The Pennsylvania State University

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# CORRELATED METALS AS VISIBLE AND ULTRAVIOLET TRANSPARENT CONDUCTORS

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by

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#### ABSTRACT

While modern physics offers accurate descriptions of many material classes such as conductors and insulators, there are some peculiar subgroups that lie outside complete theoretical understanding. One such class is that of correlated materials where the coulombic interactions between electrons are simply too strong to be ignored. These materials have been observed to exhibit profound properties due to the interplay between the charge, spin, and orbital moment of their *d*- and *f*- electrons. The complex interactions between these electrons are extremely sensitive to defects, chemical composition, and external stimuli, making it decidedly difficult to experimentally verify theoretical models and predictions. This problem is further amplified by the inherent difficulty in synthesizing many of these complex, multicomponent materials which host intriguing properties arising from a sizeable electron correlation. Even with advances in modern thin film growth techniques such as molecular beam epitaxy and pulsed laser deposition, high quality material synthesis remains one of the leading challenges in the field of experimental correlated materials. In addition, the recent discovery of certain correlated metals as transparent conducting materials has added a technological desire to expand material solutions beyond the conventional composition and design space of transparent conductors.

This thesis addresses three open questions in the field of experimental correlated materials using the perovskite correlated metals SrVO<sub>3</sub> and SrNbO<sub>3</sub>: how can electron correlations be utilized in room temperature applications, how does disorder and anisotropic scattering influence properties arising from electron interactions, and how does film orientation affects electronic transport in correlated metals. The first question is addressed through the experimental verification of SrNbO<sub>3</sub> as an effective UV transparent conductor which was found to have an optical transmission up to 94% at a wavelength of 280 nm with a resistivity of  $2.36 \times 10^{-4} \Omega$ cm. The second question is then addressed by investigating the influence of disorder in SrVO<sub>3</sub> films where a robust Fermi liquid phase was found to exist at low temperature. The scattering prefactor in the Fermi liquid phase was

This thesis is structured as follows. First, an introduction to traditional metals, correlated metals, and electron-electron interactions is presented in Chapter 1. A short review of transparent conductors in the visible and ultraviolet regions as well as recent developments in the growth of correlated metals along the polar [111] direction are also included. Chapter 2 provides a review of the experimental growth techniques and characterization methods used for these correlated materials. Chapter 3 then delves into the structural, electrical, and optical characterization techniques used in this thesis. Exploration into room temperature applications for correlated materials begins in Chapter 4 with the theoretical and experimental investigations of SrNbO<sub>3</sub> as a visible and ultraviolet transparent conductor. Chapter 5 expands this investigation by examining the role of Sr vacancies in sputtered  $Sr_xNbO_3$  films. The effects of material quality and the entanglement of electron-electron scattering and disorder are then studied in Chapter 6 with SrVO<sub>3</sub> in the polar [111]-orientation and the subsequent, unexpected effects on the electronic transport.

transport were observed in comparison to [001]-oriented films.

The work presented here offers insights to both technological advances and fundamental research of correlated materials. This dissertation offers fertile ground to inspire future advancements in the fields of experimental correlated metals, transparent conducting materials, hybrid MBE, and topological materials.

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## **Chapter 1: Introduction**

The field of materials science and condensed matter in particular hinge on the underlying fundamental physics that drive material properties. An in-depth understanding of these physical phenomena and how they can be utilized is an invaluable asset for materials design. Some research and development fields have remained in a rut of innovation, caught in a material design paradigm that has little developmental future. To break through this logiam of development, one must be willing to examine the utilization of a new physical phenomenon or material class. One material class that offers the potential to bring breakthroughs to multiple fields is that of correlated materials. Unlike traditional materials where the electron-electron interactions can largely be ignored, strong correlations and interactions exist between the electrons in correlated materials, whether it be through their charge, lattice, spin, or orbital degrees of freedom. This plethora of potential electron interactions enables a nearly boundless array of technologically valuable properties including but not limited to charge density waves,<sup>1</sup> spin-orbit coupling,<sup>2</sup> unconventional superconductivity,<sup>3</sup> topological phenomena,<sup>4</sup> multiferroics,<sup>5</sup> colossal magnetoresistance,<sup>6</sup> and a multitude of other charge ordered and spin ordered states. Despite great strides taken towards achieving a comprehensive understanding of these phenomena, much of the physics underpinning these systems and phenomena is not well established, evidenced by a lack of predictive power to identify materials in which these exotic phases would emerge.

These strong correlations typically arise in transition metal oxides (TMOs) with *d*- or *f*configurations but  $\pi$ -electron organic conductors have also been shown to demonstrate strong correlations.<sup>7</sup> These strong interactions and their inherent complexities impede the use of traditional band theory and other complex interpretations such as local density approximation and density functional theory fail to provide accurate descriptions without additional considerations. In order

H																<sup>2</sup> He	
<sup>3</sup> Li	<sup>4</sup> Be	ABX3										5 <b>B</b>	<sup>6</sup> C	7 N	8 <b>O</b>	9 <b>F</b>	<sup>10</sup> Ne
Na	<sup>12</sup> Mg	000000										<sup>13</sup>	<sup>14</sup> Si	15 <b>P</b>	16 <b>S</b>	17 <b>Cl</b>	Ar
19 <b>K</b>	20 Ca	21 <b>Sc</b>	22 <b>Ti</b>	23 <b>V</b>	<sup>24</sup> Cr	25 <b>Mn</b>	Fe	27 <b>Co</b>	28 <b>Ni</b>	29 Cu	<sup>30</sup> Zn	Ga <sup>31</sup>	Ge	33 <b>As</b>	<sup>34</sup> Se	35 <b>Br</b>	36 <b>Kr</b>
<sup>37</sup> <b>Rb</b>	<sup>38</sup> Sr	39 <b>Y</b>	40 <b>Zr</b>	<sup>41</sup> <b>Nb</b>	42 <b>Mo</b>	43 <b>Tc</b>	<sup>44</sup> Ru	45 <b>Rh</b>	<sup>46</sup> <b>Pd</b>	47 <b>Ag</b>	<sup>48</sup> Cd	49 In	50 Sn	51 <b>Sb</b>	52 <b>Te</b>	53 	54 <b>Xe</b>
55 <b>Cs</b>	56 <b>Ba</b>		72 <b>Hf</b>	73 <b>Ta</b>	74 W	75 <b>Re</b>	76 <b>Os</b>	77 <b>Ir</b>	78 <b>Pt</b>	79 <b>Au</b>	<sup>80</sup> Hg	81 <b>Tl</b>	<sup>82</sup> <b>Pb</b>	83 <b>Bi</b>	<sup>84</sup> <b>Po</b>	<sup>85</sup> At	<sup>86</sup> Rn
87 <b>Fr</b>	<sup>88</sup> Ra		<sup>104</sup> <b>Rf</b>	105 <b>Db</b>	<sup>106</sup> Sg	<sup>107</sup> Bh	<sup>108</sup> Hs	<sup>109</sup> Mt	110 <b>Ds</b>	111 <b>Rg</b>	<sup>112</sup> <b>Cn</b>	<sup>112</sup> <b>Nh</b>	114 <b>Fl</b>	115 <b>Mc</b>	116 Lv	117 <b>Ts</b>	<sup>118</sup> <b>Og</b>
				50	50		<u></u>	(2)			65					70	74
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			89 <b>Ac</b>	Th	<sup>91</sup> <b>Pa</b>	92 U	<sup>93</sup> <b>Np</b>	94 <b>Pu</b>	95 Am	<sup>96</sup> Cm	97 <b>Bk</b>	<sup>98</sup> Cf	<sup>99</sup> Es	Fm	<sup>101</sup> Md	<sup>102</sup> <b>No</b>	<sup>103</sup>

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to develop a predictive theory for correlated metals, detailed feedback from accurate experimental trends must be utilized. Many traditional thin film deposition methods that are widely used for the study of correlated materials are known to have high defect concentration levels when compared to films grown by self-regulated techniques such as *h*MBE which has been shown to produce record quality materials including SrTiO<sub>3</sub><sup>9</sup> and SrVO<sub>3</sub>.<sup>10</sup> When high defect concentrations are present in a material, it becomes difficult to deconvolute the intrinsic properties of the correlated material from those that arise due to defects. In addition, defects can completely obscure inherent material properties. Our knowledge of the properties of correlated metals is therefore limited in part by the nontrivial material synthesis. Detailed examinations of the properties that arise in the ultraclean limit of correlated materials and how they are altered as a function of increased disorder would provide invaluable datapoints for the development of predictive theories. In addition to the difficulties with material synthesis and predictive models, the vast properties enabled by electron

correlation that can be probed with high accuracy using magnetotransport measurements are typically masked by phonon scattering at room temperature.

While transition metal oxides can arrange in a multitude of crystal structures, many of which support complex electron correlations, this work focuses on those with the most commonly studied perovskite structure following the chemical formula  $ABO_3$ , shown in Figure 1-1. In this structure, the *B*-site cation is surrounded by an octahedra of anions while the *A*-site cation has a 12-fold coordination. The *A*- and *B*- sites can consist of cations covering nearly the entire periodic table, enabling a considerable number of potential combinations. The simplicity of the perovskite structure makes theoretical calculations straightforward. This, combined with the extensive potential material properties, make perovskites among the most intensely studied oxide crystal structures.

While many open questions exist in the field of correlated metals, this thesis addresses three open questions:

- How can electron correlations can be utilized in room temperature applications?
- How does disorder influence properties arising from electron interactions?
- How does film orientation affect properties arising from electron interactions?

This chapter will lay the foundation of these open questions by introducing the material discussed throughout this thesis. First, a basic introduction to the field of electron correlation physics will be discussed. Following this, the traditional design approach of transparent conductors will be contrasted by the new paradigm enabled by correlated metals. Transparent conductor figure of merits will then be compared in order to demonstrate the significant improvements offered by correlated metals. This improvement will then further be discussed in terms of UV transparent conductors and their wide application space. Following this, a brief review of [111]-oriented perovskite oxides will be presented. Finally, this chapter will conclude with some additional considerations for electron-electron interactions that arise throughout these studies.

### **1.1 Correlated Materials**

In order to contrast the electron interactions that occur in correlated materials, a brief overview of conventional conductors will be discussed. Resistivity is a second rank tensor property, present in all materials, that is commonly used to classify materials; materials with low resistivity are conductors, those with high resistivity are insulators, and those in the intermediate region are semiconductors. The distinction between these material classes can be described by the relation between the valance band, conduction band, and the highest filled state at 0 K described by the Fermi level. In conductors, the Fermi level lies in a partially filled band. In this case, the close proximity of filled and empty states of the quasi-continuous energy spectrum inside a band allows electrons to be promoted to a higher energy state by accelerating them in an applied electric field, resulting in a momentum imbalance and a net electric current. In contrast, insulators and semiconductors have a gap between the conduction and valance band, which has completely full or completely empty bands at 0 K. For insulators, this band gap is so large that only a few carriers can be thermally excited into the conduction band to contribute to the conductivity. Semiconductors have a much smaller bandgap where at non-zero temperatures, thermal energy can excite sizeable amounts of carriers into the conduction band. Each of these cases is shown schematically in Figure 1-2(a). Semiconductors are either intrinsic where thermal excitation and deexcitation is in equilibrium, like silicon, or are extrinsic where doping is required to move the Fermi level to make it conducting. The ability to change a material from the insulating limit to the conducting limit simply by changing the carrier concentration of the material has been an invaluable asset in many modern-day technologies.



Figure 1-2: (a) Schematic band diagrams of a metal, semiconductor, and insulator with single conduction and valance bands where blue indicates filled bands and  $E_F$  and  $E_g$  are the Fermi energy and band gap respectively. (b) Schematic of the *d*-band splitting as on-site Coulomb interactions (U) are turned on. (c) Evolution of the density of states as a function of U over the bandwidth (W). Adapted from reference.<sup>11</sup>

A slightly less explored phenomenon that can similarly affect the motion of the carriers is the electron correlation strength arising from their coulombic interactions. A significant deviation from the aforementioned trends occurs with the introduction of nonzero electron correlations. For example, the binary oxide NiO has a partially filled 3d band and is therefore expected to be a conductor from traditional band theory; however, a strong Coulomb potential exists between the 3d electrons resulting in their localization and causing NiO to be insulating. This effect was first observed in 1937<sup>12</sup> yet a thorough theoretical explanation was not developed until 1949.<sup>13</sup>

Consider a lattice with one electron on each site. An electron with a particular spin can move to any neighboring site that has an electron of opposite spin according to the Pauli exclusion principle; however, the probability of this transition is mediated by the repulsive Coulomb potential between the electrons (U). If U is small, electrons can easily move from site to site, allowing metallic conduction; however, if U is large the electrons are essentially locked in place even though the band is half filled. For the transition metal oxides this only affects the *d*- or *f*- bands while the oxygen *p*-bands are unaffected as shown schematically in Figure 1-2(b). The evolution of the density of states in the conduction band is further shown as the ratio of *U* to the bandwidth *W* increases in Figure 1-2(c) where the shape is described by the frequency dependent spectral weight function  $A(\omega)$  where  $\sigma_1$  is the real part of the optical conductivity.<sup>14</sup> This spectral function is measurable using angle-resolved photoemission techniques and has been used to study several correlated systems.<sup>15,16</sup>

$$A(\omega) = \frac{2m_e}{\pi e^2} \int_0^\omega \sigma_1(\omega') \, d\omega' \qquad \text{Eq. 1.1}$$

For U=0, the density of states assumes the typical ellipse shape of a metal. For weakly correlated materials where U/W is small, the electrons must be considered to be quasiparticles even though they still behave like free, i.e., non-interacting, electrons. Once a significant correlation strength is reached,  $U/W\sim1$ , Hubbard bands form alongside the narrowed free electron like quasiparticle peak as a result of the localized hopping of the electrons. Finally, the spectral weight is completely transferred from the quasiparticle peak into the Hubbard bands, completely localizing the electrons and forming a Mott insulator. The quasiparticle mass,  $m^*$ , arising from these interactions is renormalized from the band mass  $m_b^*$  by the renormalization constant  $Z_k$ , quantifying the correlation strength in a material.

$$Z_k = \frac{m_b^*}{m^*} \qquad \qquad \text{Eq. 1.2}$$

The localization of carriers as correlation strength increases has the same effect as freezing out carriers in semiconductors by decreasing temperature, causing them to return to the ionized dopant and form a localized bound state. This similarity allows correlation strength to be used as a tuning parameter similar to the way carrier concentration is used to access specific technologically beneficial regimes of semiconductors. While metal to insulator transitions play important roles in many application spaces such as ultrafast switching, memory, and neuromorphic devices,<sup>17,18</sup> this

significant alteration in correlation strength is not necessary to access unique properties. If the electron correlation strength is sizeable but not to the point of complete localization, a new regime of correlated conductors can be achieved, termed correlated metals. The metal-like conductivity of these materials allows them to be used in the same way doped semiconductors are used in applications such as transparent conductors, potentially answering the open question of how to utilize these correlated materials in high temperature applications which will be discussed in the next section.

While semiconductor functionality is well understood and technologically well established, we are not so fortunate with electron correlation. A general theory of correlated metals would be highly beneficial in their design and utilization for specific application spaces. While the elegant Drude-Sommerfeld model has been shown to accurately describe most material systems, it is ineffective for the study of correlated electron systems as it does not consider the electrons' interactions with each other, the underlying lattice, or other quasiparticles. In particular, the long range, multi-body interactions of the electrons in correlated systems make it difficult to predict and analyze their electronic properties. Computational methods such as density functional theory (DFT) and local density approximation (LDA) are widely used as predictive tools for materials design but since they are based on non-interacting quasiparticles, they fail to accurately predict the properties of correlated materials without additional considerations. Methods such as the linearized selfconsistent quasiparticle GW approximation and dynamical mean field theory (DMFT) are currently being developed to describe correlated electron materials and they become especially powerful when performed in conjunction with the well-developed methods such as DFT. DFT+DMFT methods in particular have been successful in describing a multitude of material systems<sup>19-21</sup> and have been implemented in numerous software packages.<sup>22</sup> As computation calculations are not the focus of this thesis, the reader is suggested to see the following citations for more in-depth material.11,23

Further refinement of these theoretical and computational models requires the predicted trends and phenomena to be experimentally verified. For many material systems this is challenging due to the inherent difficulty in synthesizing high-quality materials combined with the sensitivity of correlation effects to defects, strain, and stoichiometry. Furthermore, on many occasions, experimental studies on high quality materials reveal novel material properties that have not been calculated, prompting modifications to the theory. These challenges necessitate the use of high-quality thin film deposition methods such as hybrid molecular beam epitaxy, which will be further discussed in Chapter 3.

### 1.2 Transparent Conductor Design

Transparent conducting oxides (TCO) are some of the most widely utilized materials in technology today that are hardly acknowledged due to their inherent invisibility. TCOs are used in every application where the path of photons must cross the path of electrons. This means their application space extends through nearly every type of flat-panel display, LED, solar cell, and optoelectronic device. TCOs are even used in unexpected applications such as low-emissivity windows, electromagnetic shielding for computers and communications, and security circuits in windows. In principle, TCOs are a material oxymoron since typical conducting materials are reflective, such as copper, and transparent materials are usually insulating, such as glass. Creative approaches must be used to circumvent the mutually exclusive properties of conductivity and transparency. The historically tried and true method has been to take a wide bandgap semiconductor that is transparent in the spectra of interest and dope it until it becomes conductive. This design paradigm was unknowingly initiated in 1907 when thermally oxidized, sputtered Cd metal was found to have a high carrier mobility while remaining optically transparent.<sup>24,25</sup> While the current day usage of CdO is limited due to toxicity concerns, the same basic principle of using oxide

semiconductors is still widely used today. Minor improvements were realized over the following decades including the deposition of tin oxide in 1937 and indium oxide in 1953.<sup>26</sup> In the first half of the century, the application of these materials was limited to anti-static coatings and heater films in aircraft windshields,<sup>27</sup> but in the 1960's and 1970's the applications for transparent conductors started to take off with the introduction of flat panel displays and the desire to develop lowemissivity coatings for windows. Since then, tin-doped indium oxide (ITO) has dominated the field for transparent electrodes in display technology.<sup>28</sup> While ITO is widely used due to its superior optical and electrical properties, the high cost of indium limits the application space.<sup>29,30</sup> Lowemissivity coatings designed to control the heat and light through windows are typically made up of cheaper transparent conductors such as fluorine doped tin oxide (SnO<sub>2</sub>:F).<sup>31</sup> Over four billion square meters of float glass is produced per year.<sup>31</sup> If only a small percentage of this contains TCO coating, it still remains the most widely used application of TCOs. Due to decades of studies, these materials have been optimized for deposition with nearly any thin film deposition method including highly scalable methods such as magnetron sputtering, can be deposited on nearly any substrate including glass and flexible substrates, and can easily patterned using wet-etching techniques allowing for them to be easily incorporated with devices. While doped semiconductors may seem like miracle materials, they face some significant drawbacks. Solubility limitations in dopant concentrations restrict the conductivity through low carrier concentrations. The conductivity is further reduced by an enhanced ionized impurity scattering from the dopant atoms. This limitation in conductivity necessitates thicker films to meet sheet resistance requirements which in turn reduces the achievable optical transmission. In addition, optical transparency ranges are limited to the visible since they experience significant absorption in the ultraviolet (UV) and reflection in the infrared (IR).

The decades of study on the traditional approach of doping wide bandgap semiconductors have nearly ran their course. In order to discover substantial improvements, the field has moved towards more complicated structures to incorporate layers of highly conductive materials such as silver and graphene. These structures include ITO/Ag/ITO,<sup>32</sup> SnO<sub>2</sub>/Ag/SnO<sub>2</sub>,<sup>33</sup> WO<sub>3</sub>/Ag/WO<sub>3</sub>,<sup>34</sup> Ag/ZnS/Ag,<sup>35</sup>, MoO<sub>3</sub>/Graphene<sup>36</sup> to name a few. In addition, there have been investigations to completely replace doped semiconductors with 2D materials,<sup>37,38</sup> nanowires,<sup>39,40</sup> conductive polymers such as PEDOT,<sup>41</sup> and the combination of any of the above.<sup>42</sup> While some of these material systems have shown promising results, their increased complexity over single material TCOs make integration with devices substantially more difficult. The inherent complexities arising from the multi-material composition also make comparison to the single material transparent conductors difficult; therefore, the reader is directed to the following reviews for additional reading on these alternatives.<sup>43,44</sup>

To develop a new strategy for the advancement of novel transparent conductors it is first crucial to outline their ideal optical and electrical properties. First, the optical spectrum of interest must be defined; typically, this is the visible spectrum. For high transmission in this region, the reflection edge caused by the free carriers must be pushed into the IR while the optical absorption due to interband transitions must be moved into the UV. These ideal optical properties are shown schematically in Figure 1-3(a) for a visible transparent conductor. These parameters must be carefully adjusted to ensure high optical performance while maintaining a high electrical conductivity.

The reflection edge is quantified by the reduced plasma frequency, where e is the elemental charge, n is the carrier concentration,  $m^*$  is the effective carrier mass and  $\varepsilon_0$  and  $\varepsilon_r$  are the vacuum and relative permittivity respectively:

$$\hbar\omega_p = \hbar (e/\sqrt{\varepsilon_0 \varepsilon_r}) \sqrt{n/m^*} \qquad \text{Eq. 1.3}$$

For incident light with energy less than  $\hbar\omega_p$ , the electrons in the material can quickly respond to absorb and reemit the EM wave, preventing its propagation into the material and thus reducing the transparency. For light with energy exceeding  $\hbar\omega_p$ , the free moving electrons cannot respond fast enough to the electric field modulation of the EM wave so light will continue to propagate and transmit through the material with minimal reduction in intensity. This equation sets up the general expectation that conducting materials are shiny as their high carrier concentrations result in a plasma frequency inside the visible range. While at first glance it seems easy to adjust the free reflection edge, it is difficult to do so while maintaining an effective transparent conductor as it is directly tied to the electrical conductivity through the carrier concentration:

$$\sigma = e^2 \tau(n/m^*) \qquad \qquad \text{Eq. 1.4}$$

A simple reduction in the carrier concentration results in a square root reduction in the plasma frequency while the conductivity decreases linearly, offering a nonideal optimization of the desired properties. The relation between these two properties is shown in Figure 1-3(b) for typical semiconductor based TCOs ITO,<sup>45,46</sup> SnO<sub>2</sub>,<sup>47,48</sup> and ZnO,<sup>49,50</sup> as well as the elemental metals Au, Ag, Cu, and Al.<sup>51,52</sup>



Figure 1-3: (a) Schematic of the optimal optical properties of a visible transparent conductor. (b) Relation between the electrical conductivity and plasma frequency of typical metals and semiconductor based transparent conductors highlighting the carrier gap between them. Reproduced from reference.<sup>53</sup>

Here, traditional TCOs have the desired plasma frequency below the visible range; however, the reduced carrier concentration that enables this also reduces the conductivity nearly two orders of magnitude from traditional metals. In addition, increased ionized impurity scattering further reduces the maximum achievable conductivity by decreasing the carrier relaxation time  $\tau_{ph}$ . If doping concentrations were increased, this scattering time would be further reduced by  $\Delta \tau$  and conductivity would decrease as shown for Al doped ZnO. While traditional metals do not experience these issues since ions are electrostatically screened by the mobile charge carriers, their high carrier concentrations exceeding  $5 \times 10^{22}$  cm<sup>-3</sup> result in plasma frequencies that lie either inside the visible or beyond. The high conductivities of metals have driven some studies for their use as transparent conductors; however, in order to be effectively used as transparent conductors they must be extremely thin (<10 nm) in which case it is difficult to establish continuous films even when using wetting layers.<sup>54</sup> The extreme differences between these material classes leaves a carrier gap between ~2×10<sup>21</sup> to 5×10<sup>22</sup> cm<sup>-3</sup>, precluding any materials from sitting in the ideal low  $\omega_p$ , high  $\sigma$  regime.

