Epitaxial growth, structure, and thermoelectric properties of CaMn- and V-based oxides

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Cover: SEM image of vanadium oxide film.

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Abstract

This thesis is focused on physical vapor deposition, epitaxy, and structural characterization of CaMnO_3 and VO_2 . Environmentally friendly and abundant materials are important for energy savings in applications, e.g., thermoelectrics for waste-heat recycling and thermochromic materials for passive indoor-temperature regulation. CaMnO_3 is thermoelectric and VO_2 is thermochromic at attractive temperatures for waste heat recycling and passive indoor-temperature regulation, respectively. The two material systems in this thesis were grown by reactive magnetron sputtering. A two-step synthesis process was investigated where rock-salt $(\text{Ca,Mn})\text{O}$ was grown by sputtering followed by an annealing step to form the perovskite CaMnO_3 . CaMnO_3 was alloyed with Nb with the purpose to enhance the thermoelectric properties by increasing the number of free carriers, resulting in $\text{CaMn}_{1-x}\text{Nb}_x\text{O}_3$ ($x = 0 - 0.10$) films. CaMnO_3 was grown on Al_2O_3 and LaAlO_3 while VO_2 was grown on muscovite (mica), phase-pure films of the metastable B phase and the stable M1 phase could be grown by controlling the gas flow and pressure. The mica substrate is a material with weakly interacting van der Waals layers in the structure that enable van der Waals epitaxy for the stable VO_2 film in M1 phase. The thickness effect on electrical properties in the thermochromic region was investigated as well as proving van der Waals epitaxy. This thesis therefore provides an overall contribution to the understanding of film structure and the control thereof and how it affects the properties of the film.

Keywords: Thin film, PVD, Oxides, Epitaxy, XRD

Preface

This PhD thesis is the result of my studies in the Energy Materials unit of the Thin Film Physics Division at the Department of Physics, Chemistry, and Biology (IFM), at Linköping University. My main supervisor has been Per Eklund with Biplab Paul and Fredrik Eriksson as co-supervisors. Some of the contents of these chapters have previously been published in my Licentiate Thesis (No. 1811; Linköping Studies in Science and Technology, ISBN 978-91-7685-262-0)

I am grateful for the financial support from Swedish Foundation for Strategic Research (Future Research Leaders grant to my supervisor Per Eklund), the Swedish Energy Agency under project 46519-1, and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No. 2009 00971). The European Research Council, the Swedish Research Council, and the Knut and Alice Wallenberg Foundation are also acknowledged for their financial support to co-workers that has been involved in the project. I also acknowledge ÅForsk and Kungliga Vetenskapsakademien (KVA) for financial support to conferences and travel costs and CeNano for financially supporting my collaboration with the Theoretical Physics group at IFM.

During the course of research underlying this thesis, I was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden.

Populärvetenskaplig Sammanfattning

Behovet av elektricitet globalt sett ökar och förväntas öka i framtiden. Detta sätter hårt tryck på vårt redan ansträngda klimat på jorden. En stor bov i konsumtionen av elektricitet är restvärmen som bildas. Klassiska glödlampor, som baseras på att en metalltråd värms upp så att den börjar glöda, är ett exempel på saker som är ineffektiva och genererar mycket restvärme som inte används. Detta har lösts med effektivare ljuskällor såsom lampor baserade på lysdioder (LED-lampor). Det finns även många andra processer som genererar värme som inte utnyttjas. Friktion är ett exempel, andra är avgasrör och skorstenar. Om vi kunde ta vara på denna restvärme skulle verkningsgraden drastiskt öka inom många områden. Om man drar restvärmetänket ett steg längre kan man också se att vi människor genererar värme som inte utnyttjas, och den värmen skulle exempelvis kunna användas till att driva bärbar elektronik.

Ett annat problem är den höga energikonsumtionen i byggnader, särskilt klimatreglering inomhus. Till exempel utgör kylning av rum nästan 10 % av den globala elkonsumtionen, eller motsvarande 1 GtCO₂ (100 000 000 ton CO₂). Om vi kan implementera sätt att passivt hålla ute värmen i varma klimat, eller kylan i kalla klimat, kan vi göra en stor insats för att reducera energikonsumtionen.

Ett sätt att återvinna restvärme är med hjälp av termoelektriska material. Sådana material har förmågan att omvandla värme till elektricitet. Denna förmåga är baserad på Seebeck-effekten, uppkallad efter Thomas Seebeck som upptäckte den i början av 1820-talet. Termoelektriska material fungerar genom att materialet har en varm och en kall sida. På den varma sidan rör sig elektronerna snabbare än på den kalla sidan. Denna skillnad resulterar i att fler snabba elektroner kommer röra sig mot den kalla sidan än tvärt om och en ström/spänning har skapats i materialet. Ju bättre materialet är på att upprätthålla värmeskillnaden, leda elektricitet samt har hög Seebeck-koefficient, desto högre verkningsgrad har materialet som termoelektriskt material. Tyvärr är det få material som leder värme dåligt och elektricitet bra samt har hög Seebeck-koefficient. Därför är många material ineffektiva som termoelektriska material.

För att lösa problemet med den höga energikonsumtionen av byggnader kan material som passivt ändrar egenskaper tillämpas. Till exempel så släpper fönster in mycket värme från solen. Denna värme kan minskas med en tunn film som kan blockera delar av värmestrålningen när det blir varmt ute. Detta kan lösas med termokroma material som ändrar färg eller optiska egenskaper vid temperaturskillnader. Om de används på rätt sätt kan fönsterna släppa genom både synligt ljus och värmestrålning när det är kallt ute. När det blir varmare ändrar filmen optiska egenskaper och blockerar värmestrålningen men släpper fortfarande genom det synliga ljuset. På detta sätt minskas behovet av kylning av rum när det är varmt.

För att kunna använda termoelektriska material eller termokroma material i stor skala måste de bestå av miljövänliga, billiga och vanligt förekommande ämnen. Därför har jag under min forskning undersökt oxider (syreföreningar) av kalcium och mangan (CaMnO_3) samt vanadin (VO_2) vilka är ofarliga, relativt billiga och vanliga material. VO_2 är termokrom och CaMnO_3 har hyfsade termoelektriska egenskaper. Mitt arbete har varit att undersöka om tillverkningsprocessen kan förenklas och ta materialen ett steg närmare industriell tillverkning. Jag har till exempel visat innebörden av olika tillväxtmetoder som inte/otillräckligt utforskats för materielsystemen samt tittat hur egenskaper påverkats av defekter och sammanhängande kristaller i filmerna. Detta har stor betydelse för forskning då enkla och billiga processer är viktiga för tillämpning av materialen samt att små ändringar i strukturen har extremt stora effekter (bra och dåliga) på egenskaperna hos filmerna.

List of Included Papers

Paper I

Formation mechanism and thermoelectric properties of CaMnO_3 thin films synthesized by annealing of $\text{Ca}_{0.5}\text{Mn}_{0.5}\text{O}$ films

E. Ekström, A. le Febvrier, D. Fournier, J. Lu, V.L. Ene, N. Van Nong, F. Eriksson, P. Eklund and B. Paul

Journal of Materials Science 54, 8482-8491, doi:10.1007/s10853-019-03496-7 (2019).

Paper II

The effects of microstructure, Nb content and secondary Ruddlesden–Popper phase on thermoelectric properties in perovskite $\text{CaMn}_{1-x}\text{Nb}_x\text{O}_3$ ($x = 0\text{--}0.10$) thin films

E. Ekström, A. le Febvrier, F. Bourgeois, B. Lundqvist, J. Palisaitis, P. O. Å. Persson, O. Caballero-Calero, M. S. Martín-González, J. Klarbring, S. I. Simak, F. Eriksson, B. Paul and P. Eklund

RSC Advances 10, 7918-7926, doi:10.1039/C9RA10007E (2020).

Paper III

Epitaxial growth of CaMnO_{3-y} films on LaAlO_3 (11 $\bar{2}$ 0) by pulsed direct current reactive magnetron sputtering

E. Ekström, A. Elsukova, J. Grasland, J. Palisaitis, G. Ramanath, P.O.Å Persson, B. Paul, F. Eriksson, A. le Febvrier and P. Eklund

Submitted

Paper IV

Stabilization of phase-pure B phase VO₂ on mica by pulsed DC reactive magnetron sputtering

E. Ekström, S. Hurand, M. M. Yildizhan, A. Elsukova, P.O.Å. Persson, B. Paul, G. Ramanath, A. le Febvrier, F. Eriksson, and P. Eklund

In manuscript

Paper V

Microstructural control and property switching in stress free epitaxial VO₂ films on mica

E. Ekström, S. Hurand, A. le Febvrier, B. Paul, F. Eriksson, G. Ramanath, and P. Eklund

In manuscript

My contributions

Paper I

I performed the XRD measurements, summarized and analyzed the data and wrote the manuscript.

Paper II

I planned the study and did the synthesis. I analyzed the samples by XRD, XRR, SEM, Seebeck coefficient and four-point probe. I wrote the manuscript.

Paper III

I co-supervised the student who did the depositions. I analyzed the sample by XRD, Seebeck measurements, Four-point probe and SEM. I wrote most of the manuscript.

Paper IV

I planned the study, performed the synthesis. I analyzed the samples by SEM, XRD, XRR, Seebeck measurements, and four point probe. I wrote the manuscript

Paper V

I planned the study, performed the synthesis. Measured and analyzed the samples using SEM, XRD (θ -2 θ , Pole figures, RSM), and XRR. I wrote the manuscript.

Papers not included in the thesis

Paper I

Optical and mechanical properties of amorphous Mg-Si-ON thin films deposited by reactive magnetron sputtering

Authors: S. Ali, B. Paul, R. Magnusson, **E. Ekström**, C. Pallier, B. Jonson, P. Eklund, J. Birch

Surf. Coat. Technol. 372, 9-15, doi:10.1016/j.surfcoat.2019.05.015 (2019).

