%$ Cu/(Cu+Cr) ratio) is formed, while in the oxygen rich condition a predominately Cr_2O_3 rich phase is present.

A reduced oxygen content in the carrier gas also leads to higher conductivities as demonstrated in Fig. 5.12. Previously compressed air was used during growth, but reducing the oxygen content by introducing a mix of nitrogen in the carrier gas leads to more conductive

CuCrO_2 . The optimum nominal oxygen partial pressure in the carrier gas is around 5% before the conductivity drops again. In very low oxygen partial pressure the films do not have enough oxygen to form oxides and the precursors are left on the surface of the substrate.

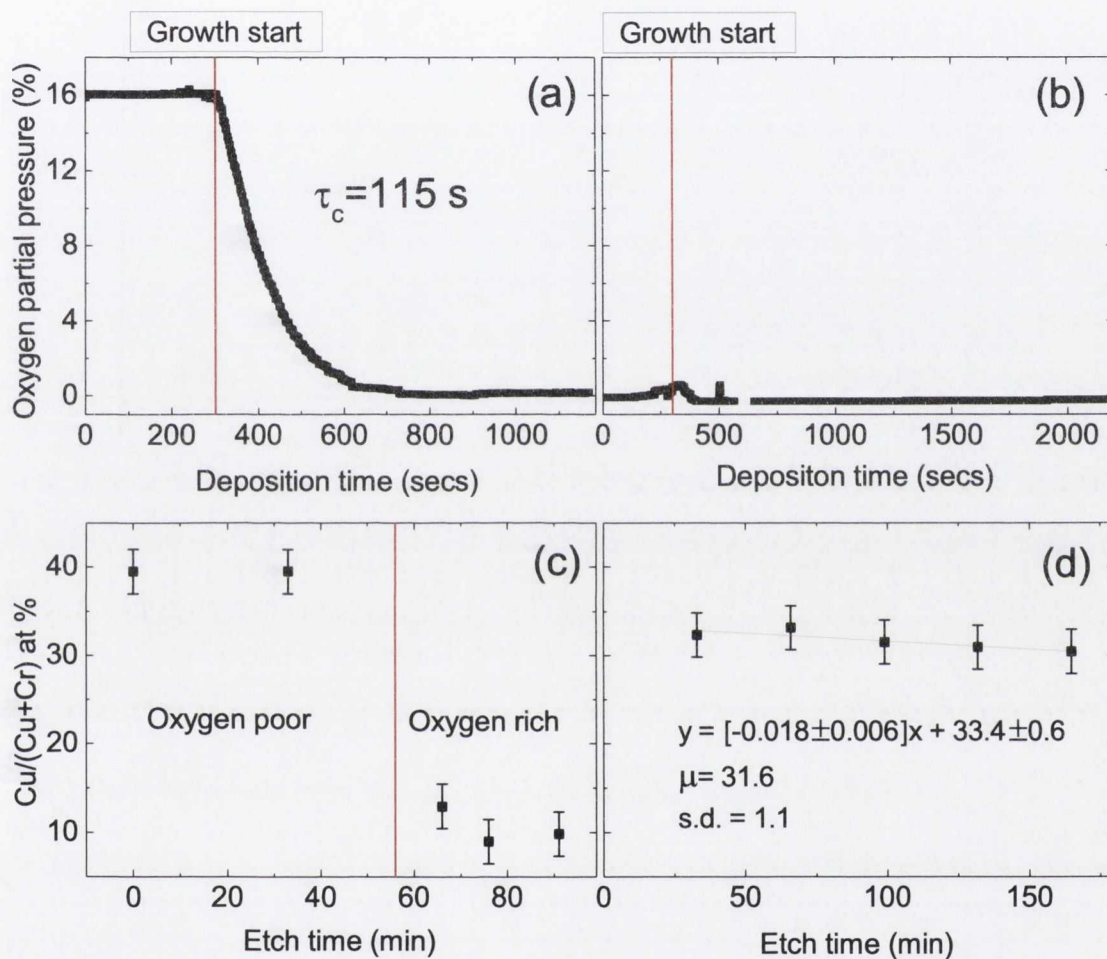


Fig. 5.11 (a) The oxygen partial pressure during growth for a non-evacuated chamber. (b) The oxygen partial pressure during growth for an evacuated chamber. (c) The corresponding XPS determined $\text{Cu}/(\text{Cu}+\text{Cr})$ atomic ratio for (a) showing the lower Cu content in the oxygen rich conditions as a function of etch time. (d) The XPS ratio showing a consistent Cu content throughout the film, with an average value of 32%.

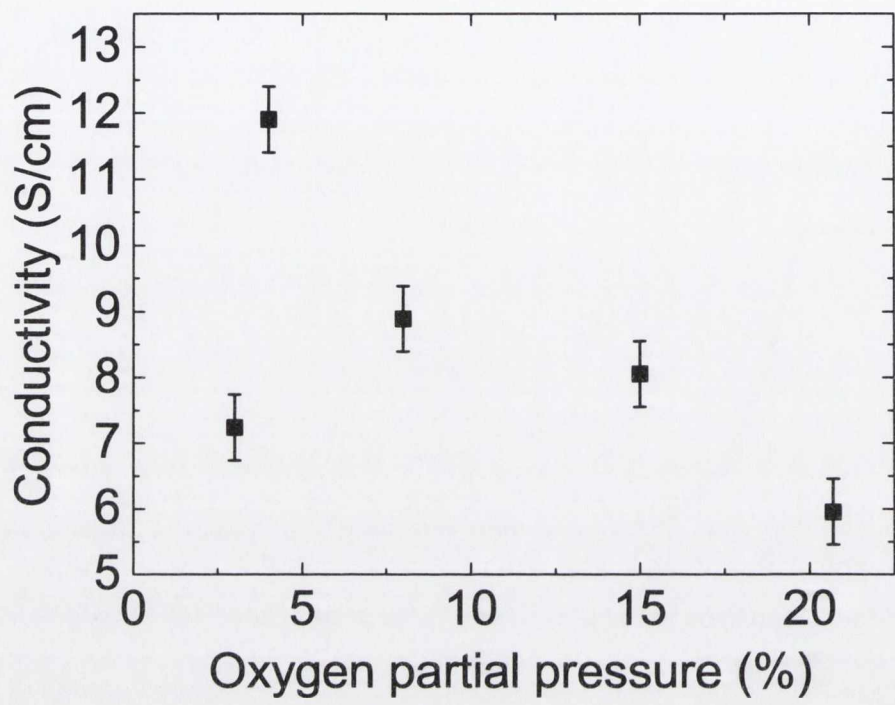


Fig. 5.12 The dependence of the conductivity on the oxygen partial pressure. A reduced oxygen partial pressure results in higher conductivity samples.