While it may appear that this is the limit of optimization, there is a hidden third dimension in the  $\omega_p - \sigma$  map enabled by alterations to the electron effective mass through correlation effects. This additional dimension is shown in Figure 1-4 where the conductivity and plasma frequency are plotted as a function of the renormalization constant  $Z_k$ , defined in Eq. 1.2 as the correlation strength. Following Eq. 1.3 and Eq. 1.4, decreasing  $Z_k$  results in a decrease in both  $\omega_p$  and  $\sigma$ . This result can be rationalized through the fact that as correlation strength increases, electrons begin to couple to electrons in their spatial proximity, effectively slowing their dynamic response in the crystal, thus limiting the electrical conductivity and decreasing the plasma frequency. While the correlation strength of a particular material cannot be freely adjusted between 0 and 1, it can be used to identify materials which would otherwise be ignored for use as transparent conductors. For example, a material with noninteracting electrons and a carrier concentration of  $2.3 \times 10^{22}$  cm<sup>-3</sup> is predicted to have a  $\omega_p$  of ~5.6 eV, making it highly reflective throughout the visible spectrum. However, if  $Z_k$  is allowed to vary,  $\omega_p$  can be reduced below the visible range at the cost of some conductivity performance. Three such iso-carrier lines are shown in Figure 1-4 for the correlated metals: SrNbO<sub>3</sub>,<sup>55</sup> SrVO<sub>3</sub>,<sup>53</sup> and SrMoO<sub>3</sub>.<sup>56,57</sup> Each of these materials have conductivities exceeding that of any traditional TCO, as seen from their projection onto the  $\sigma - Z_k$  plane, while maintaining a plasma frequency near or below the visible range as seen from their projection onto the  $\omega_p - \sigma$ plane. In addition to these three materials, other correlated materials are shown including LaNiO<sub>3</sub>,<sup>58,59</sup> Sr<sub>2</sub>RuO<sub>4</sub>,<sup>60,61</sup> SrRuO<sub>3</sub>,<sup>62,63</sup> CaVO<sub>3</sub>,<sup>53</sup> and CaMoO<sub>3</sub>.<sup>64</sup> Note that data for some materials comes from multiple sources; therefore, this figure is only a guide to how materials behave and should be updated as more uniform datasets become available.



Figure 1-4: Schematic for the optimization of the plasma frequency ( $\omega_p$ ) and conductivity ( $\sigma$ ) using the carrier concentration and correlation strength ( $Z_k$ ). Traditional metals (gray) and doped semiconductors (orange) lie on the  $Z_k=0$  plane while correlated metals (blue) exist in the extended dimension.

The realization of this additional dimension was first utilized by Zhang, *et al* to circumvent the conventional design approach of doping wide bandgap semiconductors and use materials with a high effective mass resulting in a high conductivity while maintaining the reflection edge below the visible range.<sup>53</sup> The existence of this dimension enables an entirely new class of materials to be considered as transparent conductors, creating a new starting point to optimize the design of transparent conductors.

While this is a revolutionary discovery, it only addresses the reflection edge of the transparency window; in addition, considerations must be made to reduce or avoid interband transitions with energies in the visible to ensure an interband absorption edge in the UV. Reducing absorption in a desired spectrum is significantly more difficult than maintaining a specific reflection edge, but it can be solved. The contributions to optical absorption will be outlined for the case of SrVO<sub>3</sub>. For this we will only consider interband transitions with energies in the visible spectrum. In SrVO<sub>3</sub> there are eight bands involved in interband transitions with energies lower than 3.6 eV, marking the edge of the visible spectrum. These are the three highest oxygen bands,  $2p^1$ ,  $2p^2$ , and  $2p^3$ , and the conduction bands  $e_g^1$ ,  $e_g^2$ ,  $t_{2g}^1$ ,  $t_{2g}^2$ , and  $t_{2g}^3$  as highlighted in Figure 1-5(a). Each transition between these bands is an electric dipole transition and must obey the Pauli exclusion principle. Due to this, the strength of the interactions can vary and therefore must be calculated using the dipole matrix element. The square of the calculated dipole matrix element  $(M^2)$  for each main transition in  $SrVO_3$  is shown in Figure 1-5(b-f) with the visible range highlighted. If the occupancy of the transition is the same, the transition is forbidden. These forbidden transitions are shown as red in Figure 1-5(b-f), while available transitions are shown as blue. Here it can be seen that almost all transitions that occur in the visible spectrum either have a low dipole matrix element or are forbidden transitions that do not increase the absorption coefficient.



Figure 1-5: (a) Band structure of SrVO<sub>3</sub> with all interband transitions lower than 3.6 eV indicated in addition to band labels and shape labels for which  $t_{2g}$  band is involved in each transition. (b)-(f) The dipole matrix element, M2, and energy difference,  $\Delta E$ , for each specific transition along the Brillouin zone. Red symbols indicate that the initial and final state of the transition are of the same occupancy so it is repressed and is not involved in optical absorption. Blue symbols indicate transitions to different occupancy that are involved in optical absorption. (g) The major contributions to the dielectric function as a function of energy. Figure reproduced from reference.<sup>53</sup>

Through this in-depth examination of the optical absorption in  $SrVO_3$ , we can identify the interband transitions that significantly contribute the optical absorption. From this we can reduce the dipole matrix elements of all transitions in the visible, suppress transitions through changing the occupancy of the problematic transitions, or further isolate the conduction bands to move transitions to energies outside the visible spectrum. Of these, the positioning of the conduction bands, specifically the  $t_{2g}$  bands in this case, is the easiest to utilize. For example, the positioning of these bands is caused in part by the electronegativity difference between the transition metal cation and the oxygen anions. Increasing this electronegativity difference results in all transitions between the oxygen 2p bands and the  $t_{2g}$  bands to move apart relative to one another. Perovskite materials are ideal to realize such changes due to their ability to populate different elements at the crystal lattice sites. In the case of SrVO<sub>3</sub>, the transition metal V would simply have to be substituted partially or completely to another transition metal with a smaller electronegativity that still promotes electron correlations such as Nb. This exact case of tuning correlated metals as transparent conductors will be further highlighted in Chapter 4 where the switch from SrVO<sub>3</sub> to SrNbO<sub>3</sub> was found to shift the absorption edge to higher energies, enabling a highly efficient UV transparent conductor.

#### **1.3 Transparent Conductor Figure of Merit**

The performance of transparent conductors is dependent on how well electrons and photons are conducted through the material. Therefore, the figure of merit (FOM) must include some terms that describe the transparency and the conductivity of the material; however, the optimal choice of these terms is not straightforward. One of the earliest FOM was simply defined to be the ratio of optical transmission T and sheet resistance  $R_s$ .<sup>65</sup> While this FOM is straightforward to interpret, it does not strike a good balance between the transmission and sheet resistance as it strongly favors
materials with a low sheet resistance. If this FOM is maximized for a given material, it yields a transmission of 37% which is physiologically perceived to be opaque.

Due to this, it was modified by Haacke in 1976<sup>66</sup> to be more in line with what humans perceive to be transparent:

$$\phi_{Haacke} = \frac{T^{10}}{R_s}$$
 Eq. 1.5

This modification ensures that the highest FOM occurs at 90% transmission which is the point at which an object physiologically appears transparent; however, the exponent of the optical transmission can be adjusted according to the requirements of the comparison. An additional, hidden factor of this FOM is the film thickness that is encompassed in both  $R_s$  and T.

Another commonly used FOM focuses on the intrinsic, bulk properties of the material to ensure a thickness independent comparison as shown in Eq. 1.6. Here, the FOM is defined simply as the ratio of the electrical conductivity to the optical absorption.

$$\phi_{\sigma/\alpha} = \frac{\sigma}{\alpha} = -\frac{1}{R_s ln(T+R)}$$
 Eq. 1.6

It should be noted that for most of these comparisons, the transmission is typically taken at a single wavelength, usually 500 or 555 nm where the human eye is most sensitive,<sup>67</sup> while a spectral range relevant for the application would provide a better comparison. Figure 1-6 demonstrates the differences between Eq. 1.5 and Eq. 1.6 for a variety of transparent conductors in the visible spectrum.



Figure 1-6: Optical transmission of various transparent conducting materials as a function of sheet resistance with constant FOM lines corresponding to (a) the Haacke FOM (Eq. 1.5) and (b) the  $\sigma/\alpha$  FOM (Eq. 1.6). The location of an ideal transparent conductor for each FOM is marked by a blue star. The effective mass ( $m_e$ ) and renormalization constant ( $Z_k$ ) are indicated by the size and color of the datapoints.

This comparison consists of elemental metals,<sup>51,52</sup> commonly used doped semiconductors including ITO,<sup>45,46</sup> TiO<sub>2</sub>,<sup>68</sup> CdO,<sup>26</sup> BaSnO<sub>3</sub>,<sup>69</sup> ZnO,<sup>49,50</sup> SnO<sub>2</sub>,<sup>47,48</sup> correlated metals including VO<sub>2</sub>,<sup>70</sup> SrVO<sub>3</sub>,<sup>53</sup> SrMoO<sub>3</sub>,<sup>56</sup> SrNbO<sub>3</sub>,<sup>55</sup> CaVO<sub>3</sub>,<sup>53</sup> chalcogenides including NbSe<sub>2</sub>,<sup>71,72</sup> TiS<sub>2</sub>,<sup>73,74</sup> TiSe<sub>2</sub>,<sup>75,76</sup> as well as MgB<sub>2</sub>,<sup>77</sup> ZrZn<sub>2</sub>,<sup>78</sup> BaFe<sub>2</sub>As<sub>2</sub>,<sup>79</sup> and Ni<sub>3</sub>Ga.<sup>80,81</sup> These images help illustrate the strengths and limitations of each commonly used figure of merit. The Haacke FOM, shown in Figure 1-6(a), provides a good balance of optical transmission and sheet resistance; however, the inclusion of film thickness in the FOM leaves a poor comparison between experimental data which typically have different thicknesses. For instance, the metals here have a thickness of approximately 10 nm while the doped semiconductors are on the order of hundreds of nm. The second FOM,  $\phi_{\sigma/\alpha}$  shown in Figure 1-6(b), equally weights the intrinsic properties of conductivity and optical absorption. This creates an awkward weighting of the electrical and optical properties where 4× reduction in in the optical absorption can simply be compensated by a 4× improvement in conductivity. This leads to highly conductive but opaque materials such as silver to have the same FOM as transparent but insulating materials such as CdO. In contrast, this simple intrinsic relationship eliminates the contributions of interfacial effects which can be engineered to further improve the optical transmission.

The limitations of each FOM can be somewhat rectified if the materials are plotted as a function of their actual optical transmission and sheet resistance as shown in Figure 1-6. In this case if a specific transmission or sheet resistance is required for an application, the material with the best FOM can be easily determined.

### **1.4 Ultraviolet transparent conductors**

While the research and development of transparent conductors has been primarily focused on the visible range, few have considered the enormous untapped potential that exists in the rest of the electromagnetic spectrum. Here we discuss the significance of developing transparent conductors in the ultraviolet (UV) region and highlight specific applications throughout the entire UV spectrum. Finally, we discuss the current options and developmental strategies for UV transparent conductors with a focus on adjusting the paradigm to correlated metals.

UV light is typically associated with sunlight; however, only about 10% of the electromagnetic radiation emitted from the sun lies in the UV. In addition, ozone in the atmosphere greatly absorbs the lower wavelength UV light, preventing the majority from reaching sea level.<sup>82</sup> The difference between the solar irradiance and the irradiance that reaches sea level is outlined in Figure 1-7(a). Ultraviolet light extends from the visible range starting at a wavelength of 400 nm to highly energetic X-rays at 10 nm. The UV spectrum is subdivided into regions with somewhat different bounds depending on the discipline involved. These regions with their respective boundaries relevant to this work are UVA (320-400 nm), UVB (280-320 nm), UVC (100-280 nm), near UV (300-400 nm), middle UV (200-300 nm), far UV (120-200 nm) and extreme UV (10-100 nm) as shown in Figure 1-7(b).



Figure 1-7: (a) Standard solar spectra (black line: ASTM E490)<sup>83</sup> compared to the solar spectra at sea level (red line: ASTMG173)<sup>84</sup> after atmospheric absorption. (b) Diagram outlining the regions of interest for this thesis in the visible and UV.

As the UV spectrum consists of many distinct regions with vastly different photon energies, each region has its own separate applications as outlined in Figure 1-8. UVA and UVB light are commonly associated with acute effects such as sunburns and tanning in addition to chronic effects such as skin cancer. In contrast, exposure to these wavelengths has a major upside in allowing our bodies to synthesize vitamin D<sub>3</sub> from 7-cehydrocholesterol in our skin.<sup>82</sup> UVA and UVB light can be used in a plethora of applications from both a commercial and an industrial standpoint. For instance, UV phototherapy is commonly used to treat psoriasis and other dermatology procedures<sup>85,86</sup> and photochemotherapy uses a UV light source to activate orally administered photosensitizer drugs at the location of tumors, preventing adverse effects in other locations in the body.<sup>87</sup> UVB light is also used to regulate the secondary metabolism in plants making it widely used in horticulture.<sup>88</sup> Some types of 3D printing methods including stereo lithography and digital light processing utilize a UV light source to locally photopolymerize specific areas in a vat of liquid monomers, oligomers, and photoinitiators.<sup>89</sup> Standard tanning beds use UVA and UVB light is weighted

differently to negate some of the harmful effects.<sup>90</sup> UVA and UVB light is also widely used for security purposes including high-density optical recording,<sup>91</sup> banknote identification, counterfeit detection, and ID security devices.<sup>92,93</sup>



# **UV Application Space**

Figure 1-8: General overview of the application space in the UV.

UV light is most widely known for its disinfection abilities in the UVC range. The germicidal effect of sunlight was first shown in 1877;<sup>94</sup> however, the effect could not be utilized on a large scale until the development of mercury vapor lamps which were able to apply UV light with sufficient intensity. The disinfection property of UV light arises from the damage it inflicts on the nucleic acids in microorganisms such as bacteria, protozoa, viruses, algae, and molds. When high intensity UV light hits a microorganism, the high energy of the photons severely damages DNA and RNA, inhibiting their replication and leading to the inactivation of the organism. In addition, this exposure can form new bonds between neighboring nucleotides, resulting in dimers which also prevents replication.<sup>95</sup> Even though high intensity light is detrimental to microorganisms, exposure to UV light from the sun has resulted in evolution driven natural

defenses to repair pathways through photoreactivation;<sup>96</sup> therefore, high light intensity is a necessity to ensure full deactivation and disinfection. Due to the high intensities required for deactivation and the harmful nature of high energy UV light on the human body, these technologies are primarily used for disinfecting inanimate objects.

UVC light has long been targeted to assist with the disinfection of drinking water, which has continuously been an important issue worldwide.<sup>97</sup> The World Health Organization estimates that over 785 million people worldwide lack access to a safe drinking water source and at least two billion people use a water source that is contaminated by feces.<sup>98</sup> While technologies such as chlorination, advanced filtration, and reverse osmosis exist, they either have significant downsides or are not applicable on a large scale. Specifically, chlorination has been shown to cause major adverse health effects ranging from birth defects to cancer.<sup>99</sup> The key challenge is to provide clean drinking water to the entire human race; therefore, it is highly desirable to put additional emphasis on UV disinfection of water to circumvent the downsides of traditional approaches. Further development of this technology will enable a cheap and environmentally benign solution to disinfect water on a massive scale. In addition to water disinfection, UV disinfection of air and surfaces in general has become more widespread in the past year due to studies demonstrating its effectiveness in deactivating SARS viruses including COVID-19.<sup>100,101</sup> Currently, UV light is being used to disinfect N95 masks, hospitals, currency, and buses to name a few. UV light has also been widely used for disinfection in the processing and packaging of food and beverages where it is highly desirable to replace toxic chemicals.<sup>102</sup>

In all of these applications, mercury vapor discharge lamps are used to generate high intensity UV light. UV lamps are most commonly seen in plant grow lights, tanning beds, and black lights that are typically used in many aesthetic capacities combined with materials containing phosphors that absorb and re-emit the light as vibrant visible colors. These lamps work on the principle that high energy arcs in a low-pressure, inert gas vaporizes and ionizes small amounts of mercury into a plasma that produces UV light. Even though they are widely used, they have serious downsides including toxic byproducts from both manufacturing and disposal, high energy consumption from the high voltage requirements to induce electric breakdown and ignite a plasma, as well as throughout operation, bulky form factors, high operating temperatures, and long warm up times. These lamps also emit a wide spectral range of intensities which makes them ill-suited for applications that require a high intensity light source at a specific wavelength. Due to these significant downsides, there is currently a strong desire in the industry to replace these mercury vapor lamps with UV LEDs which are environmentally friendly, have lower fabrication costs, lower power consumption, and longer life times. In addition, UV LEDs have low operating temperatures which is beneficial for applications such as 3D printing, polymerization, and food processing where excess heat has an adverse effect on the products. UV LEDs also have an extremely small form factors compared to mercury vapor lamps, allowing them to be easily integrated into any existing product or process.<sup>103</sup>

AlGaN based LEDs are well positioned to replace mercury vapor lamps as the most widely employed UV light source. AlGaN is a ternary material with a tunable bandgap ranging from 3.4 to 6.1 eV, allowing it to be optimized for specific optical applications between 200 and 365 nm.<sup>104</sup> While the basic LED structures exist, the external quantum efficiency of UV LEDs is less than 11%, partly due to the low light extraction efficiency (LEE) due to sizeable UV light absorption of the electrical contact layers.<sup>105,106</sup> While technologically and economically acceptable solutions are known for LEDs emitting in the visible spectrum, e.g. by using a TCO such as ITO, no suitable material solution exists for the UV range. TCOs encompassing the traditional design of a transparent conducting electrode, such as ITO ( $E_g = 3.8 - 4.0 \text{ eV}$ )<sup>107</sup> and Al doped ZnO ( $E_g = 3.3 - 3.7 \text{ eV}$ )<sup>108</sup> have much lower band gaps than those required to transmit UV radiation generated by AlGaN, even when taking into account the Burstein-Moss shift for degenerate doping. These relatively small band gaps lead to large absorption coefficients exceeding 1.0×10<sup>5</sup> cm<sup>-1</sup> in the UV range of interest, making them unsuitable for UVB and UVC LEDs.<sup>109</sup> Choosing ultra-wide band gap semiconductors such as  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> ( $E_g = 5.3 \text{ eV}$ )<sup>110</sup> or  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> ( $E_g = 4.9 \text{ eV}$ )<sup>111</sup> alleviates the problem of low optical transparency; however, these materials have a significantly higher electrical resistivity since donor states are further away from the conduction band edge, thus exacerbating the activation of free carriers. Under optimal doping conditions of 10% Sn,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> was found to have a carrier concentration of only  $3.7 \times 10^{19} \text{ cm}^{-3}$ , while further increase of dopant concentrations resulted in a significantly reduced crystal quality and increased electrical resistivity.<sup>112</sup> A similar undesired resistivity increase for large dopant concentrations was observed in  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> as well.<sup>113</sup> In addition, heavily Sn doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> showed a significant band gap decrease from 5.3 eV down to 4.12 eV, attributed to a lattice parameter increase to accommodate the larger Sn atom in the lattice, concomitant with an undesirable shift of the interband absorption edge, making it less transparent in the UV.<sup>13,15</sup>

The lack of an effective transparent electrode in the UV has forced UV LEDs to adopt alternative LED architectures such as the thin film flip-chip architecture in order to spread current.<sup>115,116</sup> Further development of high performance UV TCOs would increase the design space for LEDs, allowing for simple and thus more cost effective LED architectures. Even though there is currently no reasonable option for a transparent conductor in the UV, the UV LED market was valued at 348.9 million USD in 2020 and is expected to reach one billion USD by 2026 resulting in a CAGR of 20.1%.<sup>117</sup> Implementation of an effective UV TCO technology could rapidly enhance the market share of UV LEDs, allowing a pragmatic shift away from mercury vapor lamps to environmentally benign, low power UV LEDs.

While the traditional TCO design methodology fails to provide suitable candidates for the UV spectrum, the correlated metal approach remains highly favorable. Unlike for visible applications, the reflection edge does not need to be pushed into the IR, allowing the utilization of materials with a lower correlation strength that are not useful in the visible range due to their higher

reflectivity. In addition, this allows for a higher carrier concentration and electrical conductivity, permitting higher figure of merits and lower required film thicknesses. The key difficulty in designing UV TCOs is the onset of interband absorption in the UV, necessitating the identification of materials with sufficiently isolated conduction bands. This can be done most thoroughly by data mining publicly available databases with standardized computable formats such as the Materials Project<sup>118</sup> and using first order descriptors such as a low imaginary part of the dielectric function to identify potential correlated, UV transparent conductors. Alternatively, crystal chemistry arguments can be put forward to identify metallic systems with a large energy separation between the conduction and valance bands. For instance, simply increasing the electronegativity between the transition metal cation and oxygen anions in a perovskite material would increase the energy difference between the O 2p and transition metal  $t_{2g}$  bands, reducing the absorption in the UV. This method was applied to the currently well-known visible transparent conductor SrVO<sub>3</sub> to identify SrNbO<sub>3</sub> as a UV transparent conductor and serves as the focus of Chapter 4 where SrNbO<sub>3</sub> was found to have an optical transmission up to 90% while maintaining an electrical resistivity

### **1.5** [111]-oriented perovskite thin films

comparable to the leading visible transparent conductor ITO.

The growth of perovskite oxides has long been focused on [001]-oriented films due to the low surface energy of the {001} facets and the inherent stability of the growth front. Using thin film growth methods, the effects of material composition, epitaxial strain, and deposition conditions are frequency analyzed while the effect of film orientation has been largely ignored. The properties of thin films often have an orientation dependence, especially if interfaces govern the properties, allowing the film orientation to be used as a new design knob for material design.