Paper II

Phase evolution of radio frequency magnetron sputtered Cr-rich (Cr, Zr) 2O₃ coatings studied by in situ synchrotron X-ray diffraction during annealing in air or vacuum

Authors: L. Landälv, L. Rogström, J. Lu, D. Ostach, F. Eriksson, M. Junaid, N. Ghafoor, **E. Ekström**, C.L. Hsiao, H. Leiste, M. Ahlgren, E. Göthelid, B. Alling, L. Hultman, M. Stüber, N. Schell, J. Birch, P. Eklund

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1 INTRODUCTION AND RESEARCH QUESTION

Today's society is heavily reliant on electricity and the demand is predicted to increase.^{1,2} This is a major issue as we are trying to reduce global warming. Part of the solution is to generate electricity and energy from renewable and/or nonfossil sources, e.g. solar cells, wind power, nuclear power, and hydropower, and avoid the fossil energy sources of fossil gas, oil, and coal.^{3,4} Another way to tackle this problem is to increase the energy efficiency of the technologies we use. For example, the light emitting diode has greatly decreased the energy consumption of lighting systems. It was even predicted to cut the energy consumption of lighting with more than half.⁵ This was not an overestimation, as LEDs today have a 25 times longer lifetime and are about 10 times more efficient than incandescent light.^{6,7} The electricity/energy need could be greatly reduced if we could find similar technological breakthroughs in other areas.

With this in mind, I have researched materials which may ultimately be able to contribute to much-needed improvements in energy efficiency, by exploiting their thermoelectric and thermochromic properties. More than 70% of the world's energy consumption is lost due to heat.⁸ Thermoelectric modules can recycle some of that waste heat, and thermochromic materials can be utilized to passively regulate the temperature inside buildings. Both could have a substantial effect on the energy consumption if realized to widespread application.

Thermoelectric materials can generate electricity from a temperature gradient. Thus, if something generates waste heat, a thermoelectric module could be applied to recycle the heat into electricity. It can also be used to power smaller devices that works at low power using a weak heat source, e.g., body heat. Another strong point is that they have no moving parts allowing for long and maintenance-free operation, which has been proven in space missions, e.g., Pioneer 10, Voyager 1, and Voyager 2 which were launched between 1972 and 1977 and the Voyagers are still operating at this date. However, there are issues with the conventional

thermoelectric materials used. They are either toxic, expensive, or rare which prevents realization into more widespread applications.

I have therefore investigated materials that consist of abundant elements that are more environmentally friendly.⁹⁻¹¹ Oxides were chosen as they can operate at relatively high temperatures as they, generally, are chemically stable in air. Among oxides for thermoelectrics, the p-type materials have a higher figure of merit than n-type materials. To make an all-oxide module viable, the n-type material has to be improved. Therefore, the n-type CaMnO_3 has been researched in this study. The material was grown by PVD and different synthesis routes, e.g., post annealing or direct growth was investigated. Within these synthesis techniques, alloying with niobium was utilized to increase the electrical conductivity of CaMnO_3 .

Thermochromic materials, which changes optical properties when exposed to temperature changes, have many applications. Many people are familiar with color changing mugs, mood rings, or beverage containers that change color when cooled. However, thermochromic materials that change optical properties in other parts of the spectra than the visible light might be less known to the general public. For instance, VO_2 exhibits a phase transition at around 67 °C for which the infrared (IR) properties are affected. VO_2 is transparent in the IR range below 67 °C and the transparency is reduced in the high temperature phase. Additionally, VO_2 is fairly transparent in the visible spectra. These two optical properties make a good combination for using VO_2 on windows to reduce the IR heat transfer through the window when it is hot outside. However, for use near room temperature, the transition temperature needs to be reduced, which is challenging because many efficient methods also affects the IR modulation negatively making the material less useful.¹² Additionally, accurately determining the effect if, e.g., doping is further complicated by the phase transition's sensitivity to microstructural changes as well.¹³

I have grown VO_2 on mica, a substrate that allows for so-called van der Waals epitaxy, a type of growth that differs from conventional epitaxy in that it allows for large lattice mismatch without introducing strain in the film. This was utilized to investigate the hysteresis behavior of the

resistivity around the phase transition where the film thickness/correlation length was varied. Additionally, vanadium oxide has many phases and polymorphs, and we show that many can be grown fairly easily on mica by tuning the gases pressure/flow during deposition.

The applications ultimately targeted can increase energy efficiency, but in-depth understanding of thin-film synthesis and property control of these materials is required. To this end, the aim of my thesis work is to elucidate the role of different growth techniques, substrates, and sputtering parameters on the resulting epitaxy and film structure, and to contribute to overall understanding of the synthesis-microstructure-property correlations in these challenging materials.

2 BACKGROUND

2.1 HISTORY OF OXIDES FOR THERMOELECTRICS

The research on oxides as candidates for thermoelectric materials gained momentum in the late 1990's, for instance, Na_xCoO_2 in 1997¹⁴ and $\text{Ca}_3\text{Co}_4\text{O}_9$ in 2000.¹⁵ Many other oxides, such as layered cobalt oxides (Ca_xCoO_2 , CaCo_2O_5 , and the other above mentioned), layered oxychalcogenides (BiCuSeO), ZnO , In_2O_3 , perovskite oxides (SrTiO_3 , CaMnO_3) to name a few,¹⁶⁻¹⁹ have been researched since.

The p-type oxides are the best performing so far with reported dimensionless figure of merit (ZT) higher than unity at 923 K for doped BiCuSeO ²⁰ and 800 K for Na_xCoO_2 ²¹. The n-type oxides are struggling to achieve ZT higher than 0.5.²² There is therefore a need to improve the n-type materials to realize an all oxide module with high efficiency. The focus on this paper is partly on CaMnO_3 which is a well-known perovskite studied for its magnetic properties. It is a n-type material which is gaining more interest for its thermoelectric properties and enhancement thereof.

2.2 THE MATERIALS SYSTEM CaMnO_3

In this thesis, the slightly distorted perovskite CaMnO_3 is studied. An ideal perovskite is cubic with the ABX_3 structure, where X is most commonly oxygen. The A ion is situated in the middle of the lattice and is smaller than the B ion which is situated in the corners of the lattice cube. The sizes of the ions determine the distortion of the perfect cube. The Goldschmidt tolerance factor can be used to determine the distortion of the structure.²³ The Mn ion in CaMnO_3 is too large in conjunction with Ca ions in the perovskite. This results in a Goldschmidt tolerance factor of ~ 0.88 which commonly results in an orthorhombic structure, which is true for CaMnO_3 . The distortion is manifested as tilts of the MnO_6 octahedra as can be seen in Figure 2.1. (b).

CaMnO_3 is studied for its thermoelectric properties and, e.g., magnetic properties^{24,25} and interesting structure²⁶. CaMnO_3 as a thermoelectric material started to gain interest in 1995.²⁷ Approaches to improve the

thermoelectric properties of CaMnO_3 are most commonly alloying on the A or B site, or more recently co-alloying.

The most common synthesis method of CaMnO_3 is by solid-state reaction, but there are studies where other synthesis methods are explored, such as; a gas phase reaction synthesis,²⁸ chemical coprecipitation method,^{29,30} glycine–nitrate synthesis,^{31,32} electrostatic spray deposition,³³ and soft chemistry synthesis.^{34,35} Many of these synthesis techniques have proven successful for synthesizing CaMnO_3 with improved thermoelectric properties compared to the solid state reaction method. One common denominator is denser films or finer grain-structure. However, sample characteristics, e.g., stoichiometry and texture are also influencing the thermoelectric properties. Thus, comparing properties between studies are difficult as a complete sample characterization is not always performed and there can be large differences in the reported thermoelectric properties as shown below. Note, see the chapter on thermoelectricity for more information on how the different properties affect thermoelectricity.

- resistivity $0.12\text{--}20\ \Omega\text{cm}$.³⁶⁻³⁸
- Seebeck coefficient $-200\text{ to }-550\ \mu\text{VK}^{-1}$.^{27,37-39}
- thermal conductivity $2.8\text{--}4.1\ \text{Wm}^{-1}\text{K}^{-1}$.^{27,36,38,39}

The resistivity, compared to conventional thermoelectric materials, is the main issue for this material. A substantial effort has been made to decrease the resistivity by alloying the material on either the Ca or Mn site, or both. Examples of investigated elements on the Ca site are La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb and Bi⁴⁰⁻⁴⁶ and Mo, Ru, Nb, Ta, W and Si^{37,38,47-50} on the Mn site. Wang et. al. concluded that the size and weight difference between the Ca^{2+} and alloyant plays a role on the thermoelectric properties. The conductivity is governed by polaron hopping in the $\text{Mn}^{4+}\text{-O-Mn}^{4+}$ structure. By introducing A^{3+} , Mn^{3+} is formed and the $\text{Mn}^{3+}\text{-O-Mn}^{4+}$ framework has a lowered resistivity. In the

process, the Seebeck coefficient is lowered due to increased amount of charge carriers. The thermal conductivity is insensitive to carrier concentration as the largest contribution is from the lattice vibrations. Therefore, the thermal conductivity is sensitive to both distortion in the lattice and weight differences of atoms. To lower the thermal conductivity the alloyant should be larger/smaller than the parent element and heavier/lighter, where mass difference is the dominating factor.

Purely alloying CaMnO_3 with one element has been unsuccessful at increasing the thermoelectric performance to be useful in applications. Therefore, many newer studies apply co-alloying. Both dual alloying on the same ion side or both sides are investigated.⁵¹⁻⁵⁹ Most studies show no improvement or marginal improvement as compared to single alloyed CaMnO_3 . However, it has been shown that dual alloying by Bi and Cu can have strong enhancement of the thermoelectric properties of CaMnO_3 .⁶⁰ This enhancement is more connected to the CuO phase that formed in the grain boundaries. Alloying with elements is therefore most likely not enough to increase the properties to useful regimes. Instead, engineering of the structure similar to the CuO incorporation in the grain boundaries is most likely needed.