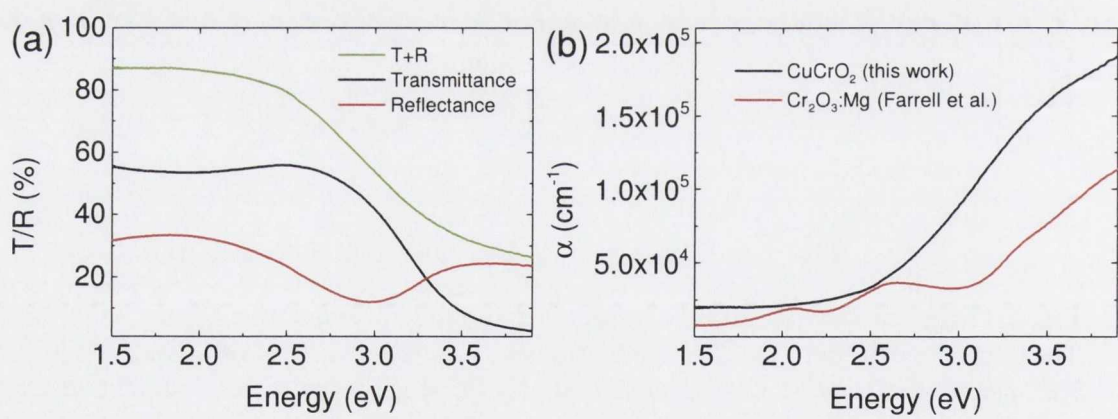


Fig. 5.13 (a) Transmittance and Reflectance of a 70 nm film. (b) The absorption spectra of Cu deficient CuCrO₂ is compared to Cr₂O₃:Mg [9]. All measurements were taken with air as a reference.

5.6 Optical properties

The sum of the total transmittance and total reflectance is plotted as a function of energy for 70 nm film in Fig. 5.13. The reflectivity of the films is high, with the reflectance as large as 25%. The reflectance loss can be mitigated by an anti-reflective layer if the films were used in a stacked layer. The transparency is still relatively high, with around 55% for similar thicknesses. The high transparency of the material is another indication that the phase is not CuCr_2O_4 as the spinel phase has been found to be very absorbant, even in thin film form [127]. The absorption spectra of Cu deficient CuCrO_2 is compared to $\text{Cr}_2\text{O}_3\text{:Mg}$ [9] in Fig. 5.13(b). The two absorption peaks at 2.1 and 2.6 eV are well known for Cr_2O_3 and are absent in our films.

The highest FOM of these films is 350 μS surpassing the previous value of 151 μS [6]. This FOM can favor high conductivity, low transparency films. However the Haacke's FOM ($\langle T \rangle^{10}/R_{sh}$) penalizes lower transparency material, and our films exhibit values of 1.5×10^{-7} comparable with the highest reported Haacke's FOM for a delafossite. As these films can be deposited at relatively low temperature, and on amorphous substrates (which gives it further advantages in industrial process considerations), this material is competitive with the majority of available *p*-type TCOs.

Transmission and reflectance measurements can be quickly measured and are helpful to assess the figure of merit of TCOs in general. Great care however has to be taken in order to extract optical parameters of thin films out of such measurements. This is because transmission measurements are not sensitive to small changes in the refractive index and variations in film thickness, or to roughness and scattered losses in polycrystalline material. Incorrect referencing can also systematically skew results. Direct calculations of *n* and *k* are therefore error prone and lead to large variations in reported values of refractive index [130]. To assess the optical constants of the Cu deficient CuCrO_2 properly we deposited a similar film on crystalline silicon substrates to minimize interface roughness as well as on glass.