Traditionally, the growth of perovskite films has been avoided on substrates with [110]and [111]-orientations due to the polar surface arising from individually charged layers. Figure 1-9 demonstrates the arrangement and charge of individual layers in a typical perovskite oxide, SrTiO<sub>3</sub>, oriented along the [100], [110], and [111] directions. For the standard [100]-orientation it is comprised of alternating layers of SrO and TiO<sub>2</sub> which have zero net charge, indicating a low surface energy. If the crystal is rotated such that [110] is out of plane, the alternating layers become SrTiO and O<sub>2</sub> which have a charge of 4+ and 4- respectively, resulting in a polar surface. Similarly, [111]-oriented SrTiO<sub>3</sub> has alternating layers of Ti and SrO<sub>3</sub> with a charge of 4+ and 4- respectively.



Figure 1-9: Arrangement and effective charge of the individual layers in (a) [100]-, (b) [110]-, and (c) [111]- oriented SrTiO<sub>3</sub>.

The polar stacking sequence in the higher index orientations gives rise to the emergence of electric dipoles detrimentally affecting the growth, potentially driving the formation of unexpected phases, undesired [001]-orientations, and unwanted exposed facets as the film attempts to minimize its surface energy.<sup>119,120</sup> Typically these unfavorable conditions along these high energy directions trigger film growth to proceed in island growth mode as the film attempts to grow along a lower energy facet, resulting in rough or completely disjoined films.

The ability to synthesize thin films along different orientations opens a new avenue for strain engineering both single films and superlattices as biaxial strain will distort the crystal along a different plane giving rise to distorted Fermi surfaces, potentially giving rise to alternate electronic transport. In addition, the [111]-oriented surface in particular offers exciting opportunities as its surface structure resembles a buckled honeycomb lattice similar to 2D systems, potentially enabling novel topological properties. Numerous theoretical calculations have been performed predicting the modified properties of many perovskite systems grown in the [111]-orientation including nontrivial band topologies,<sup>121,122</sup> ferroelectricity,<sup>123,124</sup> Dirac semimetal phases,<sup>125</sup> spin-nematic phases,<sup>121</sup> the quantum spin Hall effect,<sup>126,127</sup> and the quantum anomalous Hall effect.<sup>128–131</sup>

Although a plethora of exotic phenomena have been predicted to exist in [111]-oriented perovskite layers, few have been experimentally realized due to the inherent difficulties in synthesizing high quality [111]-oriented perovskite films and superlattices. One successful study was the growth of [111]-oriented NdNiO<sub>3</sub> and LaNiO<sub>3</sub> thin films which were shown to exhibit the coexistence of polar displacements and reasonable conductivity.<sup>132</sup> Additionally, SrRuO<sub>3</sub> thin films grown on [001]-, [110]-, and [111]-SrTiO<sub>3</sub> substrates were found to exhibit higher saturation magnetization in the [110]- and [111]-oriented films.<sup>133</sup> It should be noted that the [111] films in this study had a non-uniform surface morphology with high film surface roughness values up to 4 nm, which likely resulted in an unreasonable comparison to the [001] films with a step terrace structure.

Typically, high energy growth techniques operating far from thermodynamic equilibrium have been utilized to overcome the effects of the high energy [111] surface, such as pulsed laser deposition (PLD) which has been used for the growth of SrRuO<sub>3</sub>,<sup>134–136</sup> SrFeO<sub>3</sub>,<sup>137</sup> La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>,<sup>138</sup> AlFeO<sub>3</sub>,<sup>139</sup> NdNiO<sub>3</sub>,<sup>140</sup> SrIrO<sub>3</sub>,<sup>141</sup> LaFeO<sub>3</sub>,<sup>142</sup> BaTiO<sub>3</sub>,<sup>142</sup> LaAlO<sub>3</sub>,<sup>143</sup> PbTiO<sub>3</sub>,<sup>144</sup> and Ba<sub>0.94</sub>La<sub>0.04</sub>SnO<sub>3</sub><sup>145</sup> or such as sputtering for the growth of SrTiO<sub>3</sub>,<sup>119,146</sup> NdNiO<sub>3</sub>,<sup>147</sup> and GdMnO<sub>3</sub>.<sup>148</sup> Even though these are highly energetic techniques, they do not provide direct and easy compositional control and therefore do not guarantee high quality, atomically smooth films. In addition to these growth techniques, many studies have claimed that the effects of the polar interface can be avoided by metallic screening of the surface charges. This can most easily be

observed in the case of using conducting [111]-oriented SrRuO<sub>3</sub> as a buffer layer material. BiFeO<sub>3</sub> has been shown to immediately adopt a 3D growth mode when deposited on insulating SrTiO<sub>3</sub>; however, when deposited using a conducting SrRuO<sub>3</sub> buffer layer it formed an atomically smooth film.<sup>149</sup> An identical transition in growth modes was also observed for SrFeO<sub>3</sub> grown on a SrRuO<sub>3</sub> buffer layer.<sup>137</sup> Studies on the growth of SrRuO<sub>3</sub> on SrTiO<sub>3</sub> identified that it did not immediately assume a smooth growth mode.<sup>134,135</sup> Instead, it initially adopted an island growth which eventually coalesced into a 2D atomically smooth surface at around 10 nm. This 2D growth mode was found to eventually relax back into a 3D island growth at thicknesses exceeding 50nm, likely due to film exceeding the critical thickness. The boundaries of each mode were found to be altered by the growth temperature and deposition rate.<sup>135</sup> This initial 3D growth mode likely arose due to a critical surface coverage to successfully screen the polar interface. Others studies have reported films as thin as 2.3 nm but have not reported on the surface morphology to confirm the coherency of the film.<sup>136</sup> These studies demonstrate that a high electrical conductivity of the deposited material does not guarantee an atomically smooth surface and that other considerations must be made to ensure high quality film growth.

In addition to phase pure films, superlattices have been proposed to further demonstrate unique properties arising from the unusual interactions between layers. For instance, the buckled honeycomb interfaces of [111]-oriented superlattices result in the interfacial B-site cations to be equidistant to 3 B-site cations of the same species and 3 B-site cations of the next layer as opposed to 1 and 5 for [001]-oriented superlattices respectively, increasing the interaction between the B-sites of different layers. In addition, the buckled honeycomb interface in bilayer structures is similar to that of 2D materials such as graphene, giving rise to Dirac points in the band structure. These effects make [111]-oriented heterostructures an ideal platform for designing topologically nontrivial states such as Chern insulators<sup>150</sup> or to realize effects such as the quantum spin Hall effect.<sup>126,129,130</sup>

To realize such properties, atomically smooth and abrupt interfaces are required, necessitating a mastery of high-quality synthesis which has yet to be accomplished for many of the essential material systems. One example experimental study was the growth of La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>/SrRuO<sub>3</sub> superlattices which were observed to exhibit the magnetocaloric effect.<sup>151</sup> Another study utilized strain engineering on [111]-oriented paramagnetic LaNiO<sub>3</sub>/ferromagnetic LaMnO<sub>3</sub> superlattices where an exchange bias emerged as a function of the layer thickness, inducing magnetism in the paramagnetic LaNiO<sub>3</sub> layers.<sup>152</sup> Some other successfully synthesized superlattices include BiFeO<sub>3</sub>/BiCrO<sub>3</sub>,<sup>153</sup> LaAlO<sub>3</sub>/LaNiO<sub>3</sub>,<sup>154</sup> LaCoO<sub>3</sub>/SrTiO<sub>3</sub>,<sup>155</sup> LaNiO<sub>3</sub>/CaMnO<sub>3</sub>,<sup>156</sup> and BiFeO<sub>3</sub>/LaFeO<sub>3</sub>.<sup>157</sup>

Further development of [111]-oriented perovskite growth will be discussed in Chapter 7 with the successful growth of [111]-oriented SrVO<sub>3</sub> using the self-regulated growth mode enabled by *h*MBE. These films were found to have a higher residual resistivity ratio than [001]-oriented films grown by any other method, allowing the observation of pronounced nonlinearities in the transverse Hall resistance at low temperatures. Detailed studies such as this provide invaluable resources for the future development of novel films and superlattice structures.

## 1.6 Additional considerations for electron interactions

A full discussion of the individual interactions of electrons in correlated materials, while useful, would far exceed the space limitations of this thesis; therefore, only a brief discussion of the most relevant considerations is made here. A brief introduction to classical electronic transport leading into Fermi liquid theory is covered followed by a discussion on electron-electron scattering. This section then concludes with a discussion of other electron scattering phenomena.

### 1.6.1 Landau Fermi liquid theory

Here the basic concepts of Fermi liquid theory are summarized and discussed in a sufficient capacity to lay the foundation for the interpretation of the experimental data presented in Chapter 6 and Chapter 7. Further details and derivations can be found in the following references.<sup>158,159</sup>

The conventional theoretical framework to describe electronic transport in simple materials follows the semiclassical Drude-Sommerfeld approach. Here, electrons are assumed to be non-interacting and to follow the Pauli exclusion principle. This restriction in energy states is accounted for by the Fermi-Dirac distribution.<sup>160</sup> The energy of the highest energy electron at zero temperature can then be expressed by the Fermi energy  $E_F$  as shown in Eq. 1.7 where  $\hbar$  is the reduced Planck's constant, m is the mass of the electrons, and n is the carrier concentration.

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$$
 Eq. 1.7

The velocity of electrons is described by the Fermi velocity  $v_F$  as shown in Eq. 1.8 where  $k_F$  is the Fermi wavevector.<sup>160</sup>

$$v_F = \sqrt{\frac{2E_F}{m}}$$
 Eq. 1.8

In an applied electric field, the noninteracting free electrons are accelerated until they collide with scattering sites that are deviations from an ideal periodic potential. The collisions offer a relaxation mechanism for the electrons to dissipate momentum such that a quasi-equilibrium state is achieved in which momentum gain by acceleration and momentum loss by scattering are balanced. The type of deviation resulting in the collision does not matter, it could a phonon, impurity, or defect. What matters is that these collisions occur after a relaxation time,  $\tau$ , where the distance between successive collisions for carriers traveling at velocity  $v_F$  is the mean free path or scattering length, *l*. These collisions then give rise to the electrical resistivity following Eq. 1.9.<sup>161</sup>

$$\rho = \frac{m}{e^2 n\tau}$$
Eq. 1.9

Surprisingly, this simple approximation is sufficient for most applications even though it does not consider the coulombic interactions between electrons. In some material systems, the coulombic interactions between the electrons are significant and it must therefore be considered as an interacting many-body system. In 1956 Lev Landau developed a theory on interacting Fermi systems to explain the properties of He<sup>3+</sup> which has since been a cornerstone in modern physics and has been widely used to explain the low temperature behavior of electrons in metals and many correlated systems.<sup>158,162</sup> Starting with a non-interacting Fermi gas, the ground state's energy levels are occupied to the Fermi energy with the occupation obeying the Pauli exclusion principle. All states above  $E_F$  are unoccupied and the boundary between the occupied and unoccupied states forms the Fermi surface in momentum space. For this non-interacting Fermi gas, the Fermi surface is considered to be spherical in three dimensions and circular in two dimensions. As electron interactions are adiabatically turned on, the eigenstates of the non-interacting system must evolve continuously and smoothly into the eigenstates of the real, interacting system, designated a Fermi liquid. The endpoints of this transition are shown schematically in Figure 1-10 along with the occupation distribution.



Figure 1-10: Cross section of a Fermi surface in (a) a non-interacting system and (b) an interacting system where states in the narrow region with width contribute to electron-electron interactions. This distribution is further shown as the density of states in (c) where the discontinuity Z occurs at the Fermi wavevector  $k_F$ .

Since these excitations consist of their own energy plus that of their interactions with all other fermions, they are considered to be quasiparticles. If such quasiparticles accounting for the electron-electron interaction are present, their scattering interactions in a three-dimensional system approximated by a spherical Fermi surface at a finite temperature can be determined using straightforward energy and momentum conservation arguments.<sup>163</sup>

Consider the projection of the Fermi surface shown in Figure 1-10(b) where there exists a thermal layer at the edge of the Fermi surface with width  $\sim k_B T$ . Take two electrons in the initial states  $K_1$  and  $K_2$  that scatter into the final states  $K_3$  and  $K_4$  respectively where each state lies in the thermal layer. Each electron experiences a change in energy of  $E(K_3) - E(K_1)$  and  $E(K_4) - E(K_2)$  respectively where the conservation of energy requires that:  $E(K_1) + E(K_2) = E(K_3) + E(K_4)$  and the conservation of quasimomentum requires that:  $K_1 + K_2 = K_3 + K_4$ .

The scattering rate of any particular electron, for example in  $K_1$ , can be presented as a summation over all potential scattering partners where the probability for electrons in occupied states  $K_1$  and  $K_2$  to scatter into empty states  $K_3$  and  $K_4$  respectively while obeying the conservation laws is given by  $P(K_1, K_2, K_3, K_4)$ .

$$\tau_{ee}^{-1}(K_1) = \sum_{K_2, K_3, K_4} P(K_1, K_2, K_3, K_4)$$
 Eq. 1.10

In three dimensions,  $K_1$  is fixed so there are nine variables due to the summations over  $K_2, K_3$  and  $K_4$ . The conservation of quasimomentum and energy can then be used to reduce this to five independent variables. The conservation of quasimomentum  $K_1$  is fixed which fixes  $E(K_1)$  resulting in two independent energies since one additional energy must be fixed.

$$\tau_{ee}^{-1}(K_1) = \sum_{q, E(K_2), E(K_3)} P(q, E(K_2), E(K_3))$$
 Eq. 1.11

This restriction causes the number of states available for scattering with energies  $E(K_2)$ and  $E(K_3)$  to be proportional to  $k_BT/E_f$  for each independent energy variable since each electron must be located in the thermal shell of the Fermi surface. Therefore, for three dimensions  $\tau_{ee}^{-1} \propto T^2$ . This result then gives rise to  $\rho \propto T^2$  when combined with Eq. 1.9, a key experimental descriptor for Fermi liquids.

### 1.6.2 Electron-electron scattering

While it has been shown that electron-electron scattering results in a *T*<sup>2</sup> dependent resistivity, electron-electron scattering can further be classified into three distinct groups: normal electron-electron scattering (NEES), Umklapp scattering, and Baber scattering. Each of these events contribute to the resistivity with a different magnitude given by the scattering prefactor A<sub>ee</sub>. NEES events are collisions in which momentum is conserved and therefore do not relax momentum or contribute to the resistivity. Umklapp scattering events occur when the scattered wave vectors lie outside the first Brillouin zone, necessitating their translation back inside resulting in a transfer of momentum to the lattice. These events typically occur if the carrier concentration and Fermi surface are large enough such that the Fermi wave vector is at least 1/4<sup>th</sup> the width of the Brillouin zone. Finally, Baber scattering occurs when electrons of different masses interact, allowing lighter electrons to conduct current while the heavy electrons act as a sink.<sup>164</sup> Scattering between these two 'reservoirs' results in a momentum transfer even if it would normally be a NEES event. This type of scattering more generally occurs due to anisotropic scattering due to hot and cold Fermi surface pockets.

The identification of multiple momentum relaxation mechanisms associated with electronelectron scattering makes it difficult to provide a specific quantitative expression for the prefactor  $A_{ee}$ . Commonly, a dimensional analysis argument is put forward to determine the material specific contributions to the prefactor  $A_{ee}$ . Following  $\rho = A_{ee}T^2$ ,  $A_{ee}$  must have units of  $[VmA^{-1}K^{-2}]$ . Assuming that the electron scattering occurs on a length scale  $(l_{ee})$  and are quantized by the quantum conductance  $(G_0)$  we arrive at Eq. 1.12.<sup>165</sup>

$$A_{ee} = \frac{1}{G_0} \left(\frac{k_B}{E_F}\right)^2 l_{ee}$$
 Eq. 1.12

The characteristic e-e length scale can alternatively be expressed by the scattering cross section as  $k_F \sigma_{cs}$ . This scattering cross section is simply a measure of probability that electron-electron scattering will take place.

$$A_{ee} = \frac{1}{G_0} \left(\frac{k_B}{E_F}\right)^2 k_F \sigma_{cs}$$
 Eq. 1.13

Making the reasonable approximation that the Fermi surface is spherical such that  $k_F = (3\pi^2 n)^{1/3}$  and  $E_F = \hbar^2 k_F^2 / 2m$  where *m* is the electron mass, the dependence of A<sub>ee</sub> can be shown to only be dependent on the scattering cross section and the carrier concentration.

$$A_{ee} = \frac{4m^2 k_B^2}{3\pi^2 \hbar^4 G_0} \frac{\sigma_{cs}}{n}$$
 Eq. 1.14

This expression for  $A_{ee}$  closely follows Baber's original derivation of the temperature dependent resistivity shown in Eq. 1.15 as the scattering cross section encompasses the band and mass information of the interacting electrons. This resistivity dependence on the electron scattering arising from carrier channels with different carrier masses was found to follow Eq. 1.15 where it was dependent on the carrier concentration *n*, the electron mass *m*, the width of the s-band  $\xi$ , and the function H which depends on the ratio of electron masses  $\beta$ , and the screening constant *q*. <sup>164</sup>

$$\rho = \frac{\pi^2 e^2 m^2}{16nh^3} \left(\frac{kT}{\xi}\right)^2 H(\beta, q)$$
 Eq. 1.15

A similar expression for  $A_{ee}$  has been derived for polaron mediated electron-electron scattering in SrTiO<sub>3</sub> where the same dependencies were revealed.<sup>166</sup> The similarities to these specific scattering prefactors indicate that the result from the dimensional analysis argument is a reasonable approximation for the total prefactor from all momentum relaxation mechanisms.

### **1.6.3** Additional electron scattering events in metals

Basic interpretations of experimental transport measurements can be made through the determination of the resistivity scaling factors. The electrical resistivity is related to the intrinsic material properties as shown in Eq. 1.9. While there are some cases where the effective mass and carrier concentration are temperature dependent, they are not related to electron scattering events; therefore, the discussion here is limited to the effects of scattering on the carrier relaxation time,  $\tau$ .

For this discussion we consider electrons in the classical sense where they are free to move within the metal with a velocity equal to the Fermi velocity. As the electrons move, they scatter from deviations from a perfect crystal whether it be the thermal lattice vibrations (phonons), point defects such as impurities and vacancies, or extended structural defects such as grain boundaries, threading dislocations, and stacking faults. Each type of deviation is associated with a unique scattering cross section giving rise to individual relaxation times. For sequential noninteracting scattering processes where energy is conserved, these individual processes can be combined using the inverse sum rule known as Matthiessen's rule as shown in Eq. 1.16. This straightforward relation allows each contribution to be considered individually and summed for the total effect to the relaxation time, and therefore the resistivity.

$$\frac{1}{\tau_{total}} = \sum_{i} \frac{1}{\tau_i} = \frac{1}{\tau_{phonons}} + \frac{1}{\tau_{defects}} + \frac{1}{\tau_{grain \ boundaries}} + \dots \qquad \text{Eq. 1.16}$$

Crystalline defects such as impurities, vacancies, and grain boundaries that have temperature independent scattering cross sections make up the residual resistivity at the lowest possible temperature,  $\rho_0$ , which can be used as a material quality metric in the form of the residual resistivity ratio  $RRR = \rho_{300K}/\rho_0$ , where  $\rho_{300K}$  is the resistivity measured at room temperature.

Conversely, electron-phonon scattering is highly temperature dependent and is the dominant scattering mechanism at most temperatures. Phonons are lattice vibrations that are quantized by the boundary conditions of the crystalline lattice. In a 3D crystal with N atoms, the

three spatial directions impose 3N discrete phonon modes, each with an energy of  $\hbar\omega$ . As temperature increases, these modes become populated resulting in larger amplitude oscillations in the crystal. The maximum angular frequency of the normal modes occurs at the Debye temperature,  $\Theta_D$ , described by Eq. 1.17 where  $v_s$  is the speed of sound and V is the volume of the crystal.<sup>167</sup>

$$\Theta_D = \frac{\hbar v_s}{k_B} \left( 6\pi^2 \frac{N}{V} \right)^{1/3}$$
 Eq. 1.17

At temperatures above  $\Theta_D$ , all normal modes are populated. The temperature dependence of phonon scattering to the resistivity is described by the Bloch-Grüneisen model given in Eq. 1.18 where *B* is a material dependent constant.<sup>168</sup>

$$\rho(T) = B\left(\frac{T}{\Theta_D}\right)^5 \int_0^{\Theta_D/T} \frac{t^5}{(e^t - 1)(1 - e^{-t})} dt$$
 Eq. 1.18

Here it can be perceived that at temperatures  $T \ll \Theta_D$  where only the low energy phonon modes are being populated, the integral goes to zero resulting in a  $T^5$  temperature dependence. Around the Debye temperature this dependence begins to transition to that of temperatures  $T \gg$  $\Theta_D$  where the resistivity dependence is proportional to T. As phonon modes become populated, they rapidly increase the number of electron-phonon collisions. Once all modes are populated, the scattering only increases linearly with temperature.

Far below the Debye temperature where few phonon modes are populated and their contribution to the resistivity is minimal, many exotic scaling behaviors can be observed. For instance, magnons in ferromagnetic materials can give rise to a  $T^2$  or a  $T^{9/2}$  dependence, where the exponent depends on the exchange mechanism.<sup>169,170</sup> This low temperature region is also home to localization effects arising from specific defects such as Anderson localization and the Kondo effect. Anderson localization arises from significant levels of disorder which sets up energy barriers preventing the movement of electrons. These barriers force the electrons to hop to sites where the initial and final energies are close, resulting in resistivity scaling of  $T^{1/2}$  to  $T^{1/4}$  depending on the

geometry of the sample and the types of defects.<sup>171</sup> The Kondo effect arises from electrons scattering off magnetic impurities, diverging the resistivity as temperature reaches 0 K.

As a general guideline, the previously discussed temperature scaling relations of resistivity in addition to some uncommon relations are summarized in Table 1-1. Note that care must be taken when applying these scaling dependences to a real system since multiple effects can take place at the same temperature. For example, a temperature dependent resistivity following  $\rho(T) = AT^2 + BT^5$  could appear to have  $T^3$  or  $T^4$  scaling for a finite temperature region.

Table 1-1: Temperature dependent resistivity scaling for various scattering events, theoretical models, and reasonably unexplained experimental observations. Here,  $\Theta_D$  is the Debye temperature which typically ranges between 200-600 K and  $T_F$  is the Fermi temperature which is typically a few eV.