In the last 5 years, an increasing interest in thermochemical energy storage (TCES) at high temperature can be seen for alloyed CaMnO_3 .⁶¹⁻⁶⁵ Basically, CaMnO_3 stores energy as it releases oxygen during the heating process and releases heat when oxidizing during the cooling down process. TCES has a promising technology as the efficiency and energy density is high as compared to other energy storage technologies.⁶⁶

For the first two papers in this thesis, the synthesis method used consists of two steps where $(\text{Ca,Mn})\text{O}$, Figure 2.1 (a), was grown on sapphire using reactive magnetron sputtering from elemental Ca and Mn targets. The as-deposited films were annealed to induce a phase transformation to CaMnO_3 , Figure 2.1 (b). The third paper utilizes pulsed DC magnetron reactive sputtering to grow CaMnO_3 without the annealing step.

Fig. 2.1. Structure of (Ca,Mn)O (a) and CaMnO₃ (b).

2.3 VANADIUM DIOXIDE

Vanadium oxide is a material with numerous phases as illustrated in the phase diagram in Figure 2.2.⁶⁷ As seen in the phase diagram, the oxygen-to vanadium ratio in vanadium oxide ranges from 0 – 2.5. Many vanadium oxides usually have several polymorphs, e.g., M1, M2, B, R and A are polymorphs of VO_2 where M1, M2 and B are monoclinic. R and A are tetragonal.

Fig. 2.2. Phase diagram of Vanadium Oxide as calculated by Kang.
Reproduced with permission,⁶⁷ Copyright 2012, Elsevier B. V.

VO_2 has the monoclinic M1 structure at room temperature. At 67 °C⁶⁸, a phase transition to rutile R phase occurs. This phase transition is a so-called thermochromic phase transition, i.e., a phase transition where the color of the material changes. However, the interesting optical changes are in the IR range, where VO_2 changes from transparent to opaque when transforming from M1 to R phase. Therefore, VO_2 is proposed to be a candidate for smart windows for autonomous indoors climate control. In this phase transition, other properties than optical changes as well, e.g., several orders of magnitude in electrical conductivity and the Seebeck coefficient drastically changes as well. Thus, switches⁶⁹ is also an attractive application for VO_2 .

An intermediate phase exists during the phase transition. The intermediate phase is still under debate.^{70,71} However, it is believed that the intermediate state is the result of the melting of the V – V dimers in the M1 phase resulting in a change from semiconducting to metallic material. This change is followed by the straightening of the zigzag pattern in the M1 phase. The nature of the phase transition is not fully understood, but the literature^{71,72} points towards an intermediate metallic phase that forms in parallel with the electrical transition. The resulting rutile phase is then formed at slightly higher temperatures than the insulating to metallic transition. An explanation for this behavior is that the V – V dimers in the monoclinic phase melts and the localized electrons are free to move, effectively transforming the more insulating phase to a metallic phase. These dimers are forming a zigzag pattern and when the rutile phase is formed, the zigzag pattern is lost, and the vanadium ions forms a straight chain instead.⁷¹

Fig. 2.3. Schematic illustrations of the room temperature stable M1 phase, intermediate M2 phase, and high temperature rutile R phase.

The phase transition is characterized by a hysteresis, as shown in Figure 2.4 (From **Paper V**), where the electrical conductivity evolution with temperature is shown for VO₂ films at different thicknesses on muscovite substrates. The hysteresis is formed due to an offset in critical temperature when going from cold to hot phase and the reverse. The shape of the hysteresis depends on a multitude of properties, e.g., strain, grain size, film thickness, doping, stoichiometry, defects etc., making predicting and understanding the hysteresis challenging.⁷³⁻⁸⁰

Fig. 2.4. Conductivity evolution with temperature for VO₂ films in M1 phase at film thickness 17nm, 26 nm, 62, nm and 180 nm for (a), (b), (c), and (d), respectively. The red curve represent heating and blue curve represent cooling.

Paper 4 investigates the metastable B phase. The B phase and M2 phase share space group but are otherwise dissimilar in terms of properties and crystal structure. B phase exhibits promising high temperature bolometric properties^{81,82} and can be improved by doping with, e.g., W.⁸³

3 PHYSICAL VAPOR DEPOSITION AND FILM GROWTH

Physical vapor deposition (PVD) covers a wide variety of deposition techniques, e.g., cathodic arc deposition, evaporative deposition, pulsed laser deposition and sputtering. All PVD techniques generally use a condensed material which is turned into vapor and transported to a substrate where it condenses. This chapter will focus on sputtering as it is the technique used in the thesis.

3.1 VACUUM SYSTEM

Vacuum is essential for plasma-based PVD. The vacuum is not only needed for a clean and empty environment, but also for ignition, at relatively low voltage (100-1000 V), of the plasma¹. Especially for ultrahigh vacuum conditions, the vacuum system often consists of two chambers, one main chamber for the process and the other (load-lock chamber) for loading and unloading samples into the main chamber. The chambers also have different instruments connected to them, e.g., pressure gauges, vacuum pumps, gas analyzers and more. The vacuum chamber used in this thesis is described in detail elsewhere.^{84,85} A picture of it is shown in Figure 3.1.

3.2 SPUTTERING

Two different sputtering techniques are utilized in this thesis, radio frequency (RF) reactive magnetron sputtering and pulsed direct current (DC) reactive magnetron sputtering. To explain how these works, this section is split up into five subsections about DC sputtering, magnetron sputtering, reactive sputtering, pulsed DC sputtering and finally RF sputtering.

¹ Plasma is one of the four states of matter and, probably, the most common in the universe. Ionized gas(es), charged ions and free electrons make up the plasma. The plasma is quasineutral, meaning the plasma is positively or negatively charged at micro-scale but neutral at the macro-scale.

Fig. 3.1. Picture of the PVD system used. Photo by the author.

3.2.1 DC Sputtering

In DC sputtering, a gas is inserted in a vacuum chamber, typically argon (Ar). This gas is turned into a plasma by applying voltage between the cathode and anode. Stray electrons are accelerated towards the anode (substrate) and collisions with the gas produces ions and electrons by electron impact ionization, eq. 3.1.⁸⁶

This in turn causes more collisions. A cascade of these events is the mechanism behind the plasma ignition. As an added effect the formed ions are accelerated towards the cathode (target material) where the impact knocks out both the target material and more electrons which further feeds the plasma. The sputtered material moves in lines and collides with constituents in the plasma. The rate of collisions depends on

the mean free path of the sputtered material. Finally, the sputtered species hit the chamber walls or the substrate where the film develops.

The sputtering technique used in early sputtering is called diode sputtering. It has the benefit of sputtering from the whole target whereas magnetron sputtering does not, as explained in next subsection. However, it has some significant drawbacks. The sputtering rate is much lower compared to magnetron sputtering. Typically a few 100 Å/min for metals with diode sputtering compared to up to μm/min for some metals using magnetron sputtering.⁸⁶ Consequently, magnetron sputtering is the preferred technique today.

3.2.2 Magnetron Sputtering

Magnetron sputtering uses similar setup as DC sputtering with the distinct difference that magnets are positioned behind the target. In a lab system, they are typically cylindrical and most commonly placed in an outer circle with one magnet, or solid piece of iron, in the middle as demonstrated in Figure 3.2 (a). The central magnet and outer magnets have opposing poles creating a magnetic field as visualized in Figure 3.2 (b) and (c). The effect of this magnetic field is that electrons are confined close to the target which in turn enhances the plasma density. The densification of the plasma greatly enhances the sputtering rate and forms a racetrack on the target. This means that more material per second will be sputtered away than for diode sputtering and a lower operating sputtering gas pressure is achievable, increasing the chance for the sputtered species to reach the substrate while also retaining more of its original energy. All these effects result in a high deposition rate and faster film growth. The magnets are often configured in an unbalanced type II mode, where the middle magnet is weaker than the other ones, shown in Figure 3.2 (b). The reversed configuration (type I) is shown in 3.2 (c). Type II configuration is more common because this allow some electrons to escape the magnetic field of the magnetron and move closer to the substrate where they can ionize sputtering gas atoms. By applying a bias voltage to the substrate, these ions can be attracted to the growing film surface to stimulate the adatom mobility and hence the microstructural evolution of the film.

Fig. 3.2. Schematic view of magnetron top view (a) and a slice of the magnetron and the formed magnetic field from type II configuration (b) and type I configuration (c).

3.2.3 Reactive Sputtering

For reactive sputtering, a mixture of Ar and O₂ gas was used in the present work. Other common reactive gases are N₂, C₂H₂ and CH₄ used for deposition of nitrides and carbides, respectively. The addition of O₂ allows the direct deposition of the desired oxide film on the substrate. However, the presence of reactive gas in the chamber drastically reduces the sputtering rate due to so called poisoning of the target. The target readily reacts with the reactive gas, forming an electrically insulating layer on the target surface, which dramatically reduces the sputtering rate. As an example, the relation between poisoning of a Ca target and O₂ flow was studied by investigating the target voltage as a function of O₂ flow, as shown in Figure 3.3.

Fig. 3.3. Poisoning study on Ca target.

At O₂ flow below 0.5 sccm, the target is in metallic mode. Above 0.5 sccm, the target undergoes a rapid change to poisoned mode due to the complete oxidation of target surface at O₂ flows of around 1.25 sccm. This results in steep change of target voltage to a saturated value. However, with further reduction of O₂ flow the decrease in target voltage does not follow the same path as before, resulting in hysteresis as seen in Figure 3.3. The challenge with reactive sputtering is to control the stoichiometry of the film. Sputtering in the transition region, generally, results in high quality films with high sputtering rates. This is not easily

achievable in our system as the process is unstable and the target is easily poisoned. Small fluctuations of O₂ flow can result in target poisoning, and the recovery of the target to metallic mode becomes impossible without reducing the oxygen flow. However, in industrial applications, the use of feedback control system enables the process to be stable in the transition region.