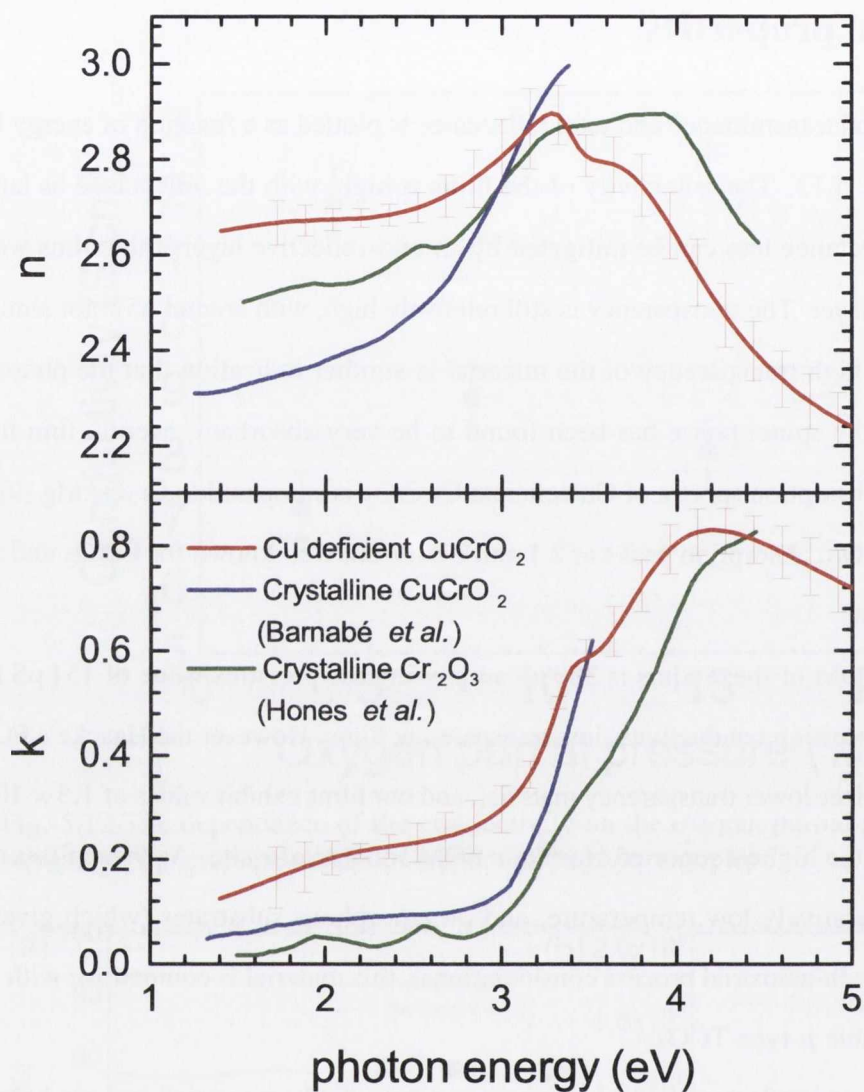


Fig. 5.14 A comparison of the n and k for Cu deficient CuCrO_2 with published data of crystalline Cr_2O_3 and CuCrO_2 included. [128, 129].

The film thickness was determined independently by XRR. Ellipsometric measurements on these films were used to model the optical constants of the films, the derived optical constant were then used to model the normal incidence transmission and reflectance measurements on samples deposited on glass to assess the consistency of the results. Fig. 5.14 compares n and k of the Cu deficient CuCrO_2 with published data of crystalline Cr_2O_3 and CuCrO_2 [128, 129]. The reference data chosen were similarly measured by ellipsometry on smooth polycrystalline

thin films allowing for a more systematic comparison. As seen by the increased k , the Cu deficient CuCrO_2 is significantly more absorbing in the visible range than both crystalline materials, yet transparent enough for a high figure of merit. The onset of the fundamental absorption in CuCrO_2 is lower than Cr_2O_3 . In Mg doped crystalline CuCrO_2 (where doping is required to improve the electrical performance) it is already known that the absorption is significantly higher. For samples of similar conductivity, the absorbance between 2-3 eV can be up to three times higher compared to low doped samples [131]. This is in line with our k -values for Cu deficient CuCrO_2 . This indicates that the Mg-doping introduces deeper mid gap states as well as increased Urbach energies very similar to those introduced by intrinsic defects in our films. This not only explains the good electrical performance of our films but also indicates that defect complexes of Mg in conjunction with adjacent intrinsic defects are crucial to understand crystalline CuCrO_2 itself.

5.7 Electrical and thermoelectrical measurements

Hall effect measurements were performed on the films using a 12 T magnetic field and contacts in the *Van der Pauw* configuration. However it was not possible to extract a reliable Hall signal to obtain a mobility value. This would set an upper limit of $\approx 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ on the mobility. The Bosman and van Daal limit of $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ would suggest that the transport in these films is limited by SPH [132]. The SPH model has already been applied to CuCrO_2 as it is known as a polaronic material [83]. In this scenario free electrons/holes tend to form polarons due to the high electron-phonon coupling. A polaron is the charge carrier, and its collective influence on the surrounding charge state, which moves sluggishly in comparison to the band conductor's free carrier picture. The SPH conductivity can be expressed as:

$$\sigma T = \sigma_0 \exp \left[\frac{-W}{k_B T} \right] \quad (5.1)$$

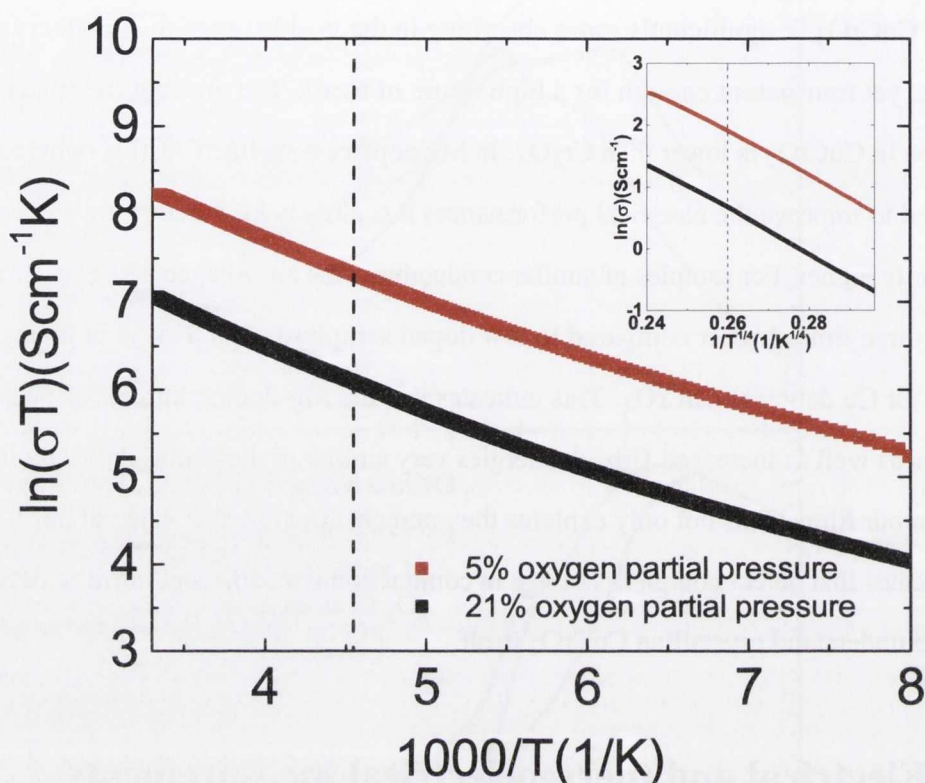


Fig. 5.15 The small polaron conductivity dependence on temperature for samples with and without optimized oxygen partial pressure. The inset shows the VRH conductivity. The dashed line in both plots indicates 220 K.

Where k_B is Boltzmann's constant, σ_0 is a constant, and W is the hopping activation energy. This is the same relation as defined in Eq. 4.3, where σ_0 has been used to simplify the expression. The temperature dependence of the conductivity was measured for various samples. The result for 5% and 21% nominal oxygen partial pressure growth is shown in Fig. 5.15 plotted using σT . The SPH model can be used to obtain W values of 65-70 meV decreasing for increasing conductivity, in the 220-300 K range. Below approximately 220 K the conductivity data deviates from the dependence expected for this model. This is due to a crossover in the conduction mechanism to VRH which has a $T^{-1/4}$ temperature dependence. The inset of Fig. 5.15 shows this dependence. The $T^{-1/4}$ dependence at low temperature