Scattering event/model/system	Temperature dependence	~Temperature Range
Kondo Effect	Log(T)	$T \ll \Theta_D$
Anderson localization	$T^{1/2} - T^{1/4}$	$T \ll \Theta_D$
Electron-phonon (fully populated)	T	$T \gg \Theta_D$
Itinerant-electron ferromagnetism <sup>172</sup>	T <sup>3/2</sup>	$T \ll T_F$
Marginal Fermi-liquid model <sup>173</sup>	T <sup>5/3</sup>	$T \ll T_F$
Electron-electron	$T^2$	$T \ll \Theta_D$
Electron-magnon <sup>169</sup>	$T^2$	$T \ll \Theta_D$
Electron-phonon (Bloch-Wilson limit) <sup>174</sup>	$T^3$	$T \ll \Theta_D$
Electron-two magnon <sup>170</sup>	$T^{9/2}$	$T \ll \Theta_D$
Electron-phonon (populating modes)	$T^5$	$T \ll \Theta_D$

## 1.7 Scope of this work

This work focuses on three areas of development for correlated metals: pushing correlated transparent conductors into the UV with  $SrNbO_3$ , investigating the interplay between disorder and the electrical properties of  $SrVO_3$ , and examining the effect of film orientation with [111]-oriented  $SrVO_3$ . The materials discussed in this thesis,  $SrVO_3$  and  $SrNbO_3$ , were grown using *h*MBE and

In Chapter 4, the ability to shift transparent conducting correlated metals into the UV is demonstrated using SrNbO<sub>3</sub> which is shown to have a transmission up to 90% at a wavelength of 280 nm while maintaining resistivities comparable to the leading visible transparent conductor ITO. Chapter 5 goes on to demonstrate the successful transition to depositing SrNbO<sub>3</sub> using RF-sputtering as well as discuss the utilization of large Sr deficiencies as an additional tuning parameter for the transmission window. In Chapter 6, the wide range of crystalline quality enabled by *h*MBE is utilized to examine the dependence of the electronic transport of SrVO<sub>3</sub> on temperature and disorder. In this work, a robust Fermi liquid is shown to exist at low temperatures where the scattering prefactor is altered due to anisotropic scattering of the Fermi surface. Finally, the growth of SrVO<sub>3</sub> thin films is demonstrated along the thermodynamically unfavorable, polar [111]-orientation using *h*MBE in Chapter 7. This simple alteration in film orientation was found to result in pronounced nonlinearities in the transverse Hall coefficient when compared to traditional [001]-oriented films.

## **Chapter 2: Growth of correlated oxide materials**

In order to experimentally obtain fundamental insight into the intrinsic physics of correlated materials it is vital to synthesize high quality materials that are free from defects giving rise to extrinsic scattering sites, potentially obscuring the true physical phenomena from the material. In this thesis, this is accomplished through the growth of epitaxial thin films using hybrid molecular beam epitaxy (*h*MBE), a technique which offers superior growth kinetics over other, more conventional techniques, enabling a significant decrease in the unintentional defect concentration. The growth of thin films is a complex non-equilibrium kinetic process, requiring a thorough understanding of a wide variety of processes and techniques. In this chapter we will discuss the basic growth processes including absorption, nucleation, and growth. First, the kinetic processes that take place during growth will be discussed, then the types of thin films growth modes and defect types will be highlighted. The most commonly used thin film growth methods for correlated oxide materials will then be discussed with a focus on with RF sputtering and *h*MBE. Finally, this chapter will conclude with an overview of the deposition chambers and methods used in this thesis.

## 2.1 Growth processes

Achieving the delicate balance of the growth conditions in order to meet the simultaneous requirements of stoichiometry, crystallinity, epitaxy, and uniformity is a key challenge in the synthesis of thin films. To meet these criteria, a thorough understanding of the growth and kinetics in thin film growth processes is necessary. Each of these processes can be influenced in numerous ways, opening new routes for the optimization of film quality and their desired material properties.

To get an idea of the inherent tunability of thin film growth, the basic thermodynamic, kinetic, and growth processes are discussed in the following subchapters. For more detailed descriptions of these processes, the reader is suggested to see Zangwill (1988)<sup>175</sup> and Oura, *et al* (2003).<sup>176</sup>

### 2.1.1 Physical and chemical adsorption

A crucial step to film growth is the accumulation of atoms at the growth surface. As molecules from the vapor phase are incident on the growth front and get within a few atomic distances, they experience an attractive force from the surface atoms. The interaction energy between the substrate surface and an incident particle can be modeled using the Lennard-Jones potential where *r* is the distance between the atom and the surface,  $\varepsilon$  is the potential well depth, and  $\sigma$  is the distance where the potential between the substrate surface and the incident particle is zero.

$$V(r) = 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$
 Eq. 2.1

Incident atoms with sufficiently low energy will be captured in the energy potential well and adsorb into the film through physical adsorption (physisorption). This potential well is shown for the physisorption process in Figure 2-1(a). Physisorbed atoms remain mobile on growth front and are able to laterally move on the surface, hopping between surface sites. These ad-atoms are able to diffuse along the surface, colliding with surface features and each other. If a physisorbed atom gains enough thermal energy it can either desorb from the surface or undergo a further interaction called chemical adsorption (chemisorption) by hoping into the lower potential well as shown in Figure 2-1(b). Chemisorption involves the formation of a chemical bond of the deposited material to the substrate and is therefore a much stronger interaction than physisorption. This chemisorption process typically occurs near step edges on the growth surface that act as nucleation sites. Since some of the physisorbed adatoms desorb from the surface, the sticking coefficient, defined as ratio of the arriving chemical species remaining on the growth front to the total amount of chemical species provided, is smaller than unity. The value of the sticking coefficient is not only dependent on the species provided, but also on the growth temperature and the rate at which the material is deposited since extremely high growth rates result in material being buried before it is able to desorb. These growth processes are shown schematically in Figure 2-1(c).



Figure 2-1: (a) Schematic of the potential energy for physical adsorption demonstrating the conditions for thermalization for thermal desorption of atoms at the growth front. (b) Schematic of the potential energy for chemical adsorption. (c) Schematic demonstrating the surface process that occur at the growth front.

### 2.1.2 Thin film growth modes

Once the adsorbed species accumulate on the growth front and form a film, the individual atoms can assemble into different compositions and polymorphs depending on the energetics at the growth front and the stoichiometry of the absorbed species, resulting in either a single phase or multiphase film. Factors such as epitaxial strain are typically utilized to energetically stabilize a specific phase where the structure and lattice parameter of the substrate and film are somewhat matched, leading to a film that is well-oriented with respect to the substrate. The atoms can further arrange in an ordered fashion with a single orientation, referred to as single crystalline film, in an ordered fashion but different orientation – a polycrystalline film, or an amorphous film in which the adsorbed species lack any long-range order, as shown in Figure 2-2.

For thin films where the desired outcome is to study the intrinsic properties of the film, single phase, single crystalline films are targeted as the crystal structure is uniform across the entire film, there are few defects, and there are no grain boundaries to convolute property measurements. To achieve a single crystal film, the growth temperature needs to be high enough to maximize surface mobility yet low enough to prevent thermal desorption. The growth rate must also be slow enough to allow the deposited material to diffuse to a stable position before it becomes buried by the next layer of material. For most MBE applications this rate is around 1 nm/min. In addition, for many material systems, this requires the use of epitaxial growth where a lattice matched single crystal substrate is used to provide a template for the film to form and orient itself. The substrate should also be atomically smooth and clean of any defects to prevent their transfer to the film.



Figure 2-2: Types of arrangements of material assuming a single phase deposited on a substrate. (a) Films comprised of atoms arranged coherently in a periodic lattice are referred to as a single crystal. (b) Films made up of domains of coherently arranged atoms that have different orientations are referred to as polycrystalline. (c) Films with atoms arranged completely randomly with no coherency are amorphous.

In contrast to a single crystalline film, a polycrystalline film has domains of different crystalline orientations. This typically occurs when the growth temperature is not high enough to fully crystalize the deposited material or when the film is grown on a substrate that does not have the same symmetry. For example, if a film with 4-fold symmetry such as SrNbO<sub>3</sub> is grown on a substrate with 6-fold symmetry such as GaN with significantly different lattice parameters (See section 5.3), the film will have multiple, energetically equivalent ways to orient on the substrate and therefore form twin domains. A similar effect can arise if the film and substrate have the same

symmetry but have significantly different lattice parameters. For example, if a  $SrVO_3$  film  $(a=3.842\text{\AA})^{177}$  was grown on MgO substrate  $(a=4.211\text{\AA})$ ,<sup>178</sup> even though they share the similar cubic symmetry, they have a lattice mismatch of over 8% which could result in an ordered film with domains or simply a relaxed film.

Finally, if the randomness is at the atomic level where there is no long-range order established whatsoever, the film is amorphous. This most commonly occurs if the film is grown at a temperature significantly below its crystallization temperature. In this case, there is not enough thermal energy for the deposited material to move and locate an energetically preferred position before being buried by additional incident material. Deposition at room temperature typically satisfies this requirement; however, some materials such as transition metals require deposition at cryogenic temperatures to be amorphous.<sup>179</sup>



Figure 2-3: Schematics of the growth modes determined by the wetting characteristics and surface energies of the film, substrate, and vacuum. (a) When  $\gamma_{sv}$  is smaller than  $\gamma_{sv} + \gamma_{fv}$ , the deposited material will ball up on the substrate, leading to Volmer-Weber growth. (b) When  $\gamma_{sv}$  is larger than  $\gamma_{sf} + \gamma_{fv}$ , the deposited material will wet on the substrate. Schematic representations of (c) the Volmer-Weber growth mode, (d) layer-by-layer growth, (e) the Stranski-Krastanov growth mode, and (f) step flow growth.

Once the conditions have been met to accumulate material on the growth surface, the growth process can proceed in several different manners, governed largely by the surface or interfacial energies between the substrate, film, and vacuum in addition to the substrate temperature and lattice mismatch. The three interfaces to consider are between the substrate and film ( $\gamma_{sf}$ ), between the substrate and vacuum ( $\gamma_{sv}$ ), and between the film and vacuum ( $\gamma_{fv}$ ). Assuming the particles deposited on the surface are spherical, the contact angle can be expressed using Young's

equation:<sup>176</sup>

$$\gamma_{sv} = \gamma_{fv} + \gamma_{sf} \cos(\theta)$$
 Eq. 2.2

For 3D island growth,  $\theta > 0$  resulting in the following interfacial energy condition:

$$\gamma_{sv} < \gamma_{fv} + \gamma_{sf}$$
 Eq. 2.3

In this case the surface tension of the film exceeds that of the substrate; therefore, the film wants to minimize its contact with the substrate. Incoming ad-atoms will prefer to be on top of existing atoms instead of the substrate, effectively balling up on the substrate as shown schematically in Figure 2-3(a). As film deposition continues it will adopt the Volmer-Weber growth mode or island growth mode as shown in Figure 2-3(c).

For the opposite case where the substrate has the highest surface energy, incoming adatoms will prefer to be in contact with the substrate, wetting the film on the surface since  $\theta = 0$ , corresponding to:

$$\gamma_{sv} \ge \gamma_{fv} + \gamma_{sf}$$
 Eq. 2.4

In addition to the interfacial energies, the structural differences between the film and substrate play a role in the film growth. For epitaxial growth, the crystal symmetry of the substrate surface must be compatible with the symmetry of the desired film. Following this, the film lattice parameter  $(a_f)$  and substrate lattice parameter  $(a_s)$  must be considered. If the film lattice parameter is larger than that of the substrate, the film will need be compressively strained to grow epitaxially.

If the film lattice parameter is smaller it will need to be stretched or tensile strained to grow epitaxially. This strain is quantified by the lattice mismatch:

$$f = \frac{a_f - a_s}{a_s}$$
 Eq. 2.5

For homoepitaxial growth, where the grown film is identical to the substrate, there is no lattice mismatch and the interface essentially vanishes. In this case, or for heteroepitaxial growth where the lattice mismatch between the film and substrate is small ( $f \approx 0.8\%$ ), the growth proceeds as layer-by-layer growth, also known as Frank-van der Merve growth as shown in Figure 2-3(d) and a smooth film will form. If the lattice mismatch is too large, the film lattice attempts to adjust to the substrate at the expense of elastic deformation. The first few layers may be able to adopt a layer-by-layer growth but the growth front will eventually exceed the range of the adhesion forces, thus relaxing the strain and causing the film to adopt an island growth mode as shown schematically in Figure 2-3(e).

The final case discussed here is step-flow growth that occurs under the same surface energy conditions as layer-by-layer growth. In order to achieve step-flow growth, the substrate must be slightly miscut by a few degrees to provide well-oriented terraces or steps of monatomic height. As long as the terrace widths are shorter than the mean diffusion lengths of the ad-atoms, the deposited ad-atoms will diffuse to these step edges as they are the most energetically favorable site to bond, resulting in a smooth film mimicking the terraces from the substrate.

## 2.1.3 Defects in thin films

Defects in a crystalline material play a significant role in both the formation of thin films and their resulting properties. While defects are usually thought to be undesired, the presence of specific defects can enable or improve certain properties. For example, the dopant atoms in semiconductors are defects intentionally added to control the electrical conductivity.<sup>180</sup> In addition, point defects can add new electronic states to the material that affect the optical properties. Defects typically add additional optical transitions beyond those of the intrinsic material, thus increasing the optical absorption; however, these additional transitions may be in competition with those arising from the intrinsic material and thus improve the optical transmission in a specific region. For example, if the additional optical transitions from defects dominate the optical response in a spectral range that is of no interest (e.g., the IR), which then weakens the intrinsic transitions in the spectral range of interest (e.g., the visible), then defects can be beneficial to optimize material performance beyond the intrinsic limits.

Due to the variability of defect utility, instead of attempting to remove all defects from a system it is significantly more beneficial to have control over the level of defects. Defect formation during film growth can be controlled to a certain extent by the growth method chosen and growth parameters employed. Defects fall into three broad classes: point defects, line defects, and planar defects. Point defects are defined as a single atom that is out of place. Examples include foreign atoms on an interstitial site, vacancies on either a cation or anion site, or substitutional dopants. These point defects can also arrange in an ordered manner to form a domain of a specific symmetry. Line defects are a disruption of a perfectly periodic arrangement along one dimension. Linear defects, such as dislocations, commonly occur at film-substrate heterointerfaces to accommodate and alleviate strain originating from a significant film-substrate mismatch, such as in the case of SrNbO<sub>3</sub> grown on LSAT. One example is an edge dislocation which occurs when an extra plane of atoms is introduced, distorting the lattice. This distortion is described using the Burgers vector which quantifies the direction and magnitude of the atomic displacement. An example of an edge dislocation along with its associated Burgers vector is shown in Figure 2-4(a). The Burgers vector is calculated from the comparison to the ideal lattice.

Another type of line defect is a screw dislocation which occurs if the lattice planes are slipped in a helical path along a linear defect. An example of a screw dislocation is shown in Figure

2-4(b). Unlike edge dislocations, pure screw dislocations have a Burgers vector parallel to the linear



Figure 2-4: (a) Distortion of the perovskite lattice due to an edge dislocation with the associated Burgers vector determined from the comparison to the ideal lattice. (b) STEM image of a screw location in  $Sr_xNbO_3$  on LSAT. (c) Schematic of stacking faults in perovskites. (d) STEM image of a stacking fault in SrVO<sub>3</sub> on LSAT reproduced from reference.<sup>181</sup>

Finally, planar defects are two-dimensional and occur when two dissimilar materials are stitched together along a plane or when the stacking order of a crystal is interrupted, causing a disruption in periodicity. Typical [001]-oriented  $ABO_3$  perovskite films consist of alternating AO and  $BO_2$  layers; however, if the stacking order is changed by adding, removing, or substituting an individual layer, then a stacking fault occurs. This effect is shown schematically in Figure 2-4(c) where a single AO layer is replaced by a CO layer and where a  $BO_2$  layer is removed, resulting in neighboring AO layers which is commonly described as a Ruddlesden-Popper (RP) fault. Such RP

faults are commonly observed in films grown under *A*-site rich conditions such as Sr-rich SrVO<sub>3</sub> on LSAT as shown in Figure 2-4(d).<sup>181</sup> If these stacking faults assume an ordered arrangement, a new RP phase is formed which follows the formula  $A_{n+1}B_nO_{3n+1}$  where an extra *AO* layer is added for every *n* perovskite layers.<sup>182</sup>

## 2.2 Thin film growth techniques

Thin film synthesis methods can be categorized into two main groups: physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques. In CVD techniques, the supplied species undergo a chemical reaction before becoming incorporated into the film. This is not the case with PVD techniques where material species are physically ejected towards a substrate from a condensed matter source, whether it be through thermal evaporation or ablation. As this work mainly involves PVD techniques, this section will summarize and discuss the advantages and shortcomings of the three most common PVD techniques used for depositing correlated metals; sputtering, pulsed laser deposition, and molecular beam epitaxy.

### 2.2.1 Sputtering

Sputtering is one of the most widely used thin film deposition techniques due to its rapid deposition rates in conjunction with its low setup and operating costs, allowing it to be easily integrated into research laboratories and industrial processes alike. The basic premise of sputtering is the transfer of material from a target to a substrate. To accomplish this, the target material is biased, causing ions in a plasma to accelerate into it, these collisions eject or 'sputter' atomic sized fragments of the target material towards the substrate. In a typical sputter deposition process, the deposition chamber is pumped out to high vacuum using turbomolecular pumps or cryogenic pumps to evacuate any unwanted background gases and contaminants. The chamber is then backfilled with a sputtering process gas, typically an inert gas (e.g. the noble gas argon) is used to prevent an incorporation of the process gas into the deposited material. A plasma is ignited by applying a high voltage bias at a cathode located behind the sputter target while the deposition chamber acts as the anode. Electrons are then accelerated away from the cathode and some number collide with the atoms of the process gas and ionize them. This avalanche of free moving charged particles results in an electric breakdown and ignition of a plasma. These ionized and positively charged argon ions are accelerated towards the cathode and collide with the target material causing atoms to be ejected with enough kinetic energy to reach the substrate and the surrounding chamber walls. This process is shown schematically in Figure 2-5. Deposition rates can be increased to some degree by maximizing these collisions by increasing the deposition pressure or by using a higher molecular weight processing gas; however, this also reduces the kinetic energy of the sputtered material. Many modern sputtering tools utilize magnetron sputtering which employs strong permanent magnets to further confine the plasma near the target, leading to increased deposition rates.

As the target material is ejected through high energy collisions, the sputtered material strikes the substrate with energies ranging from tens to hundreds of  $eV^{183}$  which can aid in the crystallization of the film but can also detrimentally affect the film quality through either the formation of defects or through re-sputtering low Z number elements causing non-stoichiometry. In addition, larger chunks of the target can be eroded and incorporated into the film without crystalizing properly.<sup>184</sup> The formation of these defects can be somewhat avoided through the use of off-axis sputtering where the target is positioned at angles up to 90° off of the substrate. In this case, the substrate is not directly in the line of sight of the target and the ejected material must undergo several collisions with the process gas before striking the substrate causing a lower, more uniform energy of impinging material. While this method allows for much higher crystalline

quality, it comes at the cost of a greatly reduced deposition rate. This tradeoff is highly desirable when investigating intrinsic material properties and has been widely used to produce high quality epitaxial films and heterostructures.<sup>185–187</sup>

The sputtering process can be categorized into four primary types: direct current (DC), pulsed DC, radiofrequency (RF), and high-power impulse magnetron sputtering (HiPIMS).<sup>184,188</sup> DC sputtering exactly follows the process outlined previously and is restricted to sputtering metals such as Cu, Ti, and Ag. Sputtering an electrically insulating target, such as a dielectric or ferroelectric material, will result in a charge buildup on the target surface, reducing the high electric field and preventing the plasma from being sustained. One method to circumvent this charge buildup is to use pulsed DC sputtering which pulses the usual bias followed by a reverse bias to clear the charge buildup. The pulsing frequencies employed in this method are typically in the kHz range.<sup>189</sup> Alternatively, a RF sputtering voltage can be used which delivers power at radio frequencies in the MHz range, preventing the buildup of charge.<sup>184</sup> The final major sputtering type is HiPIMS which delivers high peak power densities at low duty cycles to reduce the significant heat generation at the target. This allows for the formation of a plasma with a much higher density and a larger fraction of ionized species than traditional sputter processes.<sup>188</sup> In addition, the plasma generation is highly tunable as the voltage, pulse width, and repetition rate can be freely changed. This allows greater control over the stress, adhesion, and functional properties of the film, making this technique of great interest for high quality material growth.<sup>190,191</sup>



Figure 2-5: Schematic representation of the magnetron sputtering process. Note that the ground on the chamber is electrically isolated from the target.

Reactive sputtering is another variation that utilizes different processing gases with the objective of the gas reacting and becoming incorporated in the deposited film. This method has been used to deposit oxides,<sup>192–194</sup> nitrides,<sup>195–197</sup> carbides,<sup>198,199</sup> sulfides,<sup>200,201</sup> and fluorides.<sup>202,203</sup> While the inert process gas, argon, can be continuously reused in the plasma, the reactive process gases become incorporated into the film and are therefore are consumed and diluted out of the gas phase. Due to this, a sufficiently high flow of the additional process gas must be ensured to maintain consistent growth conditions. Large concentrations of these additional process gases can result in the target material being poisoned, creating uneven deposition rates and film properties; therefore, care must be taken for reproducibility when utilizing reactive sputtering.

An additional benefit to sputtering is that a wide variety of geometries for substrate size, target size and shape, and growth chamber size are possible. For example, for large throughput processes where substrate rotation is impossible, the target can be made into a rectangular shape

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allowing for deposition on a roll-to-roll system.<sup>204</sup> This flexibility in addition to the ability to deposit virtually any material in a cost-effective manner continues to make sputtering one of the most widespread deposition techniques available.

### 2.2.2 Pulsed laser deposition

Pulsed laser deposition is a PVD technique similar to sputtering where a target material is ablated to deposit a thin film with a specific stoichiometry on a nearby substrate. In contrast to sputtering, the target material is ablated by precise, intense laser pulses. As the laser irradiates the material and is absorbed, it is converted into electronic excitation and thermal energy which induces evaporation and ablation of the material. This process allows for a near one-to-one transfer of the target material to the substrate, allowing the growth of films with complex stoichiometries such as complex oxide superconductors.<sup>205</sup> Most PLD systems use nanosecond-pulsed excimer lasers operating at a wavelength of 248 nm or neodymium doped yttrium aluminum garnet lasers operating at a wavelength of 266 nm since most materials have strong absorption at these wavelengths. The pulse length is on the order of nanoseconds while the repetition rate is typically on the order of 10 to 100 Hz which can be adjusted to achieve optimal growth conditions.<sup>206</sup> For most ceramic materials, the optimal laser output energy ranges from 0.5 to  $5 \text{ J/cm}^2$  corresponding to 0.2 to  $2 \times 10^8$  W/cm<sup>2</sup> for a 25 ns pulse duration. Similar to sputtering, the atomic sized species ejected from the target material have energies in excess of 10 eV which can re-eject volatile elements from the film or induce defects in the growing film due to mechanical knock-on damage pushing the atoms on energetically unfavorable lattice sites by virtue of momentum transfer. Nevertheless, PLD has been shown to produce high quality films and superlattices.


Figure 2-6: Schematic representation of a PLD deposition chamber equipped with in-situ RHEED.