3.2.4 Pulsed DC sputtering

Pulsed DC magnetron sputtering is a technique where a pulsing unit is used in conjunction with the DC unit to generate a pulsed DC voltage. The frequency is optimized for different target materials and condition and is commonly in the range of a couple tens of kHz to ~200 kHz. The pulse can be controlled by a few parameters, e.g., frequency, on time, and reverse voltage. Figure 3.4 illustrates how the different parameters influence the waveform. Pulsed DC sputtering is commonly used when sputtering in a reactive environment where an insulating layer is built up on the target (e.g., oxide in my study) effectively reducing the sputter rate or even killing the process altogether. To discharge the built-up charge on the target the applied voltage is reversed for a short time. The waveform of the pulse is different for different elements as the nature of the insulating layers are different for different elements and different reactive gases.

Fig. 3.4. Typical waveform for pulsed DC sputtering at 100 kHz with a 90 % on time and 10 % reverse voltage.

3.2.5 Radio Frequency Sputtering

RF is a sputtering technique where, instead of a DC current, an alternating current (AC) is used. The AC prevents charge build-up on the target and is therefore commonly used when sputtering isolating targets. A frequency of a few MHz is needed to efficiently use AC during sputtering and 13.56 MHz is a reserved frequency for RF sputtering. At low frequencies, roughly below 1 MHz, the ions have enough time to DC sputter for each half cycle meaning that the target and substrates alternate between being a cathode and an anode which is unwanted during sputtering. To understand the mechanisms of RF sputtering, it is important to remember that the plasma consists of free electrons and ions, and electrons are much more mobile than ions. That means electrons readily respond to an AC. The fast electrons move back and forth with the AC frequency and this movement causes collisions as described in 3.2.1. Therefore, the plasma does not depend on electrons generated from the ion bombardments on the target to stay ignited. The plasma is sustained by electrons going back and forth in the plasma, but how does the actual sputtering occur if the electrons are vibrating and ions immobile? This is because there is an additional effect due to the faster movement of the electrons and that is the self-biasing. Essentially, during the positive cycle the much more mobile electrons are drawn fast to the electrode. During the negative cycle the ions are instead drawn to the electrode. However, these are much slower, and a lower current of ions are drawn as compared to the electrons. This causes an imbalance in the net charge. To compensate for this a negative self-bias occurs, meaning the RF signal is moved to more negative characteristics.

Despite the advantages, RF sputtering has some drawbacks, it requires expensive equipment, and the sputtering rate is lower.

3.3 FILM GROWTH

The microstructural evolution during film growth is very important since it highly affects the end results of the film, e.g., its mechanical, electrical, and optical properties. There are three different stages of the film growth:

1. Condensation and nucleation
2. Coalescence
3. Continuous growth

In the first step, the adatoms condensate on the surface and either the adatoms recombine with the gas or diffuses on the surface and merges with other adatoms/clusters and eventually forms a stable nucleus. The critical size of the nucleus depends on the free energy of the volume and surface tension between film – vapor, film – substrate, and substrate – vapor. Initially, the free energy change of the system is increased due to the increased interface tension. However, at critical radius the free energy gain from going from vapor to solid is overcoming the increase in free energy due to the interface tension and a stable nucleus is formed.

The second step is coalescence, where the islands merge forming larger islands until the surface is completely covered. During this process, adatoms can land on the islands or on the exposed surface. There are three growth modes that can occur, Volmer-Weber, Frank-van der Merwe and Stranski-Krastanov. If the surface tension between film and vapor is high compared to substrate and vapor, the resulting growth mode is Volmer-Weber, meaning 3D growth of the islands. If the case is reversed the film is grown layer by layer as in the Frank-van der Merwe mode. The last mode, Stranski-Krastanov, is somewhere in between the two extremes. The growth is in layer-by-layer mode until a critical energy is built up due to, e.g., substrate-film lattice mismatch and 3D growth begins.

Fig. 3.5. Adatom recombination and nucleation and different growth modes.

The energy of the adatoms can be controlled by the deposition temperature, sputtering gas pressure, and/or the ion bombardment by adjusting the applied substrate bias voltage. Figure 3.6 (structure zone diagram of Anders) illustrates the effect of an increasing homologous temperature² and increasing kinetic energy of arriving species on the microstructure of the film.^{87,88} At low temperatures, the film is grown in a hit and stick mode where little or no diffusion occurs, and the resulting film is amorphous and under-dense. As the substrate is thermally energized, the adatoms can diffuse and form stationary grains in relation to the substrate (zone T). Competing growth occurs and the final film is structured with a preferred orientation. In zone II, sufficient energy is provided to the grains to migrate, where minimization of energy is the driving force and columnar grains are formed. In zone III, the film is composed of 3D grains showing that, at high temperatures, the crystal growth can be stopped periodically.

² Homologous temperature is the temperature of a material divided by its melting temperature in Kelvin.

Fig. 3.6. Microstructural evolution as a function of the homologous temperature and kinetic energy of arriving particles. From ref. ⁸⁸ © Elsevier B.V., reproduced with permission.

3.4 EPITAXY

Thin films are commonly grown with an epitaxial relation with the substrate. The simplest epitaxy is homoepitaxy where the substrate and film are the same material. This can result in a perfect lattice match between film and substrate and the film is promoted to follow the texture of the substrate. Homoepitaxy can be of great benefit to grow films with low number of defects at either high purity or with low amount of doping. The other common epitaxy is heteroepitaxy where the substrate and film are of different materials. This has a wide variety of benefits. By carefully choosing the substrate different textures, structures and even metastable structures can be promoted. Homoepitaxy is often associated with strained films. The strain can be utilized for changing properties of the films, for good and bad as dislocations are common. Another issue, related to the strain, is the difference in thermal expansion coefficient of the film and substrate. The film is often grown at elevated temperatures and a large difference in thermal expansion coefficient can result in high stresses and even adhesion failure of the film.

The bond between film and substrate in homoepitaxy and heteroepitaxy is driven by strong chemical forces (ionic and covalent bonds) where the atoms share electrons to form the strong bonds. In recent years, an interest in a weaker interaction between substrate and film has been growing.^{89,90} This interacting is called van der Waals forces and these forces are governed by the polarization of the atoms/molecules. The epitaxy is then called van der Waals epitaxy when there are only weak forces bonding the film to the substrate.⁹¹ There are several appealing benefits of van der Waals epitaxy. The weak interaction allows for large lattice mismatch between film and substrate without any high associated stresses in the film which would normally exist in heteroepitaxy. This is especially attractive for electronics as many components have great demands on the quality (low number of defects) and purity. The weak bonding with the substrate also allows for easy transfer to another substrate.

In my studies, muscovite (mica) was used to promote van der Waals epitaxy. Mica was used because it exhibits natural van der Waals layers within the structure. This means that it is possible to prepare surfaces with no dangling bonds on the substrate. This can be achieved for many other

substrates, e.g. other layered substrates with natural van der Waals layers⁹⁰, conventional substrates where either the surface is coated by a 2D layer, e.g. graphene,⁹² or the surface has been terminated of the dangling bonds⁹³.

A mix between conventional epitaxy and van der Waals epitaxy also exists, called quasi van der Waals epitaxy. It is commonly achieved when growing 3D material on 2D substrates which can result in weak chemical bonding between substrate and film that is stronger than van der Waals epitaxy but much weaker than conventional epitaxy. Figure 3.7 shows examples of conventional epitaxy in (a), van der Waals epitaxy (b) and quasi van der Waals epitaxy in (c).

Fig. 3.7. Schematic illustration of conventional epitaxy in (a), van der Waals epitaxy in (b) and quasi van der Waals epitaxy in (c).

3.5 PHASE TRANSFORMATIONS

The phase of a system is governed by the Gibbs free energy (G). Basically, the system strives to lower its global Gibbs free energy. An example of a phase change can be described by Figure 3.8. The system is in metastable state 1 and needs a certain energy, G_e , to overcome an energy barrier for the phase transformation to state 3 to occur.⁹⁴ In state 3, the total energy is minimized, leading to the formation of a more stable material. The added energy is commonly, but not necessarily, from heating the material.

Fig. 3.8. Example of a Gibbs free energy curve for a system with different energy states.

There are other reasons for phase transformations as well. For the transformation of $(\text{Ca,Mn})\text{O}$ to CaMnO_3 in this thesis, the added oxygen in combination with heat are the key components. It is unlikely that the material would change to the perovskite phase without surplus oxygen, as can be understood as the material goes from 50 % to 60 % oxygen. It is also common for oxides to lose oxygen during annealing, which adds another level of complexity to the phase diagram. Take the CaMnO_3 system as an example. It is believed that it undergoes two phase transitions during annealing between 800°C and 1000°C. The first transition, to tetragonal phase, occurs at around 896°C, and the second, to the cubic phase, at 913°C.⁹⁵ The exact temperature varies with, among other things, the oxygen deficiency. So does the intermediate structure as

there are reports that the tetragonal phase does not appear for oxygen deficient CaMnO_3 . Another possibility is described in ref ⁹⁶, where the material undergoes a phase transition from orthorhombic to the cubic crystal structure by order-disorder phase transition. Resulting in a structure that is oscillating between different tilt states in the Pnma structure that on average correspond to the cubic structure.

4 THEORY ON X-RAYS

4.1 INTRODUCTION AND BACKGROUND

Wilhelm Conrad Röntgen is credited as the discoverer of x-rays in 1895 and won the Nobel Prize in 1901. X-rays are electromagnetic radiation with a wavelength on the order of 0.01 to 10 nm, corresponding to energies of about 100 eV to 100 keV. This wavelength is of the same order as the atomic distances in crystals, which give them unique properties for structural characterization of crystalline materials which will be shown in this chapter.

4.2 X-RAY INTERACTION WITH MATTER

X-rays interact with matter in many ways. However, not all are relevant in this context and are therefore not described. The interactions covered in this chapter are absorption, scattering and refraction.