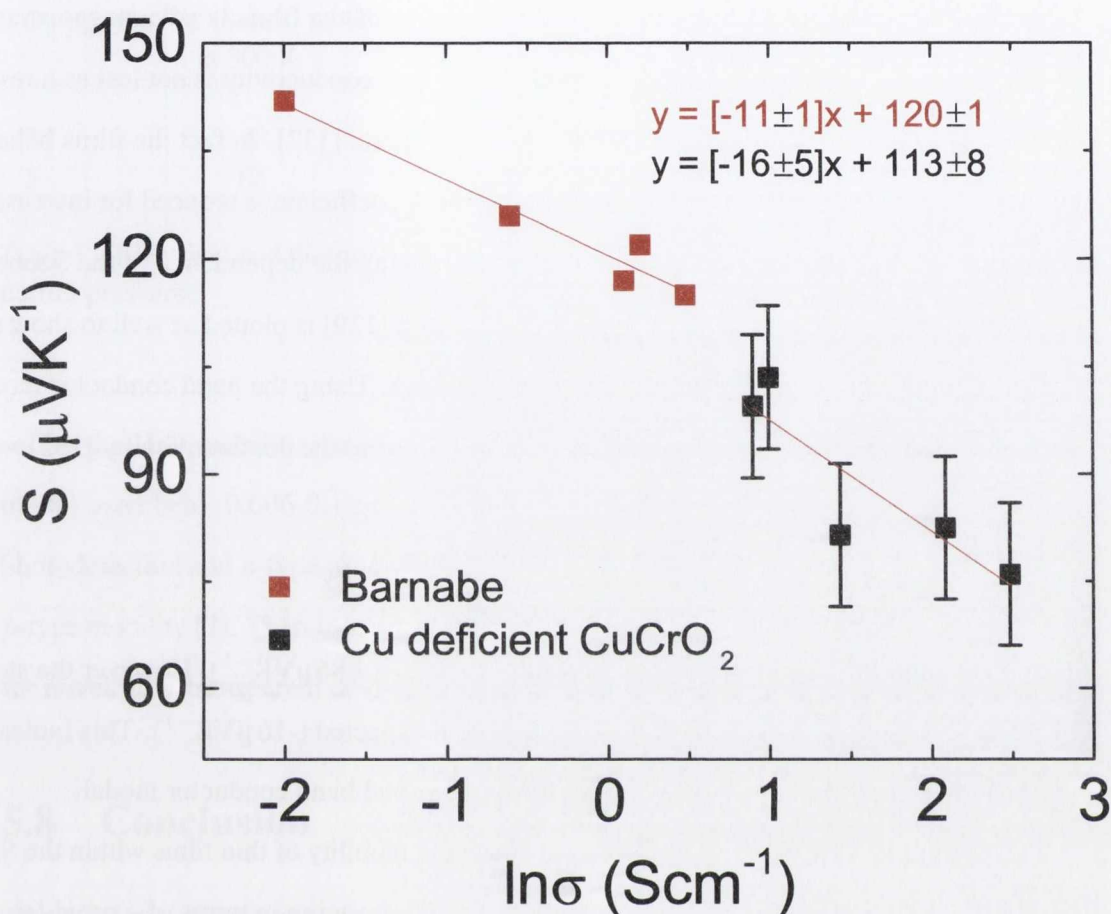


Fig. 5.16 A Jonker's plot showing the decrease in the Seebeck coefficient with conductivity. Previous work is displayed in red [129].

has been observed previously in CuCrO_2 [107], CuAlO_2 [94] and $\text{CuCrO}_2\text{:Mg}$ [89] and is typical in disordered systems with localized charge carrier states at low temperature.

The Seebeck coefficient was measured for these films, ranging from 70-100 μVK^{-1} . Previously, S values for undoped CuCrO_2 have been reported as 110-120 μVK^{-1} [108]. Our films display lower S values but higher conductivity which may originate from native defects generated from Cu vacancies as the films are highly Cu deficient. Similarly we cannot exclude small amounts of unintentional dopants such as Zn or Mg from precursor impurities, though they are below the XPS detection limit ($\sim 0.5\%$). Crystalline CuCrO_2 is usually insulating, but these films can be quite conductive (up to 12 Scm^{-1}). Retention