A schematic of a PLD deposition chamber is shown in Figure 2-6. Unlike sputtering, the deposition pressure of PLD can vary between a few Torr to ultrahigh vacuum (UHV) conditions since target erosion can be achieved without the need of a gas discharge. This wide range of pressures offers an additional tuning parameter since the addition of process gas increases scattering of the ablated material, lowering the incident energy and lessening the incorporation of defects into the deposited material. At the other end of the spectrum, the ability to deposit in UHV conditions enables the use of in-situ characterization techniques using electrons such as RHEED and electron spectroscopy methods which are not possible under higher pressure conditions when the inelastic mean free path of the electrons results in substantial scattering between the source and detector. These techniques provide real time information on the film growth and surface morphology which greatly assists in the optimization of the growth parameters.

While it is commonly assumed that the primary disadvantage of PLD is its small deposition size, typically on the order of  $5 \times 5$  mm, recently there have been significant developments on large, industrial scale PLD systems. Improvements in uniform substrate heating, laser control, and laser

rastering has enabling uniform film deposition by PLD on 12-inch wafers.<sup>207,208</sup> The true shortcoming of PLD and sputter deposition remains the high energy nature of the process which typically results in increased defect concentrations when compared to low energy techniques such as molecular beam epitaxy.

# 2.2.3 Molecular beam epitaxy

The final PVD technique discussed here is molecular beam epitaxy (MBE) which employs thermal effusion cells to supply elemental materials and compounds onto a substrate by thermal evaporation. Unlike the ablation of targets in the previously discussed methods, the evaporation of these materials and the species supplied to the growth front can be controlled to a high level of precision, allowing for highly reproducible growth of complex material systems using multiple effusion cells. MBE chambers are typically evacuated to ultra-high vacuum (~1×10<sup>-9</sup> Torr), resulting in a molecular mean free path exceeding the size of the deposition chamber. A "beam" of species supplied from an effusion cell can therefore be directed onto the growth front without being altered by unintentional interactions within the gas phase. The flux generated by each effusion cell is measured and subsequently calibrated by a quartz crystal microbalance (QCM) placed in the "beam path" at the sample position. The QCM utilizes the piezoelectric effect of the quartz which allows for a predictable, constant oscillation frequency when brought near its resonant frequency by applying an RF voltage. As material supplied from the effusion cell accumulates on the surface of the oscillating quartz crystal, the additional mass reduces the oscillation frequency. The change in mass on the crystal can then be determined by the change in frequency allowing the supply rate of the deposited material to be quantified on the order of  $1 \times 10^{12}$  cm<sup>-2</sup>s<sup>-1</sup>.

While effusion cells offer a high degree of controllability, they lack long term stability, causing the atomic fluxes to drift. These drifts can lead to non-stoichiometric ratios of elements supplied to the growth front and to the unintentional incorporation of defects. In addition, effusion cells are currently limited to temperatures below 2000°C, preventing the evaporation of certain elements such as refractory metals which have higher evaporation temperatures.<sup>209</sup> Such elements must instead be evaporated using an electron beam which results in ejected particulates with higher energies, similar to those in PLD, resulting in a lower stability and higher defect concentrations when compared to deposition with effusion cells. While these issues are critical in traditional MBE, both been shown to be resolved through the use of self-regulated growth in hybrid molecular beam epitaxy as described in the next section.<sup>209</sup>

While MBE brings many advantages to high quality film deposition, in particular the direct control of type and rate of low energy species supplied to the growth front, it is not without some drawbacks. MBE systems have a high initial setup and operating cost, long setup time for growth experiments and require a high level of routine maintenance. The inherent complexity of an MBE system and the requirement of constantly monitoring growth parameters to ensure proper growth reproducibility require sophisticated computer control, making the system prone to failure. These intricacies require complex and time-consuming troubleshooting to perform the necessary repairs. This complexity also makes it difficult to trace reproducibility errors and have resulted in other interpretations of the abbreviation of MBE, including "Many Boring Evenings" and "Mostly Broken Equipment."

### 2.2.4 Hybrid molecular beam epitaxy

High quality thin films can be most readily synthesized and reproduced by taking advantage of self-regulated growth kinetics, which prevent the incorporation of nonstoichiometric defects into the film. This method was developed for the growth of binary semiconductors, such as GaAs, where growth temperatures are chosen such that the constituents of the film have different volatilities. In the case of GaAs, the nonvolatile element (Ga) is co-supplied with the more volatile element (As). At around 600°C, the targeted line compound GaAs<sub>(s)</sub> is thermodynamically stable while excess As<sub>(s)</sub> readily evaporates, preventing incorporation and the unintentional formation of nonstoichiometric defects. Therefore, when depositing GaAs, it is possible to supply As in excess, alleviating the strict requirement of individual flux control. Instead, every Ga atom adsorbed to the growth front readily reacts with As species forming GaAs, while unreacted As desorbs from the growth surface leaving a highly stoichiometric film. The maturation of this growth approach over decades has resulted in an unparallel film quality, manifested in record low temperature carrier mobilities exceeding  $3 \times 10^7$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> in GaAs thin films<sup>210</sup> compared to bulk GaAs which is limited to  $\sim 10^4$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1,211</sup>

This highly convenient growth mode is unfortunately inaccessible for most oxide materials when using elements as source materials. For instance, when depositing SrVO<sub>3</sub> using elemental Sr and V sources in excess oxygen, Sr and V readily oxidize into SrO and VO<sub>2</sub> respectively. Since neither of these binary oxides are volatile at accessible growth temperatures, a self-regulated growth mode is not accessible. However, if one cation is instead supplied in a chemically different form, such as a metalorganic molecule with high volatility, a self-regulated growth regime can be recovered. For the case of SrVO<sub>3</sub>, elemental V can be substituted for vanadium oxytriisopropoxide (VTIP). It is hypothesized that such metalorganics, VTIP in this example, preferentially desorb on similar surfaces such as VO<sub>2</sub> and that a catalytic effect promotes thermal decomposition on dissimilar surfaces such as SrO.<sup>177</sup> Such film deposition involves both PVD and CVD processes, further complicating the kinetic processes of film growth.

The exact kinetic processes for the self-regulated growth of complex oxides are currently not well understood; however, important insight into the mechanisms can be gained through the examination of TiO<sub>2</sub> growth using the metalorganic precursor titanium (IV) isopropoxide (TTIP). These mechanisms are shown in Figure 2-7,<sup>212</sup> which outlines (a) the growth rate of  $TiO_2$ , (b) the coverage of the TTIP molecules on the surface, and (c) the TTIP incorporation rate as a function of substrate temperature. The growth process is considered as a competition between the reaction and desorption rates of the TTIP molecules and can be categorized into three distinct growth regimes depending on the deposition temperature: reaction limited, flux limited, and desorption limited. At temperatures far below 400°C, TTIP molecules entirely cover the surface but do not have enough thermal energy to react and form  $TiO_2$  or to desorb from the surface. Closer to 400°C, the surface remains saturated with TTIP molecules but they begin to decompose into volatile ligands and the non-volatile core which becomes incorporated into the film, making the growth rate reaction limited. As the temperature increases, the reaction rate of TTIP exceeds the desorption rate, resulting in a film growth rate that is limited by the TTIP flux supplied. Above 700°C, the desorption of intact TTIP molecules becomes significant and many molecules desorb before they can decompose, resulting in a desorption limited growth. These temperature dependent kinetics have been shown to be similar for binary oxide growth using other volatile metalorganic precursors including the growth of VO<sub>2</sub> using VTIP.<sup>213</sup>



Figure 2-7: (a) The deposition rate of TiO<sub>2</sub>, (b) the TTIP molecule coverage, and (c) the TTIP incorporation rate in the reaction limited, flux limited, and desorption limited regimes. (d) The growth window for SrVO<sub>3</sub> at 900°C identified by the intrinsic lattice parameter,  $a_F$ . (e) The temperature dependent growth window of CaTiO<sub>3</sub> identified by the out of plane lattice parameter, *c*. Reproduced from references.<sup>177,209,212,214</sup>

These straightforward processes rapidly become complicated with the introduction of additional elemental materials. In this case, the flux of each material as well as surface dependent reaction and desorption rates of the metalorganic must be considered. The growth window for complex oxides is experimentally determined by setting a constant elemental flux and growing a series of samples at different metalorganic pressures. The out of plane lattice parameter of the films are then determined using XRD. The growth window is then defined as the region where the film lattice parameter matches the expected stoichiometric value. Outside the growth window the lattice parameter changes due to the incorporation of nonstoichiometric defects into the film. Self-regulated growth windows have been determined for oxides including SrTiO<sub>3</sub>,<sup>215</sup> CaTiO<sub>3</sub>,<sup>214</sup> BaTiO<sub>3</sub>,<sup>216</sup> GdTiO<sub>3</sub>,<sup>217</sup> SrVO<sub>3</sub>,<sup>177</sup> CaVO<sub>3</sub>,<sup>218</sup> LaVO<sub>3</sub>,<sup>219</sup> La<sub>1-x</sub>Sr<sub>x</sub>VO<sub>3</sub>,<sup>220</sup> and BaSnO<sub>3</sub>.<sup>221</sup> The growth window of SrVO<sub>3</sub> at 900°C<sup>177</sup> and the temperature dependent growth window of CaTiO<sub>3</sub><sup>214</sup>

shown in Figure 2-7(d) and (e) respectively. The self-regulated growth of both materials occurs at temperatures in the desorption limited regime. As seen in Figure 2-7(e), the growth window widens and shifts to higher metalorganic pressures as the substrate temperature increases. The linear widening of the growth window with increasing temperature closely follows the linear decrease in the growth rate of TiO<sub>2</sub> from 700-950°C seen in Figure 2-7(c). The shift to higher pressures at elevated temperatures arises due to the increased desorption rate of TTIP, necessitating a higher TTIP flux to compensate. Furthermore, the boundaries of the growth window have different slopes, 10 mTorr/100°C for the Ti-rich side and 3 mTorr/100°C for the Ca-rich side, arising from the different reaction and desorption rates of TTIP on Ca and Ti enriched surfaces. This difference in slopes suggests that TTIP desorbs more readily on Ti-rich growth fronts. Similar evidence of an increased TTIP incorporation has been shown to occur in reactions including SrO.<sup>209</sup> While these trends have only been inferred from experiments, thorough computational investigations into the decomposition of metalorganic precursors as well as their reaction with specifically terminated surfaces are currently ongoing and promise to elucidate the intricacies of these complex kinetic processes and to develop a comprehensive understanding of the processes at the atomic scale.

While self-regulated growth is extremely advantageous, its application requires additional considerations beyond co-supplying an elemental source and a volatile metalorganic precursor. For instance, the metalorganic must be deposited in the desorption limited-regime and the surface of the elemental oxide layer must have a higher reactive surface compared to that of the metalorganic oxide, e.g.,  $R_{Sr0} > R_{V0_2}$  for SrVO<sub>3</sub>. In addition, metalorganics must be chosen that decompose into highly volatile, non-reactive products to prevent their unintentional incorporation into the film. Specifically, halide containing metalorganics should be avoided to prevent the formation of corrosive byproducts during the growth process.

Even with these restrictions, *h*MBE has been shown to be an excellent growth method for many perovskite oxides. TTIP has been used for the synthesis of  $SrTiO_3$ ,<sup>215,222</sup> CaTiO<sub>3</sub>,<sup>214</sup>

BaTiO<sub>3</sub>,<sup>216</sup> GdTiO<sub>3</sub>,<sup>217</sup> SmTiO<sub>3</sub>,<sup>223</sup> and NdTiO<sub>3</sub>,<sup>224</sup> VTIP has been used for SrVO<sub>3</sub>,<sup>10,177</sup> CaVO<sub>3</sub>,<sup>218</sup> LaVO<sub>3</sub>,<sup>219</sup> and La<sub>1-x</sub>Sr<sub>x</sub>VO<sub>3</sub><sup>220</sup> and hexamethylditin has been used for BaSnO<sub>3</sub><sup>221</sup> and SrSnO<sub>3</sub>.<sup>225</sup> In addition to these commonly used metalorganics, many other commercially available compounds exist as indicated in Figure 2-8. The self-regulated growth in *h*MBE not only simplifies stoichiometric film growth, it also enables a superior material quality that can be seen in the record mobilities exceeding 120,000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> in SrTiO<sub>3</sub><sup>9</sup> as well as record RRR values exceeding 200 in SrVO<sub>3</sub> films,<sup>10</sup> both of which far surpass the best bulk single crystals.<sup>226</sup> This superior material quality combined with the sheer number of possible material combinations as shown in Figure 2-8 renders *h*MBE one of the most promising thin film growth techniques to advance our understanding of complex physical phenomena in the ultraclean limit.



Figure 2-8: The periodic table of elements used in *h*MBE where dashed lines indicate materials that have been evaporated from elemental sources and shaded boxes indicate materials that have been supplied from a metalorganic source. The temperatures required to reach a sufficient flux as well as commercially available metalorganic precursors are indicated for most elements. Reproduced from reference.<sup>209</sup>

### 2.3 Thin film growth at Penn State

The basic capabilities of thin film deposition systems remain relatively similar from university to university; however, many deposition systems have been specially designed or modified to push the limits of the highest quality films for a specific class of materials or chemistries. In addition, the use of different components for substrate heating, precursor deployment, and base vacuum pressure can cause subtle differences in films grown in different systems. Due to this, it is highly important to outline the specific details of each thin film growth method used in this thesis for future reproduction.

# 2.3.1 Sputter system

The sputter system used in this thesis is part of a three-chamber growth cluster built by DCA Instruments Inc. consisting of a sputter chamber, an oxide MBE, and a chalcogenide MBE, all connected by in-vacuo transfer lines. This functionality allows for the inspection of the surface morphology of sputtered samples using the RHEED system installed on the oxide MBE reactor. In addition, it enables the growth of unique heterostructures consisting of oxide, chalcogenide, and sputtered films.



Figure 2-9: Views of the (a) frontside and (b) backside of the custom sputter chamber at Penn State highlighting the most relevant system components.

The sputter chamber is shown in Figure 2-9. A 1-inch and a 2-inch Kurt J. Lesker magnetron sputter source with the capability to deposit using RF and DC processes were used to deposit the  $Sr_xNbO_3$  films in this thesis (discussed in detail in Chapter 5). The system was pumped by a TMH260 turbo-pump and a Cryo-Torr 8 cryo pump allowing for a base pressure around  $1 \times 10^{-8}$  Torr. Argon was used as the main process gas and was supplied using a mass flow controller (MFC). Oxygen, nitrogen, and forming gas (5% hydrogen, 95% argon) could also be supplied in conjunction with pure argon using an additional MFC to provide oxidizing or reducing conditions. Substrates were heated using a DCA model substrate heater with a SiC heating element capable of temperatures up to 900°C. The substrate temperature was measured using a type S thermocouple which was calibrated using a pyrometer.

### 2.3.2 Hybrid molecular beam epitaxy system

The MBE reactor at Penn State is a DCA M600 MBE chamber built by DCA Instruments in 2011. The system has since been upgraded with a custom designed metalorganic precursor injection system used primarily to supply titanium and vanadium containing metalorganic precursors for the growth of titanium and vanadium-based oxide materials. The MBE control desk is shown in Figure 2-10(a) where the leftmost computer is used to process RHEED images while the middle and right computers are used to monitor the MBE and run automated scripts to calibrate sources and deposit films. The MBE chamber was pumped by a HiPace TC1200 turbo pump and a Cryo-Torr 8 cryo pump. Additional pumping speed was achieved using a cryopanel filled with liquid nitrogen, enabling a base pressure of  $1 \times 10^{-9}$  Torr after a system bake. Lower base pressures could be reached when depositing materials that getter oxygen such as Sr and La. This system was fit with a kSA 400 RHEED analysis system and can be retrofitted with an in-situ spectroscopic ellipsometer to further examine film growth in real time.



Figure 2-10: (a) MBE controls and computers. (b) Schematic of the metalorganic precursor system, reproduced from reference.<sup>209</sup> (c) Front view of the MBE chamber. (d) View of the metalorganic precursor system where the blue line indicates flow from the bubbler to the MBE and the purple line indicates the bypass path to the pumping station.

The metalorganic injection system is shown schematically in Figure 2-10(b) and the corresponding components are highlighted on an actual image of the injection system in Figure 2-10(d). The metalorganic was placed in a bubbler wrapped with heating tape to maintain a constant temperature where the metalorganic's vapor pressure was between 1 and 10 Torr,  $\sim$ 60°C for VTIP. All inlet gas lines were made up of 1/4-inch stainless steel tubing wrapped in heating tape that is maintained at a slightly higher temperature than the bubbler to prevent condensation and accumulation of the metalorganic in the line. The bubbler and all lines were further wrapped with aluminum foil for thermal isolation. Note that uniform heating over the entire inlet system was

essential to prevent hot spots that thermally decompose the precursor and cold spots that result in condensation, both of which result in clogging. An isolation valve was placed immediately above the bubbler to enable a safe point to detach and refill it in a nitrogen glove box.

A variable linear leak valve was used in conjunction with a capacitance manometer and feedback control unit to ensure a uniform precursor flow into the MBE reactor. The metalorganic gas flow was either routed to a pumping station consisting of a Cryo-Torr 8 cryo pump, or to the MBE reactor. The pumping station was used to stabilize the flow of the metalorganic precursor prior to growth and to condition new metalorganic charges. New VTIP charges in particular had to be conditioned for several hours before showing reproducible behavior. While VTIP was the only precursor used in this work, additional metalorganic precursors with sufficient vapor pressures could easily be integrated into this system. Additional details of the *h*MBE setup including the procedure to set up new metalorganic precursors can be found elsewhere.<sup>209</sup>

# 2.3.3 Substrate handling

Proper substrate handling and preparation is vital to maintaining highly reproducible growth conditions. The typical process for substrate preparation used in this thesis is as follows: substrates were immersed in an acetone bath and sonicated for 10 minutes followed by sonication in an isopropyl alcohol bath for another 10 minutes. They were then blown dry using nitrogen and visually inspected for any remaining macroscopic particles under a microscope. The substrates were then exposed to UV ozone for 5 minutes before being loaded onto the MBE transfer cart.

The MBE and sputtering systems at Penn State accept substrates up to 3 inches in diameter. Specially designed substrate holders were used to hold one or many smaller substrates, typically 10×10 mm in this work. These substrate holders were made of either tantalum or Inconel, an austenitic nickel-chromium alloy that is oxidation resistant and able to withstand temperatures in excess of 1000°C. The transfer cart is capable of holding nine sample holders at a time, largely reducing the need to vent the cart multiple times per day. Figure 2-11(b) and (c) demonstrates how 10×10 mm substrates and 3-inch silicon wafers were respectively mounted. Tantalum retaining rings were used to fasten the 3-inch wafers and substrate holders to prevent tilting and unwanted movement during transfer while tantalum clips were used for smaller square samples.



Figure 2-11: (a) View of the MBE and sputter system load lock. Sample holders for (b)  $10 \times 10$  mm and (c) 3-inch substrates which were held in place by tantalum clips. The transfer process from the (d) cart to (e) substrate manipulator to (f) transfer arm before transfer to either the sputter chamber or MBE.

The straightforward sample transfer process from the cart to the transfer arm is highlighted in Figure 2-11(d-f). For MBE growth, once the substrate was mounted in the manipulator it was visually inspected by RHEED to verify a clean surface prior to growth.

# **Chapter 3: Film characterization**

Nothing is truly discovered from thin film growth without proper in-situ and ex-situ characterization. Characterization is needed not only to measure the resulting electronic and optical properties of films but also to optimize film growth processes. If this crucial step is bypassed, considerable time could be wasted measuring the properties of films with mixed phases, incorrect stoichiometries, 3D morphologies, or any number of unwanted defects. This chapter covers the basics of the thin film characterization methods used throughout this work. First, structural characterization of thin films will be detailed. A strong focus is then given on the proper measurement and analysis of electric transport measurements. Finally, a discussion on optical measurements using spectroscopic ellipsometry will be covered.

# 3.1 Structural Characterization

In order to study the intrinsic electronic and optical properties of a material it is first essential to verify the structural quality and phase purity of the film. These measurements fall into two categories, diffraction and microscopy techniques which offer reciprocal and real space analysis of the film structure. Diffraction techniques utilize the wave-like nature of light and high energy particles, such as electrons and neutrons, to probe a material and reveal details of the crystal structure. X-ray diffraction (XRD) is the most common example of this technique and is used in the analysis of almost every type of thin film growth. Another example is reflection high-energy electron diffraction (RHEED) which is used to examine the surface morphology of thin films insitu. Microscopy measurements, such as atomic force microscopy (AFM) and scanning transmission electron microscopy (STEM), physically probe the local structure and surface morphology on the sub-nanometer scale. In this section we briefly introduce these methods and discuss their utilization for the optimization of growth conditions.

# 3.1.1 Reflection high-energy electron diffraction

In-situ characterization of crystalline thin films greatly expedites the optimization of growth conditions since time consuming ex-situ methods such as X-ray diffraction are not always necessary to observe non-stoichiometries and unfavorable growth conditions. The leading in-situ characterization method for physical vapor deposition such as PLD and MBE is reflection high-energy electron diffraction (RHEED). RHEED was first used in 1928 to study calcite crystals but was relatively unused until the inception of high vacuum equipment.<sup>227</sup> RHEED has long been used to monitor the growth of complex materials such as superconductors, complex heterostructures, and topological materials.<sup>228</sup>



Figure 3-1: (a) Image of the MBE chamber at Penn State with each component of the RHEED system labeled. (b) Phosphorous screen and CCD camera that captures the RHEED image.

RHEED systems consist of an electron gun that generates a finely focused electron beam from a heated tungsten filament source. The electrons are accelerated to a kinetic energy of 8-

20 keV. Like X-rays, this beam of electrons can be tuned to a wavelength on the order of the atomic lattice spacing, 14 keV for the materials in this thesis. This beam is then focused and collimated into a highly focused beam of electrons using a series of focusing coils which can also be used to adjust the position of the beam on the sample. The electron beam is positioned at a glancing angle of approximately  $2^{\circ}$  from the sample surface illuminating an area of about 100 µm × 1 mm. The electrons are diffracted by the atoms of the growth front and the resulting diffraction image is observed on a fluorescent screen mounted on a CF flange opposite to the electron beam gun, which is recorded by a digital camera. The image is then read and analyzed by commercially available software (k-Space Associates). The RHEED system integrated with the MBE at Penn State is shown in Figure 3-1 and a schematic of the RHEED working principle is further shown in Figure 3-2. Since we are interested in how the electron path is altered by the crystalline surface, the electrons cannot be impeded by molecules reducing their mean free path; therefore, working pressures below  $1 \times 10^{-5}$  Torr are required for the operation of RHEED, typically restricting it to PLD and MBE techniques; however, differential pumping can be used to protect the RHEED filament for systems that operate under higher pressures.