4.2.1 Absorption

Photoionization is the main contribution to the absorption of x-rays in matter. As x-rays propagate through a material, core electrons can absorb the x-ray energy and be excited to a higher electronic state or be expelled from the material. This interaction causes energy losses of the x-ray radiation which follows Beer-Lambert law:

$$I(x) = I_0 e^{-\mu x} \quad 4.1$$

where $I(x)$, I_0 , μ and x are the intensity at depth x , initial intensity, linear absorption coefficient, and the distance travelled inside the material, respectively. The linear absorption coefficient, μ , depends on both the material and wavelength/energy of the photon and can be calculated using eq. 4.2.

$$\mu = \frac{N_0 \rho_m \sigma_a}{A} \quad 4.2$$

where N_0 , ρ_m , σ_a and A are Avogadro's number, mass density, absorption cross section and atomic weight, respectively. The material dependence in eq. 4.1 is obvious, but the photon energy not so. σ_a depends on both the atomic number and the photon energy and varies several orders of magnitude with energy of photon and binding energy of electrons in different shells.⁹⁷ This strong relation is utilized in x-ray absorption near edge structure (XANES) measurements.

4.2.2 Scattering

I will only consider elastic scattering (Thomson scattering) in this section, because it is the most relevant scattering mechanism for x-ray characterization techniques. The reason inelastic scattering (Compton scattering) is of less importance for this thesis is that it does not contribute to Bragg peaks due to change in wavelength/energy. Instead, it is detected as a background noise.

In the case of elastic scattering the incoming x-rays have an oscillating electric field perpendicular to the traveling direction. This field interacts with the electrons in the material and causes them to oscillate at the same frequency as the incoming x-rays. The oscillations of the electron create an electric field which scatters the x-rays and this is called Thomson scattering.⁹⁸ The scattered intensity is described by eq. 4.3 for an unpolarized x-ray beam:

$$I = I_0 \frac{r_e}{r^2} \left(\frac{1 - \sin^2 2\theta}{2} \right) \quad 4.3$$

where I_0 , r_e , r , θ are the intensity of the incident beam, the classical electron radius, distance from the scattering center, and angle of scattering, respectively, as seen in Figure 4.1.

Fig. 4.1. Coherent scattering on an electron.

4.2.3 Refraction

Refraction is commonly used in visible light applications and is described by Snell's law, eq. 4.4 and Figure 4.2.

$$n_1 \sin \theta_1 = n_2 \sin \theta_2 \quad 4.4$$

Fig. 4.2. Schematic view of refraction.

There is, however, an important difference between visible light and x-rays. The index of refraction (n) is negative and close to unity for wavelengths in the x-ray region. This means that the x-rays only weakly refract at interfaces between different media, making lenses ineffective as focusing optics. Another limiting factor is the high absorption of x-rays. Lenses can, even with these limiting factors, be used. The lens is inverted, that is, the lens is in vacuum, and the surrounding material is a low absorption material. The percent reflected is also very low for x-rays because the index of refraction is close to unity, which makes mirrors ineffective (with the exception at low angles (see chapter 4.5.3)).

4.3 CRYSTAL STRUCTURES

A crystal can be defined as a basis (set of atoms) in an infinitely repeating three-dimensional lattice structure. The simplest case, a cubic lattice with one atom as the basis, is illustrated in 2D in Figure 4.3.

Fig. 4.3. Illustration how a basis with a lattice describe a crystal.

Because of the intrinsic nature of a crystal, the infinite repetition of the lattice, it is possible to define a unit cell made up of three vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ which, by translation of integers m_1 , m_2 and m_3 can describe the whole crystal. A unit cell can be either primitive or non-primitive. The distinction between them is that a primitive unit cell only contains one lattice point while non-primitive contains more than one. Figure 4.4 illustrate how a face centered cubic (FCC) cell (a) can be explained with a primitive cell (b). The primitive cell is much more cumbersome and harder to work with and therefore the FCC variant is used instead.

In total, there are 14 so-called Bravais lattices in three dimensions obtained by coupling the 7 crystal systems with slightly different lattice

atomic arrangements. As an example, the cubic system has three different possible atomic arrangements; primitive, body-centered, and face-centered. Each Bravais lattice refers to a distinct lattice type and describes the possible translational symmetries in a periodic crystal.⁹⁹

Fig. 4.4. The FCC cell (a) and the primitive version of the same (b).

Now we have a tool to describe what a crystal is and the structure it possesses. William Miller developed the Miller indices (hkl) which describe planes and directions in the crystal structure. Miller indices are integers which are reciprocal values of the real space distances. The plane in Figure 4.5 (a) intercepts a at 1, b at infinity and c at infinity. The reciprocal of this gives $h=1$, $k=0$ and $l=0$, and the plane is denoted as the (100) plane. If the plane is instead at $a=1/2$, b at infinity and c at infinity the corresponding Miller indices are (200). This way of describing planes avoid the use of infinity and fractions.

Fig. 4.5. Illustrating the (100) (a) and (200) (b) plane.

When x-rays are incident on a material, they can be scattered off the atomic planes. The scattered x-rays from different atomic planes can interfere constructively if Bragg's law is fulfilled (eq. 4.5), as illustrated in Figure 4.6. Thus, by using x-ray diffraction the distance between atomic planes in a crystal can be measured.

$$2d \sin \theta = n\lambda \quad 4.5$$

Here d , θ , λ and n are the atomic plane spacing, the angle between sample and incident x-rays, wavelength, and integer.

Fig. 4.6. Illustration of Bragg's law.

It turns out that it is not only Bragg's law that needs to be fulfilled for constructive interference and a diffraction peak to appear in an x-ray diffraction (XRD) measurement, also the so-called structure factor (F) plays a major role. It is defined as:

$$F = \sum_j f_j \exp(-i\mathbf{G} \cdot \mathbf{r}_j) \quad 4.6$$

where f_j , $\mathbf{G}$ and $\mathbf{r}$ are the atomic form factor, reciprocal lattice vector and distance vector to atom j ,⁹⁹ and it takes into account the internal distribution of atoms in the unit cell and describes the amplitude and phase of a wave diffracted from a crystal lattice. The reciprocal lattice vector is equal to:

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \quad 4.7$$

where $\mathbf{b}_i$ are axis vectors in the reciprocal lattice. The reciprocal lattice vector is related to d in the following way:

$$d = \frac{2\pi}{|\mathbf{G}|} \quad 4.8$$

Multiplying a reciprocal lattice vector with a real space lattice vector has the following relation:

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi\delta_{ij} \quad 4.9$$

Where the delta function is 1 when $i = j$ and otherwise 0. Using this relation, it can be understood that eq. 4.6. can be rewritten to:

$$F = \sum_j f_j \exp(-i2\pi(hx_j + ky_j + lz_j)) \quad 4.10$$

where h , k and l are the miller indices and x , y and z are the atomic positions of the base. For example, the FCC has atoms at position $(0,0,0)$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ and which results in the following form factor:

$$F = f(1 + \exp(-i\pi(h + k)) + \exp(-i\pi(h + l)) + \exp(-i\pi(k + l))) \quad 4.11$$

From this, it is clear that some hkl combination will result in $F=0$, which means zero intensity (a forbidden reflection), even though Bragg's law is fulfilled.

4.4 LABORATORY X-RAY DIFFRACTOMETER

4.4.1 X-ray Generation in lab-scale instruments

X-rays are generated in x-ray tubes, schematically illustrated in Figure 4.7. The tungsten filament in the x-ray tube is heated up by a current to temperatures where the electrons are leaving the material by thermionic emission. The electrons are accelerated to the anode by the applied bias. As the high energy electrons strike the target, two types of x-rays are generated. One part is from the continuous deceleration of electrons (generating the Bremsstrahlung continuum) and the other is the ionization process. The ionization process is when a core shell electron is excited, an electron falls back to the core shell and energy in the form of characteristic x-rays are released. Commonly a copper anode is used as the x-ray source and the two processes earlier described generate an x-ray spectrum as shown in Figure 4.8. The generated x-rays exit the x-ray tube through a beryllium window. The production of x-rays is inefficient (typically less than 1%) and most of the energy from the electrons is transformed to heat and the x-ray tube is therefore cooled with water.

Fig. 4.7. Schematic drawing of an x-ray tube.

Fig. 4.8. Image of intensity of characteristic x-rays, Bremsstrahlung, and cut-off wavelength of the Ni-filter.

4.4.2 Optics

X-ray optics can be split into two different sections, conditioning, and selective optics. Conditioning optics are focusing the beam while selective optics cuts off intensity to lower the divergence. Mirrors and capillary lenses are conditioning optics, while slits, masks, filters, crystals, and parallel plate collimators are selective in nature.

4.4.2.1 Slits

Slits are simple optics where a small rectangular opening is used which selects which part of the beam can pass. Typically, a slit on the incident path is used to select the divergence of the beam, here care should be taken to make sure the x-rays are confined to the sample dimensions. To determine the 2θ resolution, a receiving slit is used before the detector, this influences the instrumental peak broadening. To reduce the background from air scattering and other stray x-rays an anti-scatter slit is commonly used on either side of the sample. The divergence perpendicular to the x-rays is limited by the use of Soller slits which are several plates stacked together which only accept x-rays with an angle depending on the spacing and length of the plates. A mask can also be

used to limit the width of the x-ray beam to reduce artefacts from the holder.

4.4.2.2 Filter

A filter is typically used on either side of the sample in order to produce monochromatic x-rays. The filter is made of a material that has an absorption edge between the characteristic peaks of K_{β} and K_{α} (see Figure 4.8). Typically, this material has atomic number $Z-1$ if the source (target) material has atomic number Z . For this reason, a Ni-filter is used in conjunction with a Cu source and blocks x-rays with energies higher than $\text{Cu-}K_{\alpha}$. This effectively removes the $\text{Cu-}K_{\beta}$ radiation at the cost of about half the intensity of the $\text{Cu-}K_{\alpha}$.

4.4.2.3 Crystal Optics

An alternative to produce monochromatic radiation is to use a set of single-crystals. The monochromator works by diffracting only the wavelength that fulfills Bragg's law for the particular atomic plane spacing of the monochromator crystal. The same devices can be used before the detector for the examination of the direction of diffracted x-rays and they are then called crystal analyzers.

4.4.2.4 Parallel Plate Collimator

The use of a parallel plate collimator is similar to that of Soller slits, but they are rotated 90° to be parallel with the scattering plane. The benefit of using parallel plate collimators is that not only does the optics limit the divergence it only let parallel x-rays pass. The parallel plate collimator determines the resolution of the diffraction angle in the experiment.