of the p -type conductivity despite the nanocrystallinity of the films is advantageous as it means that amorphous substrates can be used. The p -type conductivity is not lost as a result of using amorphous substrates contrary to previous reports [132]. In fact the films behave similarly to Mg doping in crystalline films; the Seebeck coefficient is reduced for increasing conductivity. A Jonker plot is shown in Fig. 5.16 showing the dependence of the Seebeck coefficient on the conductivity. Data from previous work [129] is plotted as well to show the similarity between Cu deficient films and previous work. Using the band conductor model for semiconductors the Seebeck coefficient can be related to the conductivity by [133]:

$$S = \pm \frac{k_B}{e} (\ln[\sigma] - \ln[\sigma_0]) \quad (5.2)$$

Therefore a plot of S against $\ln\sigma$ should result in $\pm k_B/e$ ($\pm 86 \mu\text{VK}^{-1}$). However the slope of the dependence is an order of magnitude less than expected ($-16 \mu\text{VK}^{-1}$). This indicates that the films are degenerate, and do not follow the normal band conductor model.

The Seebeck coefficient can be used to estimate the mobility of thin films within the SPH model [9, 18] as defined in the last chapter, Eq. 4.5. Rearranging in terms of c provides,

$$c = \exp \left[\frac{2}{Q_R + 2} \right] \quad (5.3)$$

where Q_R is the reduced Seebeck coefficient, Se/k_B . The calculated c can be used to estimate the carrier concentration p of the films, via $p = Nc$, where N is the number of available carrier sites. The SPH mobility is then calculated to be $6.4 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for a sample with a conductivity of 12 S/cm (the highest conductivity at room temperature for our films). Calculated and measured electrical and thermoelectrical transport values are shown in Table 5.2. These mobility values are quite low, as expected for SPH transport. However an alternate version of the formula, which factors in the degeneracy gives $0.03 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, an order of magnitude larger [129]. It is likely that the mobility lies within the upper boundary

O ₂ pp (%)	σ (S cm^{-1}) at 300 K	W (meV)	S (μVK ⁻¹)	p (cm ⁻³) at 300 K	mobility (cm ² V ⁻¹ s ⁻¹) at 300 K
21	4	70	82	1.4 × 10 ²²	0.002
5	12	65	76	1.2 × 10 ²²	0.006

Table 5.2 Electrical and thermo-electrical transport values for films grown at different oxygen partial pressures.

set by the Hall mobility measurements and the lower boundary set by the SPH mobility model used here, 0.006-0.1 cm²V⁻¹s⁻¹. As discussed recently devices such as rectifiers, photodetectors and *n*-type junction field-effect transistors are not adversely affected by low *p*-type mobility [7]. Therefore such low mobility, high conductivity *p*-type TCOs are required for novel fully-transparent devices.

5.8 Conclusion

This Cu deficient CuCrO₂ material is the best performing *p*-type TCOs grown by solution methods to date. This is despite the relatively low processing temperatures and the solution based technique used. Room temperature conductivities as high as 12 S cm^{-1} without post-annealing were observed. In this chapter the dependence of the electrical and optical properties on the Cu content, the temperature, and the oxygen partial pressure is examined. The growth of the delafossite CuCrO₂ phase is discussed. The mobility of the holes is estimated from thermoelectrcial measurements of the films. The film properties in terms of optical and electrical properties, and crystallographic phase are very similar to doped CuCrO₂ despite the lack of any long range crystallographic order. This is a facile method to obtain a high-performing *p*-type TCO, compatible with flexible substrates. This growth method is scalable and low cost in comparison to alternative deposition methods.

Chapter 6

Conclusion

The thesis has discussed the growth and characterization of two Cr related *p*-type TCOs: Cr₂O₃ and CuCrO₂. Chapter 1 introduced the topic of *p*-type TCOs, followed by a brief discussion of the state of the art for this field. Chapter 2 outlines the experimental methods used. Cr₂O₃ was grown epitaxially on sapphire substrates, and the details of this is discussed in Chapter 3. Chapter 4 investigates the Mg doping of Cr₂O₃ and the electrical and optical properties of the films. The SPH model was deemed the most appropriate to describe the charge transport. The mobility is limited by the hopping mechanism and therefore low mobilities are obtained ($1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The thesis then explores a different but related *p*-type material, CuCrO₂. As the details of epitaxial stoichiometric films of CuCrO₂ have already been investigated [100, 102], the growth of this material was tested at relatively low temperature ($\approx 345^\circ\text{C}$) by SP. Significant improvement on previous work was obtained with conductivities as high as 12 Scm^{-1} , resulting in the best performing *p*-type TCOs grown by solution methods to date. This is of course advantageous as SP is a low cost, scalable technique.