Figure 3-2: (a) Schematic of the RHEED setup. (b) Schematic of RHEED in reciprocal space. (c) 2D representation of RHEED demonstrating the intersection of the lattice rods from the sample intersecting the Ewald sphere. Images are not drawn to scale; the Ewald sphere is much larger than the reciprocal lattice spacing. Adapted from reference.<sup>229</sup>

Due to the glancing angle and the short mean free path of electrons in materials, RHEED is extremely surface sensitive, only probing the top few atomic layers of a thin film. This surface sensitivity is the most useful aspect of RHEED since it enables a real time monitoring of the terminating layer of the film during growth. This allows growth conditions to be monitored and changed to improve crystalline and surface quality 'on the fly'. When considering diffraction, this thin probing depth indicates diffraction conditions out of the plane can be ignored; therefore, the reciprocal lattice can be considered to be a series of infinite rods arising from the reciprocal lattice points. The kinetic energy of the incident electrons sets up their momentum and corresponding de Broglie wavelength ( $\lambda$ ), which is approximately 0.1 Å for electron energies of 14 keV. This electron beam sets up an Ewald sphere with a radius given by Eq. 3.1 where *i* designates the vector to a specific diffraction rod.

$$k_i = \frac{2\pi}{\lambda}$$
 Eq. 3.1

Following this geometric construction, any point where the reciprocal lattice rod intersects with the Ewald sphere will satisfy the Bragg condition since the magnitude of the incoming and outgoing vectors have the same magnitude. Vectors that satisfy the Laue condition such that  $\Delta k = k_0 - k_i$ , where  $\Delta k$  is a reciprocal lattice vector, give rise to circles corresponding to the *i*<sup>th</sup> Laue zones. The relation between the Ewald sphere and the diffraction is shown schematically in Figure 3-2(b) and (c). Since the diffraction condition relies entirely on the point where the reciprocal lattice rods cross the Ewald sphere, this point is confined to move up and down the lattice rod as the sample is rotated.

Modifications of the film surface morphology can drastically alter the diffraction pattern in RHEED. Six distinct examples are shown in Figure 3-3. If the film is entirely amorphous, no reciprocal lattice rods are present and only a hazy background is formed. If some crystallinity is present in randomly oriented grains with the same out of plane direction, the rods are rotated around the origin in reciprocal space, forming concentric reciprocal cylinders. The intersection between these cylinders and the Ewald sphere then lead to circular diffraction patterns as shown in Figure 3-3(b). A corrugated film surface adds another dimension to the diffraction condition since electrons are able to diffract through protrusions. This sets up a 3D diffraction condition corresponding to the entire crystal structure, not only the reciprocal lattice rods, creating a RHEED pattern of points. A similar 3D diffraction pattern can occur if an unwanted secondary phase is present at the growth surface. In this case, the unwanted phase sets up a diffraction pattern that is only satisfied at specific points of the Ewald sphere. When the sample is rotated these conditions are no longer met, making the secondary phase spots 'blink on and off' as the secondary phase is rotated in and out of the diffraction condition. Films with domains arising from slight relaxation, vacancies, or defects experience a broadening of the reciprocal lattice rods causing a rod like intersection with the Ewald sphere and making it appear as a streak as seen in Figure 3-3(e). Finally, the ideal case is shown where the film forms a single crystal and is atomically smooth, giving rise to sharp points in RHEED.



Figure 3-3: RHEED images with their corresponding schematic representations for (a) amorphous films, (b) polycrystalline films, (c) films with 3D corrugated surfaces, (d) films with unexpected secondary phases where some unexpected spots in RHEED are highlighted, (e) films with domains and thus a limited lateral coherency, (f) and single crystalline films. RHEED images were taken at various points in the optimization process for films grown in this thesis.

Even though RHEED is frequently praised for its usefulness in gauging the in-situ surface morphology, it is not without its limitations. Since RHEED is a diffraction technique, it only illuminates areas that meet the diffraction condition. If 10% of the film is highly oriented and crystalline but 90% of the film is out of place, diffraction will still occur albeit at a smaller intensity; therefore, since RHEED is only a qualitative characterization method it is difficult to quantify film

quality. For example, if a film has large areas where it is atomically smooth and the only 3D features are holes, the only contributions to diffraction will occur on the atomically smooth portions since electrons entering the side of holes will likely not have enough energy to transmit through the material and reach the phosphorous screen. Two examples of this are shown in Figure 3-4. In the first case, [111]-oriented SrVO<sub>3</sub> was deposited on [111]-oriented LSAT where cation nonstoichiometry resulted in the presence of triangular holes in the film that was otherwise atomically smooth (Further discussed in Chapter 7). The spacing between the holes was on average much larger than the mean free path of the electrons used in RHEED (approximately 1 to 3 nm);<sup>175</sup> therefore, only a small number of electrons were captured in Figure 3-4(a). The second case of FeSe deposited on SrTiO<sub>3</sub> substrates had large square island growth where the electrons would need to travel more than 10 to 100 nm inside the material to diffract in transmission, resulting in a complete elimination of a 3D diffraction pattern. These cases are relatively rare but they illustrate the importance of additional surface morphology characterization.



Figure 3-4: Two examples where films appear to be smooth from RHEED but have 3D features: (a) [111]oriented SrVO<sub>3</sub> grown on LSAT and (b) [001]-oriented FeSe grown on SrTiO<sub>3</sub> by Dr. Hilse at Penn State.

# 3.1.2 Atomic force microscopy

While RHEED is a useful qualitative, in-situ technique to investigate a film's surface morphology, it is not able to quantify the surface roughness or differentiate certain surface morphologies, as seen in Figure 3-4. Atomic force microscopy (AFM) offers an ideal ex-situ approach to verify the surface morphology and correlate it back to the pattern observed in RHEED. AFM offers a height resolution of 0.5 nm and a lateral resolution on the order of the tip size used (2 nm for the SCANASYST-AIR tips used in this thesis) which allows for highly detailed 3D topographical maps of the film surface which can be compared to the 2D construction seen in RHEED.

AFM is based on the principle that all objects exert a small force on other nearby objects whether it be van der Waals, dipole interactions, or some other force. In this case the two objects of interest are the film's surface and the microscopically sharp AFM tip on a flexible cantilever. When the AFM tip is near the film's surface, the forces experienced by the AFM tip defect the cantilever. The amount of deflection is measured by reflecting a laser off the cantilever onto a photodiode. As the cantilever is deflected, force is applied on the cantilever using piezo actuators to keep the reflected laser on the center of the photodiode, adjusting for the nN-level forces arising from the proximity of the tip and the sample. The deflection and force on the cantilever can then be used to get information of the film surface. This setup is shown schematically in Figure 3-5(a).



Figure 3-5: (a) Schematic of the AFM setup. (b) Schematics describing the motion of the AFM tip in Peak Force tapping mode. Figure design reproduced from reference.<sup>230</sup>

AFM has several imaging modes that primarily depend on how the cantilever position is maintained with respect to the sample. First is contact mode where the tip of the cantilever is held onto the sample and dragged across the surface. This method simply maps the morphology by the force required to keep the cantilever on the surface. While this method is effective and relatively fast, the constant contact to the sample can cause damage to the film, cause excessive tip wear, and drag debris across the sample, detrimentally affecting the image. Next is tapping mode where the cantilever is oscillated at a constant frequency and only comes close to the sample at the minimum of every oscillation.<sup>231</sup> This significantly reduces film damage while producing a high image quality. The forces exerted by this method are small enough that single strand polymers, ligands, and DNA can be imaged in solution.<sup>232</sup> Finally there is non-contact mode where the tip is oscillated at its resonant frequency and maintained immediately above the sample. Forces arising from the substrate, such as van der Waals forces, change the oscillation frequency of the cantilever. A feedback loop is used to maintain the resonant frequency by changing the tip-to-sample distance. This information is then used to construct the topographical image of the film.

In this study, Peak Force tapping mode was used for all images. This mode is a slight adjustment to tapping mode where the tip does not oscillate at a resonant frequency; instead, the force distance curve at every lateral point on the surface is rapidly calculated in order to maintain a peak force on the cantilever. The quasi-static motion of the cantilever and the positioning of the z-piezo allow the interaction force and cantilever position to be measured and controlled in real time. A wealth of topological and nanomechanical information can be extracted from these force distance curves; however, only topological data such as surface roughness and surface morphology are used in this study. The motion of the AFM tip and cantilever in Peak Force tapping mode is shown schematically in Figure 3-5 (b). The precise force control in this mode can keep the peak force as low as 10 pN, enabling high quality surface micrographs.

# 3.1.3 High-resolution X-ray diffraction

X-ray diffraction techniques remain the most robust and accurate measurement to determine the crystalline structure, orientation, thickness, and strain of a thin film, making it the most useful tool in a film grower's characterization arsenal. When a material is exposed to X-rays, they scatter in the material and interfere with each other. If long range order exists in the material such as crystal planes, X-rays constructively interfere causing diffraction at specific angles whenever the Bragg condition is met, following Bragg's law in Eq. 3.2 where  $\lambda$  is the wavelength of X-rays, *d* is the interplanar spacing,  $\theta$  is the incident angle of the X-rays, and *n* is the order of the diffraction.

$$2dsin\theta = n\lambda$$
 Eq. 3.2

The diffraction condition is shown schematically in Figure 3-6(a) where two incident plane waves with the same phase and wavelength interact with neighboring lattice planes. One plane wave's path length is increased by  $2dsin\theta$ , resulting in constructive interference. While this is the simplest description, there are additional considerations to be made for diffraction to occur. The arrangement of atoms in a unit cell may cause X-rays to be reflected out of phase and destructively interfere even at the Bragg condition. This effect can be determined by calculating the structure factor of the crystal according to Eq. 3.3 where hkl is the Miller index of the set of lattice planes considered to give rise to diffraction, N is the number of atoms in the unit cell, and uvw are the coordinates of each atom in the unit cell. The intensity of the diffracted beam is proportional to  $|F_{hkl}|^2$ ; therefore, any non-zero structure factor will result in an X-ray intensity for the specific set of planes.

$$F_{hkl} = \sum_{n=1}^{N} f_n \, e^{2\pi i (hu_n + kv_n + lw_n)}$$
 Eq. 3.3

For single crystalline samples with one orientation, the sample must be placed in the diffraction condition using a 4-circle diffractometer where the sample can be oriented independently from the X-ray source and detector. The positioning of the X-ray source and detector along with their rotational axes are shown schematically in Figure 3-6(b). Four circle diffractometers like the one shown here have four angles that define the relationship between the X-ray source, film, and detector. These include the angle between the X-ray source and detector (2 $\theta$ ), the angle between the source and the sample ( $\omega$ ), the sample cradle angle ( $\chi$ ), and the in-plane sample rotation angle ( $\varphi$ ). This system also has X-, Y-, and Z- axis controls to adjust the sample position in the X-ray beam. Once the sample is properly oriented in the beam path, scans can be performed over specific angles where the scattered X-ray intensity is measured using the detector. The most common scans used in the analysis of thin films are as follows. Rocking curves, or  $\omega$ scans, measure the spread of the crystal plane orientations where high plane alignment results in a narrower peak width. Wide angle or high resolution  $2\theta \cdot \omega$  scans are used after aligning to a specific substrate peak to reveal the location and widths of the film peaks which give information about the film's thickness. The Scherrer equation, which is commonly used to determine crystallite sizes in powder diffraction, can also be used to determine the thickness of thin, crystalline films. The Scherrer equation is shown in Eq. 3.4 where  $\tau$  is the size of the crystal or film,  $\lambda$  is the X-ray

wavelength,  $\theta$  is the Bragg angle,  $\Delta(2\theta)$  is the broadening of the full width half max of the diffraction peak, and *K* is a dimensionless shape factor that is close to unity.

$$\tau = \frac{K\lambda}{\Delta(2\theta)\cos\theta}$$
 Eq. 3.4

In addition,  $2\theta$ - $\omega$  scans of films with atomically smooth interfaces exhibit thin film interference fringes called Kiessig fringes in addition to the film peaks, which provide further information of the film thickness.



Figure 3-6: (a) Schematic of Bragg diffraction. (b) Schematic of a 4-circle diffractometer with the relevant axis of rotation between the X-ray source, film, and detector indicated.

While X-ray diffraction is most often used to confirm the presence of a specific film orientation or to measure the film thickness, its true power comes from the ability to measure specific symmetric or asymmetric peaks. This ability enables the mapping of asymmetric peaks in reciprocal space which can be used to measure the film's in-plane and out-of-plane lattice parameters and to determine the degree of film relaxation. This ability in turn gives information about the mismatch, strain and composition gradients, chemical composition and defects of the film.

In this construction, each lattice plane in real space is represented as a point in reciprocal space. The points in which the Bragg condition are satisfied are then given by the Ewald sphere

with a radius equal to the X-ray wave vector length, and thus inversely proportional to the X-ray wavelength used  $(k = 2\pi/\lambda)$ . Assuming elastic scattering, the incident  $(k_i)$  and scattering  $(k_o)$  wavevectors have the same length, as shown in Figure 3-7. One point of the Ewald sphere, representing the Laue condition for constructive interference, is fixed at the origin of reciprocal space and the incident and scattering wave vector directions are changed using  $\omega$  and  $2\theta$  until the desired reciprocal lattice point coincides with the Ewald sphere circumference. The scattering intensity is then mapped as a series of  $\omega$ -2 $\theta$  scans at different 2 $\theta$  positions.



Figure 3-7: Schematic of the reciprocal space lattice for a strained thin film and substrate indicating the scanning patterns for a reciprocal space map. The gray semicircles indicate the areas in reciprocal space that are the non-accessible Laue zones. Figure adapted from reference.<sup>233</sup>

The diffraction space coordinates can then be expressed in terms of the angular positions using Eq. 3.5 and Eq. 3.6.

$$Q_x = 1/\lambda * (\cos(\omega) - \cos(2\theta - \omega))$$
 Eq. 3.5

$$O_{\tau} = 1/\lambda * (\sin(\omega) + \sin(2\theta - \omega))$$
 Eq. 3.6

In addition to the characterization of single crystal films, X-ray diffraction can also be used for polycrystalline samples. Scans done in the Bragg-Brentano geometry, otherwise known as coupled scans, change  $2\theta$  while maintaining  $\omega$  and are typically used in phase identification of powder or polycrystalline samples. In the case of polycrystalline samples where grains of all orientations are represented, diffraction will occur at every angle where the Bragg condition is met for a grain of a specific orientation. This allows unknown materials to be easily identified by comparing the angle dependent scattering pattern to a structural database such as the International Centre for Diffraction Data.<sup>234</sup> Further Rietveld refinement of the measured peaks can provide additional information about the sample including the stoichiometry, crystal structure, porosity, and grain size.<sup>235</sup>

All thin film XRD measurements in this thesis were performed on a 4-circle Malvern Panalytical X'Pert<sup>3</sup> MRD. X-rays were generated by impinging a copper anode with an electron beam and the characteristic X-ray spectra was then reduced into  $K_{\alpha l}$  radiation with a wavelength of 1.5406 Å using a four bounce Ge 220 hybrid monochromator. The X-ray beam was further confined using a 10cm mask and 1/4° receiving slit for most scans. Samples were either mounted on a zero-diffraction plate or an amorphous glass slide to remove any diffraction peaks arising from the sample stage. High resolution  $2\theta$ - $\omega$  scans were fit using GenX to extract the film thickness and out of plane lattice parameter as detailed in Appendix A.<sup>236</sup>

## 3.2 Electrical Characterization

Electrical transport measurements are one of the most common characterization methods applied to materials due to the vast quantity of information that can be extracted. In typical studies, information such as the material's resistivity, sheet resistance, carrier concentration, and carrier mobility are extracted; however, clever measurements can reveal highly detailed information about the Fermi surface shape, the dominant scattering mechanisms, and localization effects. In this section, the commonly used methods for characterizing the resistivity, carrier concentration, and mobility will be discussed. This section will then conclude with a thorough discussion of multicarrier transport analysis.

#### 3.2.1 Resistivity measurements

When addressing the direct resistance of a material, a layman may consider a measurement with a handheld multimeter tool. If a known current is to a material and the voltage drop is measured, Ohm's law can be used to extract its resistance. While this type of measurement is appropriate to find a material's resistance ( $R_M$ ) in many situations, it is associated with an unacceptable amount of error due to the inclusion of the resistance of the wires ( $R_W$ ) and the contact resistance between the probes and the material ( $R_C$ )

$$R = V/I = R_M + R_W + R_C$$
 Eq. 3.7

Instead of this simplistic 2-point probe technique, a 4-point probe measurement setup is used for research purposes to avoid these systematic errors. In this method, the current is applied using one pair of probes and the resistance is measured by the voltage drop through the second pair. As long as the input impedance of the voltmeter is very high, current will be prevented from flowing through the voltage probes, ensuring that all current stays within the sample and preventing the lead and contact resistances from being measured.

Typically, 4-point probe measurements are taken in one of two standardized geometries: Hall bar or van der Pauw. Hall bar geometry requires additional sample processing to etch the film into a bar like structure shown in Figure 3-8(a). In this measurement, a current is applied between opposing leads 1 and 4 while the longitudinal voltage drop is measured between leads 2 and 3. The resistivity can then be found using Eq. 3.8, were *t* is the thickness of the material, *W* is the width of the Hall bar and *L* is the distance between the legs of the bar as indicated in Figure 3-8(a).

$$\rho = \frac{V_{23} tW}{I_{14} L}$$
 Eq. 3.8

The transverse resistance, or Hall resistance, is measured using the same current probes and measuring the voltage drop between contacts 3 and 5 as shown in Figure 3-8(a). The geometric confinement forming a conducting channel out of the sample in the Hall bar reduces the effects of sample inhomogeneity which can obscure properties such as Shubnikov-de Hass oscillations and the quantized Hall effect; therefore, it is typically used when characterizing quantum and topological materials. It should be noted that since extra lithography steps are required to make the Hall bar, some additional uncertainty is introduced since the film is exposed to atmospheric gases and other contaminants which may decrease the film quality.

Unlike the Hall bar setup, the van der Pauw configuration requires no extra processing steps. This configuration assumes that (1) the sample has a uniform thickness, (2) the sample is uniformly connected and has no holes, (3) the probes are connected to the edges of the sample, (4) the contact area of the leads is much smaller than the area of the film, and (5) the sample has homogenous resistance everywhere. Under these assumptions it has been shown that the sheet resistance can be determined through an averaging procedure with leads in various locations.<sup>237,238</sup>



Figure 3-8: Schematics of the most commonly used geometries for electric transport measurements. (a) Hall bar geometry allows current to be sourced in one direction while measuring both the longitudinal  $(V_{XX})$  and transverse voltage drops  $(V_{XY})$ . Van der Pauw geometry allows for the sheet resistance and Hall resistance to be measured on arbitrarily shaped samples by measuring the (b) longitudinal and (c) transverse voltage drops.

This averaging ideally takes place in the form shown in Figure 3-8(b) where the contacts are placed on the corners of the sample. The resistance must be averaged across each side. To do this, a current is sourced from lead 1 to 2 while measuring the voltage drop from lead 3 to 4. This is expressed as  $R_{12,34} = V_{34}/I_{12}$ . This measurement repeats by moving each lead clockwise to measure  $R_{23,41} = V_{41}/I_{23}$ ,  $R_{34,12} = V_{12}/I_{34}$ , and  $R_{41,23} = V_{23}/I_{41}$ . Note that it would be sufficient to simply measure  $R_{12,34}$  and  $R_{23,41}$  as Onsager's reciprocity theorem states that  $R_{12,34}(B) = R_{34,12}(-B)$  so in the absence of a magnetic field  $R_{12,34}$  and  $R_{34,12}$  are equal.<sup>239,240</sup> Using the van der Pauw method, the following condition is met where  $R_s$  is the sheet resistance of the film:<sup>241</sup>

$$e^{-\pi R_{12,34}/R_s} + e^{-\pi R_{14,23}/R_s} = 1$$
 Eq. 3.9

For isotropic samples  $R_{12,34}$  is equal to  $R_{14,23}$ , therefore Eq. 3.9 can be reduced to:

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where  $R_{xx}$  is the average of  $R_{12,34}$  and  $R_{14,23}$  and  $\pi/\ln(2)$  is a geometry correction factor for a general 2D sheet. The transverse resistance can be measured following the probe arrangement shown in Figure 3-8(c). Since the Hall resistance does not depend on the sample geometry, no correction factor is needed. In order to extract the resistivity from the measured sheet resistance, the film thickness, *t*, must be accurately determined. In this work it is typically extracted from high resolution XRD as discussed in Section 3.1.3.

In this thesis, all magnetotransport measurements were performed on a Quantum Design Physical Properties Measurement System (PPMS) in AC-mode with a source current of 500 µm up to a magnetic field of 8 T.

#### 3.2.2 Hall data symmetrization

When measuring the Hall effect, whether using a Hall bar or van der Pauw geometry, there is an unavoidable mixing of the longitudinal resistance,  $R_{xx}$ , with the transverse Hall resistance  $R_{xy}$  due to inexact placement of the leads on the sample. This mixing can be easily identified by a nonsymmetrical B-dependent  $R_{xx}$ . This effect can be mitigated by precise placement of the probes but it cannot be alleviated completely. Fortunately, the longitudinal resistance is purely an even function of the magnetic field while the Hall resistance is purely an odd function. This allows us to mathematically separate their contributions as it falls into the form:  $f(x) = f_{odd}(x) + f_{even}(x)$ , where  $f_{odd}(-x) = -f_{odd}(x)$  and  $f_{even}(-x) = f_{even}(x)$ . Therefore, the even and odd contributions can be found by equations Eq. 3.11 and Eq. 3.12 respectively.

$$f_{even} = \frac{f(x) + f(-x)}{2}$$
 Eq. 3.11

$$f_{odd} = \frac{f(x) - f(-x)}{2}$$
 Eq. 3.12

In order to apply this to real measured data, the Hall resistance  $R_{xy,m}$  and the magnetic field  $B_m$ , the measured curve is fit numerically using an interpolation function. The even contributions from the longitudinal resistance are then removed using equation Eq. 3.13.

$$R_{xy} = \frac{R_{xy,m}(B_m) - R_{xy,m}(-B_m)}{2}$$
 Eq. 3.13

The effect of this symmetrization can be quite insignificant if the contacts are properly placed as seen from the raw and symmetrized data in Figure 3-9(b). In contrast, it can also be dramatic as shown from the raw and symmetrized data of the Hall effect data of [111]-oriented SrVO<sub>3</sub> seen in Figure 3-9(c) (Discussed in detail in Chapter 7).



Figure 3-9: Demonstration of the effect of misplaced leads in the van der Pauw geometry. (a) If leads are unintentionally misplaced,  $V_{XX}$  and  $V_{XY}$  are mixed in the transverse van der Pauw measurement. (b) In most cases the raw data is non-symmetric but close to the corrected, odd part after symmetrization. (c) In some cases, the misplacement of leads can lead to dramatic changes in the measured data yet the symmetrization process can still salvage accurate data comparable to data taken in the Hall bar geometry (see Chapter 7 for more details).