4.4.2.5 Mirror Optics

An x-ray mirror is used to collect divergent x-rays from the x-ray tube and make them parallel and directed towards the sample. A mirror is therefore very different for x-rays compared to visible light. An x-ray mirror consists of a multilayer stack with alternating high and low refractive index materials. The stacks get thicker and thicker, and the interfaces must be extremely smooth which make them hard to manufacture. The mirror reflects all x-ray wavelengths to give a high intensity on the sample, but it does not make the x-rays monochromatic.

For this reason, sometimes, mirrors are combined with crystals, so called hybrid mirrors, to achieve a monochromatic high intensity beam.

4.4.2.6 Capillary Optics

Capillary optics have a similar role as the mirror but are used when the same beam divergence is required in all directions, not only in the scattering plane. Instead of having a multilayered mirror the x-rays are guided through thin capillaries which produce a parallel circular beam. Usually used together with point focus.

4.5 MEASUREMENT TECHNIQUES

4.5.1 $\theta - 2\theta$ Measurements

The most common measurement technique is the $\theta - 2\theta$ measurement. It is used to identify the phases of the material and gives information of planes parallel to the surface. It is a symmetrical measurement where the incident angle and diffracted angle is equal throughout the measurement. When the x-rays interfere constructively, i.e., when Bragg's law is fulfilled, and the structure factor is nonzero, a diffraction peak will appear in the diffractogram.

Fig. 4.9. Example of a $\theta - 2\theta$ diffractogram from paper 2 of a Nb alloyed CaMnO_3 film grown on Al_2O_3 substrate.

The measured peak profile is a convolution of the sample broadening and the intrinsic instrumental broadening which depends on the chosen x-ray optics. An example of this measurement can be seen in Figure 4.9.

The position of the peaks gives information about the atomic plane spacings, which is related to the crystal structure. Peak broadening can be related to the grain size and microstrain, while peak shifts can be attributed to e.g., stoichiometry changes (elements) and macroscopic stresses in the material.

4.5.2 GIXRD

Grazing incidence x-ray diffraction (GIXRD) is similar to $\theta - 2\theta$ with the difference that the incidence angle is fixed at low angles. This allows the x-rays to be confined to a few hundred nm instead of a few μm in depth. This is especially useful for thin film measurements where the film can be a few nm thick only. The drawback is, however, that the measured planes are not in the same direction but will change continuously during the measurement.

4.5.3 XRR

X-ray reflectivity (XRR) is conceptually different. It does not rely on diffraction, instead the x-rays are reflected at the interfaces between two different media with different x-ray optical properties, see Figure 4.10. The reflected x-rays interfere constructively if Bragg's modified law is fulfilled:

$$2D \sin \theta \sqrt{1 + \frac{\eta^2 - 1}{\sin^2 \theta}} = m\lambda \quad 4.12$$

where D , η and m is the film thickness, complex refractive index of the material and the reflection order (integer), respectively.

Fig. 4.10. Illustration of an XRR measurement.

Fig. 4.11. Example of an XRR measurement from paper four of a 21 nm thick VO_2 film on mica.

Figure 4.11 shows a typical reflectivity profile when performing an x-ray reflectivity measurement of a thin film. At low angles, as a result of a refractive index below unity for x-rays, total external reflection occurs and at the critical angle, which is related to the electron density, the reflected intensity drops. The observed oscillations beyond the critical angle are called Kiessig fringes and the distance between two maxima (or minima) is determined by the thickness of the sample. This measurement has a few limits: the film should be thinner than about 100 nm, the surface and interfaces should be smooth enough to give specular reflection of the

x-rays, and there should be a sufficient x-ray optical contrast between the film and the substrate, i.e., they cannot have too similar refractive indices.

4.5.4 Pole Figure

A pole figure is a measurement where the orientation of a particular atomic plane is mapped out with respect to the sample orientation. In this measurement the incident and diffracted beam angles are kept constant, set to a specific plane spacing, while the sample is rotating 360° in ϕ during the measurement, this is repeated for several ψ tilts up to 85° . Figure 4.12 shows a representative pole figure, where the poles give information about the orientation of the investigated planes. Combining pole figures from the film and the substrate can be used to determine to the epitaxial relationship between the film and the substrate.

Fig. 4.12. Example of pole figures from paper one on the CaMnO_3 film grown in sapphire where (a) is performed on the 121 pole and (b) is performed on the 202 pole.

4.5.5 Reciprocal space mapping

Reciprocal space mapping (RSM) is a technique where a set of scans are utilized to map out an area in reciprocal space, e.g., a set of 2θ scans at different, but closely spaced, ω . This is performed around an area of interest, e.g., a diffraction spot. The available diffraction spots are limited by geometrical limitation (half circles shown in Figure 4.13. (a) and (b) and energy of the x-ray (radius of the Ewald's sphere/length of the k vectors). This can be performed in symmetry ($\omega = \theta$) or asymmetry ($\omega \neq$

θ), illustrated in (a) and (b), respectively. This measurement results in an intensity map as shown in (c) for the symmetric 040 peak of VO₂ and (d) for the asymmetric 130 and 031 peak of VO₂.

Fig. 4.13. Schematic image of Q space and how a measurement of symmetric peak (a) and asymmetric peak (b) is performed. RSM maps of symmetric 040 VO₂ reflection is shown in (c) and asymmetric 130/031 VO₂ reflection is shown in (d).

The maps are analyzed by peak position, FWHM and shape. Real space (d distances) and reciprocal space (q distances) are related by eq. 13.

$$q = \frac{2\pi}{d} \quad 13$$

In symmetric maps, the FWHM in z (Δq_z) is the vertical correlation length. The FWHM in x (Δq_x) is a combination of lateral correlation length and mosaicity³. This changes slightly in asymmetric mode as the mosaicity contribution causes a tilt of the RSM, meaning the mosaicity contributes to a broadening in both q_x and q_z . It is possible to deconvolute the lateral correlation length and mosaicity. By analyzing the Δq_x of several symmetric maps as the broadening from the lateral correlation length is constant while the mosaicity contribution is increasing for higher order reflections. The asymmetric RSM can be analyzed following the steps in ref. ¹⁰¹. RSM is also commonly used for analyzing film growth where the structures are closely matched and the relaxation and strain can be deduced, e.g., InGaN/GaN films.¹⁰²

³ The mosaicity of a material, in our case a thin film, is the spread of small variations between grain orientation, causing small $\Delta\phi$ and $\Delta\omega$ spread in orientations of the grains.¹⁰⁰ Note that these variations in ϕ and ω should be small and the grains should be connected by dislocations. If $\Delta\phi$ or $\Delta\omega$ gets too large the mosaicity is better described as texture.

5 DEFECTS

Thin films, and materials in general, are never perfect. The crystal lattice always contains imperfections in the form of defects. They can form during the sputtering process due to impurities, e.g., poor vacuum pressure and low grade targets that contain impurities. Defects also form due to stress from lattice mismatch, low adatom energies or many other reasons. Defects can be divided into point defects, line defects, planar defects, and bulk defects.

5.1 POINT DEFECTS

A point defect is essentially a change in the lattice that is related to changing one atom only. Even though only one atom is exchanged, it can have significant effects on the macroscopic properties. Examples of point defects are vacancies, antisites, impurities and interstitials. Vacancies are empty lattice points in the solid. The neighboring atoms will either be attracted or repelled from the vacancy causing a distortion in the crystal surrounding the vacancies. Vacancies occur naturally in all crystals. An antisite defect is formed when, e.g., a Mn ion is in the Ca ion site in CaMnO_3 . An impurity defect is similar to the antisite defect, for example an impurity defect is a Mn ion replaced by a Nb ion in CaMnO_3 . The difference between antisite defect and impurity is whether the defect atom is part of the macroscopic crystal normally or not. Impurity defects are commonly utilized to change the properties of the material. By adding small amounts (doping or alloying) of a new element the electrical properties can drastically change as in semiconductors. An interstitial defect is an atom in between lattice points in the crystals. They are usually small atoms to fit inside the lattice. Example of all point defects is shown in Figure 5.1.

Fig. 5.1. Example of a crystal lattice with point defects.

5.2 LINE DEFECTS

Line defects, or commonly called dislocations, are common in crystals. They are, as the name suggest, one-dimensional defects and are divided into edge dislocations and screw dislocations. Edge dislocations are formed by inserting an extra plane in the crystal. They can form as a result of lattice mismatch where an extra plane is formed in the film to release the associated strain, see Figure 3.7 (a). The screw dislocations can be formed due to sheer stress where a part of the lattice is shifted in regard to the surrounding as shown in the schematic Figure 5.2.¹⁰³

Fig. 5.2. Schematic illustration of a screw dislocation.

5.3 PLANAR DEFECTS

Planar defects are boundaries in the crystals, either separating grains or inside grains. Some examples of planar defects are grain boundaries, stacking faults, twin boundaries, and antiphase boundaries. Grain boundaries are formed when islands meet during the growth process. The islands can have different crystallographic orientations resulting in high or low angle grain boundaries. Controlling the grain boundaries is often important for applications as they are barriers for all kind of diffusions, propagations, and conductivities. For instance, grain boundaries act as scattering centers for electrons and phonons. Having large grains with small angle difference is therefore important for electrical conductivity.

Stacking faults, twin boundaries, and antiphase boundaries are all related to how the atomic planes are stacked. A closed packed structure, ABABAB or ABCABCABC as shown in Figure 5.3, with the wrong stacking order in the crystal is a planar defect. For example, a stacking fault can be as follows; ABABCAB. Here the normal stacking sequence is ABAB and a stacking fault at the C position is introduced in the lattice. The antiphase boundary is instead described as follows; ABABBAB. Here there is an extra B stack in the lattice. Lastly, the twin boundary can be described as a mirrored stacking; ABCABCBACBA.

Fig. 5.3. Example of closed packed structure where (a), (b), and (c) illustrates the A, B, and (c) position, respectively.