Interestingly the two materials demonstrate the importance of Cr-O octahedral cages in obtaining *p*-type conductivity. In both materials Cr has a 3+ valency and is in an octahedral environment. Work done in our group and elsewhere show that the Chromium states compose

the top of the valence band in doped and undoped CuCrO_2 , heavily influencing the electronic structure of the material [10, 11]. Similarly $\text{LaCrO}_3\text{:Sr}$, a newly investigated *p*-type TCO material with a room temperature conductivity of 15 Scm^{-1} , also has Cr in its $3d^3$ electron configuration [7]. Recently a value of 20 Scm^{-1} for Ni doped Cr_2O_3 [134] has been reported and in general this class of *p*-type TCOs show relatively high conductivity. However the hole mobility in these materials is typically low, due to the polaronic nature of the Cr-O bond. The induced polarization will inhibit the movement of charge through the material. There are some devices that are not adversely affected by low mobility [7], but routes to improve the hole mobility are of interest in this field.

By comparing poor crystalline quality material from SP with high crystalline epitaxial films it has been shown that conduction is not limited by crystalline quality as previously thought, but that once conditions are right, poorly crystalline material can have properties on par with single crystal material.

6.1 Outlook/Future work

There are a number of candidate *p*-type TCO materials that have been proposed by theoretical simulations. B_6O has a theoretically low effective mass (m_h) [135, 136]. Additionally, due to the nature of its native defects, bipolar doping of the material is theoretically possible, opening up the possibility of a bipolar homo-junction using such an appropriately doped material. The carrier concentration could be increased by doping with Si. However the synthesis of this material is difficult as pellets or targets for PLD require excessive temperatures. Similarly the compound $\text{M}_2\text{Sn}_2\text{O}_3$ where M is either K or Na has been predicted to have reasonably low effective mass ($< 0.4 m_h$) [136]. However the band gap of this material is significantly below the 3.1 eV threshold for visible light at 2.4 eV. From a synthesis perspective this material should be easier to form. However sensitive control over the oxygen environment will be required as SnO_2 will be thermodynamically more stable. The bixbyite structured V_2O_3

and its alloy with Manganese $(\text{Mn}_{0.5}\text{V}_{0.5})_2\text{O}_3$ has been reported as a candidate *p*-type TCO [137]. There are no expected native compensating defects which would hinder a high *p*-type carrier concentration, in theory. These materials are available as acetylacetonate precursors, which means the material could be grown by SP.

Beyond these theoretical predictions another candidate ternary compound is of interest, $\text{CuB}_{1-x}\text{Cr}_x\text{O}_2$. Currently the highest reported mobility from the delafossite class of materials is CuBO_2 , with a mobility of $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and a conductivity of less than 2 Scm^{-1} . The high mobility is attributed to its small Cu-Cu distance, the smallest of the delafossite class [22]. The highest conductivity in the delafossite class is attributed to CuCrO_2 (220 Scm^{-1}) [16]. A finely tuned mixture of CuCrO_2 and CuBO_2 could result in a compound that retains the high mobility of CuBO_2 and the conductivity of CuCrO_2 . There is also uncertainty over the validity of these high conductivity and mobility values, as they have not been repeated. Another hurdle is that the transparency of such a material will be quite low.

As the sophistication of theoretical models increases, the possibility of predicting potential *p*-type TCOs *ab-initio* will become more prevalent. However chance discoveries will continue to play a role in the development of material science.

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