### 3.2.3 Detailed analysis of Hall measurements

The following section is reproduced in part from: Brahlek, M. and Roth, J., et al., Hidden transport

phenomena in an ultraclean correlated metal, Under review in Nature Communications (2021)

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While Hall measurements are most commonly utilized to extract carrier concentrations and mobilities of metals and semiconductors, they are far more powerful in probing electrical properties and phenomena. In this section, the Hall effect for multiple carrier channels will be discussed. Unlike semiconductors that have a single carrier type, the transport properties of many metals are governed by multiple carrier channels that are made up of electrons or holes. The presence of these channels can give rise to nonlinearities and complicate the interpretation of Hall data.

When a magnetic field is applied normal to a film's surface, it applies a force orthogonal to the velocity vector of the charge carriers, bringing them into a circular trajectory known as a cyclotron orbit. The carriers deflected by this field build up on the edges of the material, setting up an electric field transverse to the current flow and the magnetic field direction, defined as the Hall field,  $E_H$ . The voltage drop across this region with current  $I = J \cdot w \cdot t$  is defined as the Hall resistance  $R_{xy}$  with J being the current density, t the film thickness, and w the sample width as shown in Figure 3-8a. For electrons, the Hall resistance is given by Eq. 3.14 where  $V_{Hall}$  is the Hall voltage.

$$R_{xy} = \frac{V_{Hall}}{I_x}$$
 Eq. 3.14

The electrons experience the Lorentz force from the magnetic field following  $F_L = qv_d B$ , deflecting them according to the right-hand rule in addition to a force from the built-up electric field given by  $F_E = qE_H$ . In the steady state condition, these forces are equal, allowing the measurement of the Hall voltage according to Eq. 3.15 where *B* is the magnitude of the electric field and *v* is the drift velocity of the electrons.

$$V_{Hall} = \int_0^W E_y dy = E_y w = wvB$$
 Eq. 3.15

Using the definition of the current density,  $J = q \cdot N \cdot v$  where q is the elemental charge and N is the 3D carrier density, Eq. 3.14 and Eq. 3.15 can be combined and simplified to find the expression for the Hall resistance where  $n_{2d}$  is the 2D sheet carrier concentration.

$$R_{xy} = \frac{-E_H \cdot w}{J \cdot w \cdot t} = \frac{-v \cdot w \cdot B}{q \cdot N \cdot v \cdot w \cdot t} = -\frac{B}{q \cdot n_{2d}}$$
Eq. 3.16

For a single carrier channel, the Hall resistance is negative for electrons since they are deflected in the -y direction resulting in the Hall field being oriented in the -y direction. The opposite is true if holes, i.e. positively charged particles, are carrying the electric current. For a single carrier channel, the Hall resistance is a linear function of the magnetic field with a slope inversely proportional to the carrier concentration. The 3D carrier concentration can then be determined using Eq. 3.17 where t is the film thickness extracted from high resolution XRD as discussed in Section 3.1.3.

$$N = n_{2D}t Eq. 3.17$$

For most cases this derivation is sufficient; however, for material systems with multiple carrier channels, a more detailed derivation is required to separate the contributions for each carrier type. The Hall effect can alternatively be derived by describing the average time  $\tau$  between collisions amongst the atoms in the crystal and the charge carriers with an effective mass  $m^*$  and charge q following Newton's equation of motion shown in Eq. 3.18.

$$m^* \left[ \frac{d\vec{v}}{dt} + \frac{\vec{v}}{\tau} \right] = q \cdot \left( \vec{E} + \vec{v} \times \vec{B} \right)$$
 Eq. 3.18

To simplify this, the following simplifications are made: 1) the magnetic field is defined to be normal to the film surface along the z-axis such that  $\vec{B} = (0 \ 0 \ B)$ , 2) the transport plane is assumed to only take place in the x-y plane such that  $\vec{E} = (E_x \ E_y \ 0)$ , and 3) the effective masses of the charge carriers are assumed to be independent of the transport direction. Eq. 3.18 can then be put in terms of constant drift velocity in the x and y directions where  $\frac{dv_{Dx}}{dt} = \frac{dv_{Dy}}{dt} = 0$ . Using the previous assumptions and the definition of carrier mobility where  $\mu = \frac{q \cdot \tau}{m}$ , Eq. 3.19 and Eq. 3.20 are derived.

$$v_{Dx} = \frac{1}{1 + \mu^2 \cdot B^2} \left[ \mu \cdot E_x + \mu^2 \cdot B \cdot E_y \right]$$
Eq. 3.19

$$v_{Dy} = \frac{1}{1 + \mu^2 \cdot B^2} \left[ \mu \cdot E_y - \mu^2 \cdot B \cdot E_x \right]$$
Eq. 3.20

In the presence of an electric field, carriers with a carrier concentration N with individual charge q drift in a steady-state motion with velocity  $\vec{v}_D$  and have a current density  $\vec{j} = q \cdot N \cdot \vec{v}_D$ . The current density and the electric field are related by  $\vec{j} = \sigma \cdot \vec{E}$  where  $\sigma$  is the electrical conductivity tensor  $\sigma = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} \\ \sigma_{yx} & \sigma_{yy} \end{pmatrix}$ . Utilizing Eq. 3.19 and Eq. 3.20, the vector components of the current density  $J_i$  can be related to the electric field components  $E_i$  through  $j_i = \sigma_{ij} \cdot E_j$ , resulting in:

$$\sigma = \frac{q \cdot N}{1 + \mu^2 \cdot B^2} \begin{pmatrix} \mu & \mu^2 \cdot B \\ -\mu^2 \cdot B & \mu \end{pmatrix}$$
 Eq. 3.21

In order to align this with the experimentally measured electrical resistivity, the conductivity tensor must be inverted:

$$\rho = \sigma^{-1} = \frac{1}{\sigma_{xx} \cdot \sigma_{yy} - \sigma_{xy} \cdot \sigma_{yx}} \begin{pmatrix} \sigma_{yy} & -\sigma_{xy} \\ -\sigma_{yx} & \sigma_{xx} \end{pmatrix} = \begin{pmatrix} \rho_{xx} & \rho_{xy} \\ \rho_{yx} & \rho_{yy} \end{pmatrix}$$
 Eq. 3.22

Eq. 3.22 can then be split up to find the longitudinal resistivity  $\rho_{xx} = E_x/j_x$ :

$$\rho_{xx} = \frac{\sigma_{yy}}{\sigma_{xx} \cdot \sigma_{yy} - \sigma_{xy} \cdot \sigma_{yx}} = \frac{1 + \mu^2 \cdot B^2}{q^2 \cdot N^2 \cdot \mu^2} \cdot \frac{q \cdot N \cdot \mu}{1 + \mu^2 \cdot B^2} = \frac{1}{q \cdot N \cdot \mu}$$
Eq. 3.23

and the transverse Hall resistivity  $\rho_{xy} = E_y / j_x$ :

$$\rho_{xy} = \frac{-\sigma_{xy}}{\sigma_{xx} \cdot \sigma_{yy} - \sigma_{xy} \cdot \sigma_{yx}} = \frac{1 + \mu^2 \cdot B^2}{q^2 \cdot N^2 \cdot \mu^2} \cdot \frac{-q \cdot N \cdot \mu^2 \cdot B}{1 + \mu^2 \cdot B^2} = \frac{-B}{q \cdot N}$$
Eq. 3.24

The Hall coefficient is then simply:

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$$R_H = \frac{E_y}{j_x \cdot B} = \frac{\rho_{xy}}{B} = -\frac{1}{q \cdot N}$$
Eq. 3.25

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If the carrier motion is assumed to take place in individual, non-interacting channels indexed by *i* with individual carrier concentrations  $N_i$  and mobilities  $\mu_i$ , the conductivities for the individual channels can simply be summed.

$$\sigma_{tot} = \sum_{i} \sigma_{i} = \sum_{i} \frac{q \cdot N_{i}}{1 + \mu_{i}^{2} \cdot B^{2}} \begin{pmatrix} \mu_{i} & \mu_{i}^{2} \cdot B \\ -\mu_{i}^{2} \cdot B & \mu_{i} \end{pmatrix}$$
Eq. 3.26

Inverting the conductivity tensor to determine the resistivity tensor gives rise to a complicated expression where the off-diagonal elements of the resistivity tensor follow Eq. 3.27.

$$\rho_{xy} = -\frac{B}{q} \frac{\sum_{i} \frac{N_{i} \cdot \mu_{i}^{2}}{1 + \mu_{i}^{2} B^{2}}}{\left(\sum_{i} \frac{N_{i} \cdot \mu_{i}}{1 + \mu_{i}^{2} B^{2}}\right)^{2} + \left(\sum_{i} \frac{N_{i} \cdot \mu_{i}^{2} \cdot B}{1 + \mu_{i}^{2} B^{2}}\right)^{2}}$$
Eq. 3.27

Here, the sign convention for the Hall coefficient is chosen to have a positive carrier concentration for channels with negatively charged carriers and negative carrier concentration for channels with positively charged carriers.

The nonlinearities of the Hall coefficient  $R_H = dR_{xy}/dB = d(\rho_{xy}/t)/dB$  due to multiple carrier channels can be examined using the expression for the Hall resistivity in the low magnetic field limit, i.e.  $B \rightarrow 0$ , and the high field limit with  $B \rightarrow \infty$ . In the low field limit, the second sum in the denominator of Eq. 3.27 is negligible resulting in the following expression.

$$\rho_{xy,B\to 0} = -\frac{B}{q} \frac{\sum_i N_i \cdot \mu_i^2}{(\sum_i N_i \cdot \mu_i)^2}$$
 Eq. 3.28

In the high field limit, the second term in the denominator of Eq. 3.27 dominates and resulting in:

$$\rho_{xy,B\to\infty} = -\frac{B}{q} \frac{1}{\sum_i N_i}$$
Eq. 3.29
This choice is also ideal as the ratio  $\rho_{xy,B\to0}/\rho_{xy,B\to\infty}$  is independent of the magnetic field since both expressions are linear with the magnetic field. This ratio is plotted as a function of the mobility ratio  $\mu_1/\mu_2$  and the carrier concentration ratio  $N_1/N_2$  of the two channels in Figure 3-10. The left panel describes the situation where the carriers in each channel have an opposite sign, representing the case of mixed carriers where both electrons and holes are present. The right panel describes the situation when both channels are of the same type, in this case electrons are shown. The three subpanels show the Hall resistivity calculated from Eq. 3.27 as well as the slope of the Hall resistivity for three distinct cases.



Figure 3-10: Contour plot of the ratio of the Hall resistivity in the weak and strong magnetic field limit  $\rho_{xy,B\to0}/\rho_{xy,B\to\infty}$  plotted against the ratio of the carrier mobilities  $\mu_I/\mu_2$  and carrier concentration  $N_I/N_2$  where 1 and 2 designate different carrier channels. The left plot describes a system containing an electron-like channel and a hole-like channel while the right plot describes a system containing two channels with the same carrier type. The contour corresponding to  $\rho_{xy,B\to0}/\rho_{xy,B\to\infty} = 0$  is shown in red. Subplots (i)-(iii) demonstrate three

In the case of different carrier types, two distinct regions are distinguished, corresponding to ratios of  $0 < \rho_{xy,B\to 0}/\rho_{xy,B\to\infty} < 1$  shaded in yellow and  $\rho_{xy,B\to 0}/\rho_{xy,B\to\infty} < 0$  shaded in brown. In this yellow shaded region, the slope of the Hall resistivity is smaller as  $B \to 0$  compared to the Hall resistivity at high magnetic field. This typically occurs if there are more electrons  $(|N_1/N_2| > 1)$  with higher mobilities  $(|\mu_1/\mu_2| > 1)$  than holes. This situation is shown in Figure 3-10(i). Note that the converse happens if there are more holes  $(|N_1/N_2| < 1)$  with higher mobilities than electrons  $(|\mu_1/\mu_2| > 1)$ , except the overall slope of the Hall resistivity is positive. In the brown shaded region, either the electron channel has a higher mobility than the hole channel but has a lower carrier concentration  $(|N_1/N_2| > 1 \text{ and } |\mu_1/\mu_2| < 1)$  or vice versa. For example, the case where  $|N_1/N_2| = 2$  and  $|\mu_1/\mu_2| = 0.25$  is shown in Figure 3-10(ii). In this case the slope of the Hall resistivity is positive in the low field limit and negative in the high field limit. If the electron channel instead has a lower carrier concentration and a higher mobility, the slope in the low field limit would be negative and positive in the high field limit.

In the case where both transport channels have the same carrier type, the nonlinear Hall resistivity follows the trend shown in Figure 3-10(iii). Here, the ratio  $\rho_{xy,B\to0}/\rho_{xy,B\to\infty} \ge 1$  so the slope in the low magnetic field limit is larger than the slope in the high magnetic field limit.

If this simple description of non-interacting carrier channels accurately models the nonlinear Hall resistance, the following categorizations can be made to characterize transport characteristics in a general material following the type nonlinearity observed.

• If the slope of the Hall resistance in the weak magnetic field limit is smaller than in the strong magnetic field limit, there are mixed carriers in the system, as seen in the left panel of Figure 3-10. If the slopes in the weak and strong field limit have the same sign then the

majority carrier type has a larger carrier mobility as seen in panel (i). If the slopes in the weak and strong field limit have opposite signs then the majority carrier type has a smaller carrier mobility as shown in panel (ii).

• If the slope of the Hall resistance in the weak magnetic field limit is larger than in the strong magnetic field limit, there are channels with the same carrier type but different mobilities and number of carriers, as seen in the right panel of Figure 3-10. The degree of nonlinearity increases as the ratio of the carrier ratio and mobility ratio increase while the respective conductivity in each channel remains comparable.

#### 3.2.4 Geometrical interpretation of the Hall effect in the weak magnetic field limit

The following section is reproduced in part from: Brahlek, M. and Roth, J., *et al.*, Hidden transport phenomena in an ultraclean correlated metal, in review at *Nature Comm.* (2021)

Due to the inherent complexities of electrical transport in real materials, the simplified classical picture is not sufficient and a quantum mechanical description is typically required to properly account for the band structure effects to the conductivity tensor. Therefore, the Boltzmann transport equation is typically used to derive realistic formulas for the longitudinal and transverse Hall resistivities.<sup>243</sup> This is further complicated in complex materials with multiple Fermi surfaces with complex shapes that make the Hall effect in the weak field limit non-trivial.<sup>244</sup>

These complexities can be circumvented using a tangible and straight-forward geometrical interpretation. The key points are covered as follows.<sup>245</sup> In this interpretation, the carrier motion is represented in 'scattering' space (l-space) in addition to the traditional reciprocal space (k-space).

When you move a point k around in *k*-space there is an equivalent scattering path length vector defined as:

$$l(k) = v_k \tau_k$$
 Eq. 3.30

where  $v_k$  is the Fermi velocity calculated from the band structure and  $\tau_k$  is the transport relaxation time. Note that the path in scattering space is typically much more complicated than the corresponding path in *k*-space as it can self-intersect at several points depending on the curvature of the Fermi surface. Using this straightforward transformation, the Hall conductivity  $\sigma_{xy}$  can be expressed in simple geometric terms including the area swept out by the scattering path length vector,  $A_l$ . For a two-dimensional conductor with an arbitrary Fermi surface shape,  $\sigma_{xy}$  can be represented as:

$$\sigma_{xy} = \frac{2}{R_K} \cdot \frac{\phi}{\phi_0} = 2 \frac{e^2}{h} \cdot \frac{\phi}{\phi_0} = 2 \frac{e^2}{h} \cdot \frac{B \cdot A_l}{\phi_0}$$
 Eq. 3.31

Which if expressed in units of the inverse Klitzing constant  $R_K$  (quantized Hall conductance  $e^2/h$ ), is equal to twice the magnetic flux quanta  $\phi_0 = h/e$  of the field B through  $A_l$ . This 2D representation can be generalized to any 3D Fermi surface simply by considering slices of the Fermi surface normal to the magnetic field and then integrating over all slices as shown in Eq. 3.32.

$$\sigma_{xy}^{3D} = 2 \frac{e^2}{h} \cdot \frac{B}{\phi_0} \int_{-\frac{\pi}{c}}^{\frac{\pi}{c}} A_{l_\perp}(k_z) \frac{dk_z}{2\pi}$$
 Eq. 3.32

Here, c is the out of plane lattice parameter and the subscript  $l_{\perp}$  designates that it is the projection of the scattering length vector onto the transport plane perpendicular to the applied B-field that must be used. This result is rather compelling since the complex factors influencing the Hall conductivity, namely band structure, Fermi surface curvature, Fermi velocity, and anisotropic scattering can all be separately discussed.

To get a feel for how this geometric approach is used, the simplest case will first be discussed. For a single slice of a Fermi surface that is normal to the applied magnetic field, the charge carriers will move in the x-y plane of k-space. For a spherical Fermi surface, these slice orbits will all be circular. In the isotropic limit where  $\tau_k$  is constant and not k-dependent, this translates to a similar circular trace in scattering space (*l*-space). This trace encloses an area  $A_e$  in *l*-space as illustrated in Figure 3-11(a). Note that this circular trace arises as  $l_k$  is always parallel to the wavevector k and it is electron like since the path always turns to the left.



Figure 3-11: 2D representations of Fermi surfaces in k-space (left) and traces of the scattering path length vector in I-space (right). (A) For a simple circular Fermi surface, the trace of the scattering vector is also circular. (B) As the Fermi surface becomes more complicated with sections of positive (red) and negative (blue) curvature, some Fermi velocity vectors can be parallel resulting in scattering path length vectors of different magnitudes but the same direction. (C) In cases where the sections with negative curvature have a larger Fermi velocity than those having the same direction with positive curvature, additional loops are traced in I-space with opposite handedness causing a mixed electron/hole characteristic in the Hall conductivity. (D) Opposite to (C), if the areas with negative curvature have a lower Fermi velocity, 'inner loops' are created with the same handedness resulting in strictly electron characteristics. Note that the main loops do not have to be electron like in all cases. Figure reproduced from reference.<sup>242</sup>

Fermi surfaces of real materials deviate significantly from the simple spherical case as they can consist of areas with negative Fermi surface curvature, shown schematically in Figure 3-11(b). This local curvature is defined as  $\kappa = \frac{d\theta}{dk_t}$ , the deviation from a straight line  $d\theta$  per arc-length  $dk_t$  (tangential) which is inverse to the radius of the osculating circle approximating the local bending

of the Fermi surface. These segments with negative curvature result in a nontrivial change in the scattering path length trajectory in *l*-space. Negative curvature results in parallel Fermi velocity vectors for different k-states which in turn results in parallel scattering path length vectors in lspace. This point is illustrated in Figure 3-11(b) where  $v_{F,1}$  and  $v_{F,2}$  are parallel for two non-parallel Fermi wavevectors  $k_1$  and  $k_2$ . Therefore, the corresponding path length vectors  $l_{k,1}$  and  $l_{k,2}$  are parallel and their relative lengths are dependent on their corresponding Fermi velocity vector and transport relaxation time. If the segments with negative curvature have a larger scattering path length vector than those with positive curvature, additional loops will emerge in *I*-space with an opposite handedness than the main loop. This is depicted in Figure 3-11(c) where the main loop is electron-like. The outer loops have an opposite handedness and electrons undergo a retrograde motion, thus behaving like a positively charged carrier giving rise to hole-like transport characteristics. In the case where the segments with negative curvature have a smaller scattering path length vector than those with positive curvature, the additional loops will emerge in *I*-space with the same handedness where both the inner and outer loops are electron-like, see Figure 3-11(d). This simple interpretation can already reveal which states of the Fermi surface contribute electron-like and hole-like responses to the electrical transport.

The Fermi surface geometry, the Fermi velocity, and transport relaxation time encoded in  $A_l$  have direct consequences for the Hall conductivity through Eq. 3.31. In the simplest case where there is only one main loop,  $\sigma_{xy} \sim A_l$ . For more complex Fermi surfaces such as those shown in Figure 3-11(c-d) the Hall conductivity is proportional to the sum of all enclosed areas traced out by the scattering path length vector in *I*-space where the handedness is taken into account. In the case where the inner loops are the same handedness as the main loop such as in Figure 3-11(d),  $\sigma_{xy} \sim (A_e + A'_e)$  and the transport is absent of all hole-like character. In the case of Figure 3-11(c),  $\sigma_{xy} \sim (A_e - A_h)$ . The larger the segments of negative Fermi surface curvature and the longer the scattering path length, the more pronounced hole-like character of carriers will affect the Hall

conductivity. This is intuitively clear since the larger the Fermi velocity and the longer the relaxation time of an electronic state, the stronger it contributes and thus influences the transport characteristics.