In paper 3, the antiphase boundary is observed, see Figure 5.4 which shows the stacking ABAB where A is Ca (darker atoms) and B is Mn (brighter atoms). At some point there is a change in the stacking (ABAABA). At this antiphase boundary, an increase in cation-cation distance is seen. The reason for the formation is the lattice mismatch between film and substrate causing tensile strain in the film.

Fig. 5.4. Micrograph of CaMnO_{3-y} where bright spots correspond to Mn ions and darker spots correspond to Ca ions. A dark line in the middle surrounded by Ca ions is shown, corresponding to an antiphase boundary.

6 STRUCTURAL AND COMPOSITIONAL CHARACTERIZATION

6.1 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) is an imaging technique where an electron beam is used to scan the surface. The incident electrons generate several different species. The ones commonly used for imaging are the backscattered electrons (BSE) and the secondary electrons (SE). The BSE are the electrons from the incident beam that have been backscattered due to interaction with the specimen. The probability for backscattering is higher for heavier elements and is therefore useful for imaging composition. The SE are electrons from the specimen that have been knocked out due to interaction with the incident electron beam. The SE are insensitive to composition but are useful for topographical imaging as they originate from the first few nm of the specimen.¹⁰⁴

6.2 TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy (TEM) is similar to SEM in the sense that an electron beam is used in both cases to analyze the sample. They are, however, probing different length scales and TEM operates in transmission mode. SEM has a spatial resolution in the nanometer region while TEM can image individual atoms. TEM requires special film preparation because the specimen has to be electron transparent. It is also possible to use TEM to do electron diffraction which, similar to XRD and electron backscatter diffraction in SEM, can reveal the structure of the sample. The drawback with TEM is that it requires rigorous preparation of the specimen and that only local information is possible to extract from the sample, and this might not represent the whole sample.

The TEM can be operated in different modes. In my thesis TEM mode and scanning TEM (STEM) mode are used. In short, the difference is how the beam is focused inside the microscope. In TEM, the electron beam is perpendicular to the specimen when interacting with the specimen. The electrons transmitted through the specimen are scattered. The scattered electrons are collected by lenses to focus on a camera so that the electrons

that interacted at the same point of the specimen are focused at the same point on the camera, creating an image representing the specimen. In STEM, the electron beam is focused on the specimen and scanned over the specimen similar to SEM. The scattered electrons are collected at an angle from the main beam. Depending on the angle different contrast can be achieved as the scattering angle is increasing with Z . High angle annular dark field (HAADF), imaging sometimes called Z -contrast imaging as it is highly sensitive to the atomic number, is one of the modes in STEM.

It is possible to do compositional analysis in TEM and STEM by energy dispersive x-ray spectroscopy (EDS) or electron energy loss spectroscopy (EELS), described more in detail below.

6.3 X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy (XPS) is a chemical analysis technique where the sample is irradiated with an x-ray beam which excites core shell electrons above the vacuum level, meaning leaving the material. The excited electrons are measured, both in quantity and kinetic energy. The kinetic energy (E_k) depends on the energy of the x-ray radiation ($h\nu$), binding energy of the electrons (E_b) and work function of the detector (ϕ) as shown in eq. 6.1.

$$E_k = h\nu - E_b - \phi \quad 6.1$$

The binding energy is characteristic for each element and all other constituents are known or measured in eq. 6.1. Thus, the elements in the material can be determined, and the number of electrons collected can be used for quantification.

XPS can also be used to analyze the chemical state and bonding of the atoms. For instance, different valence states of an element will have different binding energy meaning XPS is sensitive to the chemical state of the atoms. XPS can also be used to do depth profiles for the above-mentioned analysis. This is performed by using a sputtering gun to remove a few nm of material to reveal a surface deeper in the material to be analyzed.

6.4 ENERGY DISPERSIVE X-RAY SPECTROSCOPY

EDS is performed in a SEM or TEM. The incident electrons can, as previously mentioned, knock out electrons from the atoms. This leaves an empty state which gets filled by an electron in an outer shell. This process yields characteristic x-rays with energies unique for each element and corresponds to the difference in energy level of the different shells in each atom. The energy can also be released by the emission of an Auger electron.¹⁰⁴ The probability for the Auger effect is higher for lighter elements. This process is schematically described in Figure 6.1.

Fig. 6.1. Schematic illustration of characteristic x-rays and Auger electron generation.

The characteristic x-rays are collected in a detector which detects both the energy and the number of x-rays. The detector is a semiconductor (typically Li doped Si). An x-ray photon generates a photoelectron that in turn is generating electron hole pairs when moving inside the semiconductor. A cascade of events occurs, generating even more electron-hole pairs, until all of the energy is deposited into the detector. This charge is the fingerprint analyzed to determine the element inside

the specimen. A window protects the detector. This window, in older SEMs, was often made from beryllium, but today mostly a thin polymer window is used. Both types of windows limit the detection and quantification of light elements by EDS.

6.5 ELECTRON ENERGY LOSS SPECTROSCOPY

In EELS the energy loss due to sample interaction in the direct beam in TEM is analyzed. It is a powerful tool where the chemistry of the sample can be characterized. Ionization events of the core shell of the electrons in the sample can occur when exposed to the electron beam. The energy needed to ionize is highly dependent on the element. Meaning that the energy loss of the electron beam can be used as a fingerprint for analyzing the elements inside the sample. The fingerprint is sensitive to the chemical bonding of the atom and thus the oxidation state can be determined. EELS was utilized in my research to determine the elements seen in TEM and also determine the oxidation state of vanadium oxide at different areas of the film.

7 ELECTRICAL, THERMAL AND OPTICAL CHARACTERIZATION

7.1 FOUR-POINT PROBE

A four-point probe is used to measure the resistivity of a sample. It consists of four probes on a line as in Figure 7.1. The outer probes drive a current and the two inner probes measure the voltage difference. The reason for using four sensors is to avoid errors from contact resistance.

Fig. 7.1. Schematic top view (a) and side view (b).

The resistivity (ρ) can be calculated using eq. 7.1

$$\rho = \rho_s t = \frac{V}{I} t \frac{d}{s} C' * F \left(\frac{t}{s} \right) \quad 7.1$$

where ρ_s , t , V , I , d , s , C' and F are the sheet resistance, film thickness, measured voltage, induced current, sample width, distance between tips, correction factor for finite sample width, and correction factor for sample thickness, respectively. The correction factors depend on the sample geometry.¹⁰⁵ The correction factors are both close to theoretical values for infinitely thin and infinitely wide sample ($F \approx 1$ and $\frac{d}{s} C' \approx \frac{\pi}{\ln 2}$) and eq. 7.2. can be used.

7.2 VAN DER PAUW

The van der Pauw method is a more flexible method as compared to the four-point probe method as it is possible to measure arbitrary shaped thin films. Four probes in the edges of the samples are used as compared to the linear setup for four-point probe. As a result, an average sheet resistance of the sample is measured. The resistivity can be calculated by eq. 7.2. It is also possible to apply a magnetic field for Hall measurements.

$$\rho = \rho_s t = \frac{V}{I} t \frac{\pi}{\ln 2} \quad 7.2$$

Fig. 7.2. Schematic illustration of a van der Pauw measurement setup. A current is induced at one contact, e.g, A and extracted in either B or C contact (the current is run along the side of the specimen). The voltage at the opposite side is measured.

7.3 SEEBECK MEASUREMENTS

Figure 7.2 shows a scheme of a Seebeck coefficient measurement. Two thermocouples are mounted on the sample. They measure both the temperature difference and voltage difference. An electrical current can be passed through the sample for the measurement of electrical resistivity simultaneously with the Seebeck coefficient measurement in a single measurement run. During the measurement both sides of the samples are heated unevenly to maintain the same small temperature difference ΔT . The Seebeck coefficient is determined by the ratio in eq. 7.3.

$$S = \frac{\Delta V}{\Delta T} \quad 7.3$$

Fig. 7.2. Schematic view of a Seebeck measurement setup.

7.4 ELLIPSOMETRY

Ellipsometry is a non-contact measurement technique where the sample is illuminated by linearly polarized light. The interaction with the sample changes the polarization of the light. The polarization state induced by the sample is measured, and the data is modelled using different models depending on the specimen. Typically, the measurements are fast and straightforward while the modelling can be complex and time consuming. The data that can be extracted are plenty, e.g., thickness, refractive index, roughness, and more.

7.5 THERMAL CONDUCTIVITY MEASUREMENT

Determining the thermal conductivity experimentally of thin films is a nontrivial task. The measurement must determine the thermal conductivity of a thin film accurately while influenced by the much thicker substrate which it is deposited on. Two common techniques are the 3ω method and thermoreflectance.¹⁰⁶ Thermoreflectance is used in this thesis and utilizes the change in reflectance with temperature. A measurement setup is shown in Figure 7.3, where a pumping laser heats up a spot on the specimen, and a probing laser measures how the refractive index changes as the specimen cools down. A nm-thick metallic layer is commonly deposited on the films which absorbs the energy deposited by the laser and has a known reflectance change with temperature.

Fig. 7.3. Schematic view of a thermal conductivity measurement setup.

8 THERMOELECTRICS

8.1 BACKGROUND

The field of thermoelectrics started in 1821 with the rediscovery of the Seebeck effect by Thomas Johann Seebeck.¹⁰⁷⁻¹¹⁰ The effect was originally discovered by Alessandro Volta in 1794¹¹¹ but received no attention at the time. The effect observed by Seebeck was small and not much research was performed in the field until the 1950s when improved thermoelectric materials were synthesized from compound semiconductors.¹⁰⁷ A breakthrough in the thermoelectric field was achieved when the first radioisotope thermoelectric generator was used in the first space mission, Transit IV-A, in 1961.¹⁰⁷ Nevertheless, we are still not seeing thermoelectric technology taking a large role in power generation, even after its successes in remote power generation. This is mainly due to low efficiency and the fact that the best materials are tellurides for low- to mid-range applications and Si-Ge for high temperature applications.¹⁹ Tellurides are not suitable for mass production because they are toxic, expensive and, the biggest problem, rare on earth.¹⁸ Si-Ge working temperature range is in a range where there are very few applications.^{112,113}

A thermoelectric material is characterized by a high Seebeck coefficient (S), high electrical conductivity (σ), and low thermal conductivity (κ). These demands on material properties do not naturally draw oxides to mind, but they gained interest in the 1990's¹⁷ when some oxides, e.g. $\text{In}_2\text{O}_3\text{-SnO}_2$ and alloyed CaMnO_3 , were found to have good thermoelectrical properties. Thermoelectrics overall have had an increased interest in the last 20-25 years, which is due to improved synthesis methods, allowing researchers to control the materials on the nano to atomic level. Other contributions to the increased interest is the possibility to model complex materials and also characterize them experimentally.¹¹⁴

8.2 WORKING PRINCIPLE

A thermoelectric module consists of n- and p-type materials connected in series as seen in Figure 8.1. The charge carriers on the hot side move faster than on the cold side. This results in a net diffusion of charge carriers to the colder side, generating a current. Thus, thermoelectric power generation does not involve any moving macroscopic parts. Thus, it requires minimum maintenance and can reliably work over years and is therefore useful for remote applications, such as off-grid power generation and space missions.

Fig. 8.1. Schematic image of a thermoelectric module.

The efficiency is related to the dimensionless figure of merit ZT , eq. 8.1

$$ZT = \frac{\sigma S^2}{\kappa} T \quad 8.1$$

where T is the absolute temperature. S of degenerate semiconductors is inversely related to charge carrier concentration following the expression 8.2.

$$S = \frac{8\pi^2 k_b^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad 8.2$$

Where k_b , m^* , n , e and h are Boltzmann constant, the effective mass of the carrier, carrier concentration, charge, and Planck constant, respectively. σ is linearly related to carrier concentration and charge carrier mobility (μ) following the expression 8.3. The thermal

conductivity consists of a phonon (lattice) part and an electronic part, eq. 8.4. In thermoelectric materials, the contribution from phonons to thermal conductivity is usually dominant over electron contribution. The electron contribution scales with electrical conductivity as shown in eq. 8.5 where L is the Lorenz number.

$$\sigma = en\mu \quad 8.3$$

$$\kappa = \kappa_e + \kappa_p \quad 8.4$$

$$\kappa_e = L\sigma T \quad 8.5$$

Finding new materials with high ZT or improving existing ones has been a challenge for many years, and still is. The reason is that the different components that determines the ZT are correlated as seen in the above equations. By improving one component another is at the same time made worse. A common way to increase the ZT is by doping which increase the number of charge carriers (n). This increases σ , but S will at the same time decrease and an optimal doping level is found as seen in Figure 8.2.¹¹⁴

Fig. 8.2. The relation between carrier concentration and ZT , S , σ and κ is shown. From ref. ¹¹⁴ © Nature Publishing group, reproduced with permission.

Take note that there are two different optima in the above graph. Between carrier concentration 10^{19} and 10^{20} cm^{-3} , the ZT is optimized, while the power factor ($S^2\sigma$) is optimized at 10^{20} cm^{-3} . Both maxima are of

importance. Maximizing the efficiency is not always as important as maximizing the power output.

Another approach to increase the ZT is by grain boundary tailoring. The electrons have in general much shorter mean free path than phonons. By making a material with grains larger than the mean free path of electrons and in the range of phonons the scattering of phonons can be increased while the electrons are almost unaffected.⁴⁹ There are other approaches with the same basic idea, to scatter phonons, e.g. doping with heavy atoms or induce dislocations to act as a scattering centers and by making multilayers which can scatter phonons.

There are other possible applications for thermoelectrics than converting heat to energy or vice versa. They can also be used as the working material for other applications, e.g. as a thermocouple which measures the temperature, cold trap¹¹⁵ in ultra-high vacuum systems and hydrogen gas sensors¹¹⁶ where a reaction on the surface of the sensor generates heat which can be correlated with the amount of hydrogen in the air.

9 CONTRIBUTION TO THE FIELD

I have shown in **paper I** that it is a viable method to grow CaMnO_3 by a two-step approach. The synthesis method was co-sputtering using RF reactive magnetron sputtering with a post-annealing step. Growth on different faces of Al_2O_3 substrates (*c*-cut, *m*-cut, and *r*-cut) were investigated, where films on *m*-cut Al_2O_3 showed the highest power factor (PF) of $45 \mu\text{V/mK}^2$. The XRD and TEM analysis indicated that the film grown on *m*-cut Al_2O_3 had the best crystal quality which is connected to lower defect density and higher conductivity which was the main contribution to the difference in PF in this study. The influence of annealing temperature was also investigated, and it was seen that a temperature of 550°C is needed to form CaMnO_3 . Secondary orientation formation is present at all temperatures and are more pronounced at higher temperatures. This study has brought insight on the phase transition from $(\text{Ca,Mn})\text{O}$ to CaMnO_3 and the different stages of the transition at different temperatures.

In **paper II**, the CaMnO_3 films were alloyed with a few percent Nb ($\text{CaMn}_{1-x}\text{Nb}_x\text{O}_3$, $x = 0-0.10$). I found that the addition of Nb increased the film quality of both as-deposited films and annealed films. The PF is also enhanced 8 times for Nb content $x = 0.04$ to $21.6 \mu\text{V/mK}^2$ at room temperature, as compared to $2.7 \mu\text{V/mK}^2$ for pure CaMnO_3 films. This increase in PF is attributed to the increase in carrier concentration which increases the electron conductivity while decreasing the Seebeck coefficient. The increase in electrical conductivity outweighs the decrease in Seebeck coefficient. A decrease in thermal conductivity was also observed with increasing Nb content. This can be connected to lattice distortion, point defects and grain size differences. Simulations showed that the grain size of the films should effectively reduce the thermal conductivity of the films. This is of great importance as grain size tailoring is a viable option to decrease the thermal conductivity without affecting the electrical conductivity to the same extent. A secondary Ruddlesden-Popper (RP) phase was identified. The RP phase, described by $\text{Ca}_{n+1}\text{Mn}_n\text{O}_{3n+1}$, has been shown to have increasing electrical resistivity with decreasing n ¹¹⁷. To clarify, a RP phase with $n \rightarrow \infty$ would

be equal to CaMnO_3 . The Nb-alloyed films in this study exhibits higher resistivity than what many other studies has shown, and the inclusion of the higher resistivity RP phase is a contribution to this. Thus, the inclusion of random RP phases in Nb alloyed CaMnO_3 is not advantageous for thermoelectric applications. This study shows that the film structure, macroscopic and microscopic, are important parameters to control the film properties of CaMnO_3 . Specifically, the grain size in the nm range can effectively reduce the thermal conductivity. Additionally, the RP phase is elusive to detect and have negative effects on the thermoelectric properties.

A different growth method, pulsed direct current reactive magnetron sputtering, was utilized to grow CaMnO_{3-y} films in one step on $(11\bar{2}0)$ LaAlO_3 substrates in **paper III**. The lattice matching between film and substrate promotes tensile growth. Tensile growth of CaMnO_3 is known to result in under-stoichiometric films, which was verified by XPS and EDX. The cleavage orientation of the substrate resulted in improved crystal ordering as compared to previously reported studies on $(01\bar{1}2)$ LaAlO_3 . We observe dark lines in STEM images which were identified to anti-site defects forming antiphase boundaries. They are an important part of stress relaxation of the tensile stress in the film, which relaxes the film without forming dislocations. This could be important for thin films as stress relaxation without dislocations could reduce the scattering centers or reduce the effect thereof.

The metastable VO_2 B phase was grown on mica substrate in **paper IV**. The study showed that the B phase can be grown on mica which is a technologically interesting substrate as it can easily be thinned to thicknesses where it is flexible. The paper also show that vanadium oxide can be easily grown in a wide variety of phase and polymorphs by pulsed direct current reactive magnetron sputtering on mica.

Van der Waals epitaxy of VO_2 M1 phase on mica was investigated in **paper V**. M1 phased VO_2 is the thermodynamically stable form of VO_2 and is vastly researched for its thermochromic properties at 67°C . Recently, van der Waals epitaxy has gained interest and there are a handful of papers touching the topic for VO_2 . However, van der Waals

epitaxy is commonly claimed without sufficient evidence, a universal challenge for van der Waals epitaxy not limited to VO₂ or other specific materials systems. Therefore, proving van der Waals epitaxy was central for the study. This problem is highlighted and examples on how van der Waals can be strongly indicated. This study shows that the films are grown by van der Waals epitaxy. The effect of film thickness/correlation length on the film properties around the thermochromic transition (room temperature to ~100 °C) are shown. My findings give new insights on the VO₂ thermochromic transition and help to determine the van der Waals epitaxy. This will benefit the van der Waals epitaxy community and hopefully help other research properly show the existence of van der Waals. This is important as claiming van der Waals epitaxy without sufficient proof can lead to misinterpreting or overinterpreting the data and the effect of van der Waals epitaxy.

Outlook

If given more time to research CaMnO₃, I would continue to investigate the film growth on LaAlO₃ as I find the antisite defects forming antiphase boundaries combined with film relaxation interesting. I also think this phenomenon may be beneficial, not only for CaMnO₃, to other material systems as well. My hypothesis is that the anti-site defects are randomly formed and act as a nucleation centers to form antiphase boundaries. To investigate this, film growth with different adatom energies together with varied growth speed are key parameters to tune. By changing these parameters, the number of anti-site defects should be possible to control, thus the number of antiphase boundaries should be possible to control. Additionally, I believe that oxides are possible to implement in commercial thermoelectrical products. As has been shown by other studies on CaMnO₃, the efficiency can significantly increase by clever design of the microstructure and alloying.

Continue exploring the field of van der Waals epitaxy is another interesting path. I have an ongoing study on V₂O₅ possibly grown by van der Waals epitaxy combined with intercalation. V₂O₅ has natural van der

Waals layers in the structure which has room for intercalation which can tune the properties of the V_2O_5 structure.

Lastly, combining this knowledge to develop a thermoelectric module based on thin films would be interesting. This is a nontrivial task, as designing thin film components to maintain a sufficiently high temperature gradient is challenging.

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