While the previous discussion was focused on 2D conduction, it can be generalized to a 3D Fermi surface by summing Eq. 3.32 over all cross sections of the 3D surface. For cases with multiple Fermi surface sheets, the contributions from each Fermi surface sheet can also simply be summed. Once again it is convenient to express the Hall resistivity in terms of the conductivity. Following Eq. 3.22 and Eq. 3.23 it is clear that in the low magnetic field limit  $\sigma_{xy}$ ,  $\sigma_{yx} \ll \sigma_{xx}$ ,  $\sigma_{yy}$ , therefore the Hall resistivity can be approximated as:

$$\rho_{xy} = \frac{\sigma_{xy}}{\sigma_{xx} \cdot \sigma_{yy} - \sigma_{xy} \cdot \sigma_{yx}} \approx \frac{\sigma_{xy}}{\sigma_{xx} \cdot \sigma_{yy}}$$
Eq. 3.33

The longitudinal conductivity can be determined as follows. In the 2D case, the diagonal components of the conductivity are given by Eq. 3.34 where  $\theta_k$  is the angle between  $l_k$  and  $\hat{x}$ .

$$\sigma_{xx} = \frac{e^2}{h\pi} \int ds \cdot l_k \cos^2(\theta_k)$$
 Eq. 3.34

For a 2D crystal with N-fold symmetry where N > 2, the Fermi surface is divided into N identical wedges that can be mapped onto each other by regular symmetry rotations where  $\theta_k$  is changed to  $\theta_k + m\alpha$  where  $\alpha = 2\pi/N$ . Therefore, in general the longitudinal conductivity can be expressed as:

$$\sigma_{xx} = \frac{e^2}{h\pi} \int_{\Delta S} ds \cdot l_k \sum_{m=1}^{N} \cos^2(\theta_k + m\alpha)$$
 Eq. 3.35

By confining the integral to one wedge of length  $\Delta S = S/N$  and observing that  $\int ds \cdot l_k$  is no more than the product of the average magnitude of the scattering path length vector  $l_{av}$  and the Fermi surface circumference *S*, the longitudinal conductivity can be expressed as:

$$\sigma_{xx} = \frac{e^2}{h} \cdot \frac{l_{av} \cdot S}{2\pi}$$
 Eq. 3.36

For cases where we can assume that  $\sigma_{xx} = \sigma_{yy}$  such as crystal systems with four-fold symmetry in the conduction plane such as biaxially strained SrVO<sub>3</sub>, the Hall Coefficient  $R_H = \frac{\rho_{xy}}{B}$ for a 2D conductor can be found by combining Eq. 3.31, Eq. 3.33, and Eq. 3.36:

$$R_{H} = \frac{\rho_{xy}}{B} = \frac{1}{B} \cdot \frac{\sigma_{xy}}{\sigma_{xx} \cdot \sigma_{yy}} = \frac{2\frac{e^{2}}{h \cdot \phi_{0}} \cdot A_{l}}{\left(\frac{e^{2}}{2\pi \cdot h} \cdot l_{av} \cdot S\right)^{2}} = \frac{8\pi^{2}}{e} \cdot \frac{A_{l}}{(l_{av} \cdot S)^{2}}$$
Eq. 3.37

This equation can be further generalized to the 3D case by integrating over all 'slices'  $dk_z$ of the Fermi surface in the transport plane and summing over all Fermi surface sheets indexed by the subscript *j*.

$$(eR_{H})^{-1} = \frac{1}{8\pi^{2}} \cdot \frac{\left[\sum_{j} \int_{-\frac{\pi}{c}}^{\frac{\pi}{c}} l_{av,k_{z},j} \cdot S_{k_{z},j} \frac{dk_{z,j}}{2\pi}\right]^{2}}{\sum_{j} \int_{-\frac{\pi}{c}}^{\frac{\pi}{c}} A_{l,k_{z},j} \frac{dk_{z,j}}{2\pi}}$$
Eq. 3.38

Here,  $l_{av,k_z,j}$  is the average magnitude of the scattering path length vectors linked to *k*-states lying on the 'orbit of constant  $k_{z,j}$  for the Fermi surface sheet *j*,  $S_{k_z,j}$  is the circumference of Fermi surface sheet *j* sliced at constant  $k_{z,j}$ , and  $A_{l,k_z,j}$  is the total area enclosed by the scattering path length vector in *l*-space on Fermi surface sheet *j* sliced at constant  $k_{z,j}$ . Note that in the original derivation in reference,<sup>245</sup> Equation (11) has a typo leading to an erroneous factor of  $\pi$ .

This results in a direct link between the inverse Hall coefficient and band structure of a given material; specifically, the Fermi surface geometry, the Fermi velocity, and transport relaxation time which are embedded in  $l_{av,k_z,j}$ ,  $A_{l,k_z,j}$ , and  $S_{k_z,j}$ , allowing direct calculation and comparison to experimental results in the weak field, isotropic limit.

# 3.3 Spectroscopic ellipsometry

In order to determine the application value of transparent conductors it is often not sufficient to simply measure the transmission, reflection, and absorption. For many applications the optical constants, *n* and *k*, are desired to verify that no interfacial interference takes place in the device stack. In this thesis, these optical constants are determined through spectroscopic ellipsometry which measures the change in polarization of light as it reflects through the film. The change in this polarization is given by the amplitude ratio,  $\Psi$ , and the phase difference  $\Delta$ . An optical model is then made comprising of a semi-infinite substrate, film, surface roughness, and air. This model is then used to extract the complex dielectric function ( $\varepsilon = \varepsilon_1 + i\varepsilon_2$ ), film thickness, and surface roughness using a least square regression analysis. The surface roughness is typically represented using the Bruggeman effective medium approximation.<sup>246</sup> It should be noted that the thickness and roughness of the film can be measured through this technique or measured using other techniques to give a better fit of the dielectric function.

# 3.3.1 Oscillator models

The complex dielectric function is then parametrized by a series of oscillator models, typically Drude, Sellmeier, Lorentz, and Tauc-Lorentz oscillators.<sup>247,248</sup> The oscillators used in the optical characterization of the films in this thesis are as follows:

Drude:

$$\varepsilon = \frac{-\hbar^2}{\varepsilon_0 \rho(\tau E^2 - i\hbar E)}$$
 Eq. 3.39

Sellmeier:

$$\varepsilon = \frac{A}{E^2 - E_0^2}$$
 Eq. 3.40

Lorentz:

$$\varepsilon = \frac{A\Gamma E_0}{E_0^2 - E^2 - i\Gamma E}$$
 Eq. 3.41

Tauc-Lorentz:

$$\varepsilon_1 = \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi \qquad \text{Eq. 3.42}$$

$$\varepsilon_{2} = \begin{cases} \frac{A\Gamma E_{0}}{(E^{2} - E_{0}^{2})^{2} + \Gamma^{2}E^{2}} \frac{(E - E_{g})^{2}}{E} & E > E_{g} \\ 0 & E \le E_{g} \end{cases}$$
Eq. 3.43

Cody-Lorentz

$$\varepsilon_1 = \varepsilon_{1\infty} + \frac{2E_1}{\pi} P \int_0^{E_g} \frac{exp[(E' - E_t)/E_u]}{E'^2 - E^2} dE' + \frac{2}{\pi} P \int_{E_t}^{\infty} \frac{E'G(E')L(E')}{E'^2 - E^2} dE' \quad \text{Eq. 3.44}$$

$$\varepsilon_{2} = \begin{cases} \frac{E_{1}}{E} exp\left\{\frac{E - E_{t}}{E_{u}}\right\} & 0 < E \le E_{t} \\ G(E) \frac{A\Gamma E E_{0}}{(E^{2} - E_{0}^{2})^{2} + \Gamma^{2} E^{2}} & E > E_{t} \end{cases}$$
Eq. 3.45

In these oscillator equations, A is the amplitude, E is the photon energy,  $E_0$  is the resonance energy,  $E_g$  is the optical band gap,  $\Gamma$  is the broadening,  $\hbar$  is the reduced Planck constant,  $\varepsilon_0$  is the vacuum permittivity,  $\rho$  is the electrical resistivity,  $\tau$  is the mean free relaxation time,  $E_t$  is the demarcation energy between the Urbach tail and band-to-band transitions, G is a varable band edge function, and L is a Lorentz oscillator function.

In this thesis the optical properties were measured in the deep IR (0.049 - 0.75 eV) using a J.A. Woollam FTIR-VASE and from the IR to UV (0.75 - 6.5 eV) using a J.A. Woollam M-2000 rotating-compensator spectroscopic ellipsometer. As the fitting of ellipsometric data is not the focus for this thesis, the reader is suggested to read the following sources for more information.<sup>247,249</sup>

# 3.3.2 Calculation of Optical Transmittance of Freestanding Thin Films

For certain transparent conductor comparisons, it is desired to compare the optical properties of a material unhindered by potential substrate effects. Consider a free-standing film of thickness *t* with abrupt interfaces, surrounded entirely by air. The absorption coefficient of the material is given by Eq. 3.46 where  $\lambda$  is the wavelength of light and *k* is the wavelength dependent extinction coefficient.

$$\alpha = \frac{4\pi k(\lambda)}{\lambda}$$
 Eq. 3.46

For monochromatic light at normal incidence, the optical transmission coefficient *T* is then the ratio of the intensity of light at the upper and lower interfaces given by Eq. 3.47 where *R* is the reflectivity given by Eq. 3.48 and  $\phi$  and  $\psi$  are given by Eq. 3.49 where *n* is the wavelength dependent refractive index.<sup>250</sup>

$$T = \frac{I}{I_0} = \frac{(1-r)^2 + 4Rsin^2\psi}{e^{\alpha t} + R^2 e^{-\alpha t} - 2Rcos[2(\phi + \psi)]}$$
Eq. 3.47

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$
 Eq. 3.48

$$\phi = \frac{2\pi nt}{\lambda}$$
 Eq. 3.49

$$\psi = tan^{-2} \left[ \frac{2k}{n^2 + k^2 - 1} \right]$$
 Eq. 3.50

The transmission coefficient is then a function of film thickness and wavelength of the light and can vary significantly. The transmission can also experience drastic drops due to thin film The following section is reproduced in part from: Park, Y. and Roth, J., *et al.*, SrNbO<sub>3</sub> as a transparent conductor in the visible and ultraviolet spectra, *Comm. Phys.* 3, 102 (2020)

Following the considerable desire to develop correlated metals as transparent conductors as outlined in the introduction, this chapter focuses on the theoretical and experimental developments in realizing SrNbO<sub>3</sub> as a transparent conductor. The correlated metal SrVO<sub>3</sub> has previously been demonstrated as an excellent transparent conductor in the visible region, rivaling the leading semiconducting TCOs. One of the limiting factors of  $SrVO_3$  was the presence of an interband absorption edge at 2.9 eV (427 nm) thus obstructing its optical transmission over the entire visible range. This absorption edge was found to arise from interband transitions between the oxygen 2p valance bands to the unoccupied states in the vanadium  $t_{2p}$  conduction bands. If this transition could be shifted to higher energies, the optical absorption edge would be pushed out of the visible range, thus improving the overall optical transparency in the entire range of interest. Such a change could be induced by increasing the electronegativity difference ( $\Delta \chi$ ) between transition metal cation and the oxygen anions. If the vanadium cation in  $SrVO_3$  was replaced by one with a smaller electronegativity but the same electronic configuration to maintain strong electron correlations, the energy difference between the O 2p and transition metal  $t_{2g}$  bands would increase. The clearest choice is to replace the V<sup>4+</sup> cation with an electronegativity of 1.795 to the isoelectric Nb<sup>4+</sup> cation with an electronegativity of 1.690.<sup>251</sup> This substitution increases  $\Delta \chi$  by ~6%, suggesting that the absorption edge could be pushed into the UV regime; however, altering the material in such a fashion has other implications. The 4d-orbitals of Nb<sup>4+</sup> have a much larger spatial extent than the 3d orbitals of V<sup>4+</sup>, resulting in a larger orbital overlap and thus an increase in the conduction bandwidth despite the larger lattice parameter of SrNbO<sub>3</sub> (4.02 Å) compared to SrVO<sub>3</sub> (3.84 Å). This increased bandwidth results in a renormalization constant closer to unity, and thus a

smaller electron correlation strength. This reduced correlation strength then adversely affects the reduced plasma frequency, causing a blue-shift and potentially reducing the optical transmission of SrNbO<sub>3</sub> at longer wavelengths of the visible spectrum.

Bulk Sr<sub>x</sub>NbO<sub>3</sub> ceramics were first grown in 1955 and were described to assume the cubic perovskite structure with a lattice parameter of 4.024 Å.<sup>252</sup> Many follow-up studies revealed the extreme difficulty in maintaining the cation stoichiometry during synthesis; however, this experimental downside exposed that the crystalline structure of Sr<sub>x</sub>NbO<sub>3</sub> was strongly dependent on the cation stoichiometry; i.e. the Sr to Nb ratio (discussed in more detail in Chapter 5).<sup>253,254</sup> While many of these studies verified the metallic nature of SrNbO<sub>3</sub>, none investigated the optical properties in detail. Surprisingly, one study demonstrated that ceramic pellets of SrNbO<sub>3</sub> were highly absorbing in the visible yet metallic, serving as an effective photocatalyst in water-splitting reactions.<sup>255</sup> This effect was further studied using first principles calculations where Sr and O vacancies could be used to alter the optical properties.<sup>256</sup> SrNbO<sub>3</sub> thin films have been deposited by PLD from Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> targets in reducing atmospheres, either with N<sub>2</sub> process gas<sup>257</sup> or low oxygen partial pressure to help stabilize the Nb 4+ state.<sup>258,259</sup> Once again, the optical properties of these thin films were left unstudied, leaving the transparent conducting nature undetected.

This chapter will first outline the first principles calculations used to evaluate the band structure, correlation strength, and optical properties of SrNbO<sub>3</sub>. The synthesis and subsequent structural characterization of SrNbO<sub>3</sub> thin films grown by PLD will then be discussed. The electronic and optical properties as a function of film thickness will then be covered, followed by a comparison to other transparent conducting materials. Finally, this chapter will conclude with the extraction of the electron correlation strength using extended Drude analysis.

### 4.1 First Principles Calculations

The realization that the optical absorption edge can be easily manipulated by simply adjusting the electronegativity difference between the transition metal cation and the oxygen anions prompted immediate investigation using density functional theory (DFT) and dynamical mean field theory (DMFT). These calculations were performed by Dr. Arpita Paul and Prof. Turan Birol of the University of Minnesota. First principles Kohn Sham calculations were performed using the Linearized Augmented Plane Wave approach as implemented in theWien2K.<sup>260</sup> A 25×25×25 MP grid was used to converge the density of states.<sup>261</sup> All other calculation used a 12×12×12 grid which provided good convergence. Fully charge self-consistent, DFT+DMFT calculations were performed using the EDMFTF package (formerly known as DMFT-Wien2K) that uses the Luttinger–Ward functional.<sup>19,21,262</sup> On-site Coulomb interaction in DMFT was taken into account by U=6 eV, in addition to an on-site Hund's coupling of J=0.7 eV. Nominal double counting was used, which is known to give reasonable agreement with experiment in the early *d'* transition metal oxides. The on-site self-energy obtained from DMFT had a vanishingly small imaginary part on the Fermi level, and its real part was linear, hence the Fermi liquid approach used in the text was valid.

The calculated band structure for SrNbO<sub>3</sub> under compressive strain (a=3.989 Å) is shown in Figure 4-1(a) in comparison to the isoelectronic SrVO<sub>3</sub> under tensile strain (a=3.868 Å) in Figure 4-1(b). A schematic of the 1<sup>st</sup> Brillouin zone along with the high symmetry points is shown for tetragonally distorted perovskites in Figure 4-1(e). The conduction band was formed by the three bands originating from the  $t_{2g}$  manifold of the Nb 4d orbital and was intersected by the Fermi level, leading to metallic conduction. The valance band derived from the O 2p bands was found to be well below the conduction band. The energy gap between the conduction band minimum and the valance band maximum was found to be 2.3 eV, considerably larger than the energy gap of ~1 eV calculated for SrVO<sub>3</sub>.



Figure 4-1: Density of states and band structure for (a) SrNbO<sub>3</sub> and (b) SrVO<sub>3</sub> calculated by DFT. The colors correspond to the orbital character of the bands. Spectral function of (c) SrNbO<sub>3</sub> and (d) SrVO<sub>3</sub> calculated by DFT and DMFT. The conduction band width W is reduced by the renormalization constant  $Z_k$ . (e) Schematic of the 1<sup>st</sup> Brillouin zone for tetragonally distorted SrNbO<sub>3</sub> and SrVO<sub>3</sub>. Figure reproduced from reference.<sup>55</sup>

The interband absorption edge originated from a strong interband transition, either a transition from occupied states of the O 2p bands to unoccupied states of the Nb  $4d t_{2g}$  bands or from occupied states of the Nb  $4d t_{2g}$  bands below the Fermi level to the higher lying unoccupied bands derived from the Nb  $4d e_g$  and Sr 5s orbitals. For electrons to transition between occupied O 2p and unoccupied Nb  $4d t_{2g}$  states, photon energies larger than 4 eV were needed, while interband transition energies from occupied Nb  $4d t_{2g}$  to unoccupied Nb  $4d e_g$  and Sr 5s states were  $\sim 2.5-3$  eV. The energy separation between the individual bands was considerably larger compared to SrVO<sub>3</sub>, where transitions from occupied O 2p to unoccupied V  $3d t_{2g}$  states already occurred at about 2.7 eV, while interband transition energies from occupied O 2p to unoccupied V  $3d t_{2g}$  to unoccupied V  $3d e_g$  occurred at about 2.2 eV, albeit with a small dipole matrix element.<sup>53</sup>

The effect of electron correlation on the band structure was examined by comparing the DFT results to DMFT calculations for SrNbO<sub>3</sub> and SrVO<sub>3</sub>, as shown in Figure 4-1(c)-(d). Comparing the conduction band widths obtained from DFT and DMFT, the renormalization constant of SrNbO<sub>3</sub> ( $Z_k \sim 0.72$ ) was found to be larger than that of SrVO<sub>3</sub> ( $Z_k \sim 0.55$ )<sup>53</sup> confirming the anticipated reduced correlation strength of SrNbO<sub>3</sub>. This reduced correlation strength was attributed to the increased size of the 4d orbitals compared to the 3d orbitals in SrVO<sub>3</sub>, resulting in a larger orbital overlap despite SrNbO<sub>3</sub>'s larger lattice parameter. This reduction induced a blue-shift of the reduced plasma frequency compared to that of SrVO<sub>3</sub>.

### 4.2 Growth of SrNbO<sub>3</sub> films

To expedite the process of investigating this material system, the SrNbO<sub>3</sub> films in this study were grown and characterized using XRD by Daichi Oka of Ohoku University and Yasushi Hirose and Tetsuya Hasegawa of the University of Tokyo. SrNbO<sub>3</sub> thin films of varying thicknesses were grown on [001]-oriented KTaO<sub>3</sub> single crystal substrates (a=3.989 Å, mismatch=-0.85%) using pulsed laser deposition following the same procedure used in the previous study.<sup>259</sup> A ceramic target of Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> was ablated using a KrF excimer laser ( $\lambda$ =248 nm) operating at an energy fluence of 0.33-0.44 Jcm<sup>-2</sup>shot<sup>-1</sup> and repetition rate of 10 Hz. The substrates were heated to 700°C by using an infrared lamp heater. The crystal structure and thicknesses of the thin films were characterized using XRD and X-ray reflectivity using a four-axis diffractometer (Bruker AXS, D8 Discover) with a 2D area detector. XRD 2 $\theta$  scans for all samples in this study are shown in Figure 4-2. All films were found to be single phase. Note that the 40 nm film had a small Pt peak as XRD was measured after Pt contacts were applied.



Figure 4-2: XRD 2 $\theta$  scans of SrNbO<sub>3</sub> thin films of varying thicknesses on KTaO<sub>3</sub> substrates. Figure reproduced from reference.<sup>55</sup>

### 4.3 Electrical characterization

Following the synthesis of a thickness series of SrNbO<sub>3</sub> thin films on KTaO<sub>3</sub>, the electronic transport was measured in a van der Pauw geometry in a Quantum Design Physical Properties Measurement System with a source current of 500  $\mu$ A. Carrier concentration and mobility values were determined through Hall measurements using magnetic field strengths up to ±8 T applied perpendicular to the film plane. Temperature dependent resistivity was also measured down to 2.2 K to measure the RRR.

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Figure 4-3: (a) Sheet resistance of SrNbO<sub>3</sub> as a function of film thickness plotted with the fit of the inverse relationship between  $R_s$  and bulk resistivity  $\rho_0$  (black curve) and the deviation  $\Delta\rho$  due to extrinsic scattering effects captured by the Fuchs-Sondheimer model (red curve). (b) Temperature dependent resistivity of two SrNbO<sub>3</sub> thin films. (c) Carrier concentration and mobility as a function of film thickness. Thickness error determined from Debye-Scherrer analysis from XRD was smaller than the symbols. Figure reproduced from reference.<sup>55</sup>

The sheet resistance ( $R_s$ ) as a function of thickness is shown in Figure 4-3(a). The SrNbO<sub>3</sub> films with thicknesses in the range of 10–60 nm had sheet resistance values between 67.5  $\Omega$ /sq and 7.3  $\Omega$ /sq and the films' electrical resistivities varied between  $6.9 \times 10^{-5} \Omega \cdot \text{cm}$  and  $3.8 \times 10^{-5} \Omega \cdot \text{cm}$ . This variation was attributed to a larger surface scattering contribution for thinner films. The small effect of resistivity increasing from surface scattering was investigated by estimating the electron mean-free path (EMFP)  $\Lambda$  using the Sommerfeld model and calculating the contribution of the Fuchs-Sondheimer effect as follows.<sup>263,264</sup>

The EMFP is the distance electrons travel between two inelastic scattering events and can be expressed as the product of the Fermi velocity and the electron transport relaxation time. The inelastic mean free path was approximated using the Fermi velocity expression from the Sommerfeld model of a free electron gas, shown in Eq. 4.1.<sup>161</sup> For the films investigated, an average EMFP of  $(3.5 \pm 0.7)$  nm was found, which was comparable to those of transparent correlated metals SrVO<sub>3</sub> ( $\Lambda$  = 5.6 nm) and CaVO<sub>3</sub> ( $\Lambda$  = 3.9 nm),<sup>53</sup> but much lower than those of conventional metals, such as silver ( $\Lambda = 52$  nm).<sup>265</sup> This exceptionally small EMFP enables more aggressive thickness scaling than traditional material solutions.

$$\Lambda = \frac{\hbar\mu}{e} (3\pi^2 n)^{1/3}$$
 Eq. 4.1

If the thickness of a metallic film is comparable to the EMPF, the effects of surface scattering must be considered. For film thicknesses t that are on the order of the inelastic mean free path or thinner, electron scattering at the film surface will contribute and increase the sheet resistance  $R_s$  causing a deviation from the simple inverse linear relationship  $R_s = \rho/t$ . The apparent decrease in bulk electrical conductivity can then be quantitatively captured by the Fuchs and Sondheimer model shown in Eq. 4.2 where  $\kappa = t/\Lambda$  is the normalized length and p is the surface reflection coefficient ranging between 0 for diffused scattering and 1 for elastic scattering.

$$\sigma_{FS} = \sigma_0 \left[ 1 - \frac{3(1-p)}{2\kappa} \int_1^\infty \left( \frac{1}{\xi^3} - \frac{1}{\xi^5} \right) \frac{1 - e^{-\kappa\xi}}{1 - pe^{-\kappa\xi}} d\xi \right]$$
 Eq. 4.2

For the SrNbO<sub>3</sub> films in this study, the smallest experimental film thickness was about three times larger than the EMFP, therefore the additional scattering effect was relatively small. Fitting the FS model to the thickness dependent sheet resistance data of SrNbO<sub>3</sub> films gave a bulk resistivity of  $5.5 \times 10^{-5} \Omega$  cm and a surface reflection coefficient 0.66. The FS fit is shown over the thickness dependent sheet resistance in Figure 4-3(a) with the EMFP highlighted.

The residual resistivity ratios (RRR) were relatively small, as can be seen from the temperature dependent resistivity curves for SrNbO<sub>3</sub> films with 23 nm and 37 nm thickness, shown in the inset of Figure 4-3(b). The RRR values were 1.6 and 3.2, respectively, indicating that temperature independent scattering from defects significantly affected the electric conductivity at room temperature. Nevertheless, the sheet resistance values measured for SrNbO<sub>3</sub> thin films were comparable to other high-performance transparent conductors in the visible spectrum<sup>45,53</sup> and were about three orders of magnitude lower compared to current UV transparent conductor materials.<sup>105,266</sup>

The thickness dependence of the carrier mobility  $\mu$  and the carrier concentration *n* for SrNbO<sub>3</sub> thin films is shown in Figure 4-3(c). The mobility was found to be ~8 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> at room temperature, comparable to values of other correlated metals such as SrVO<sub>3</sub> and CaVO<sub>3</sub><sup>53</sup> and about an order of magnitude lower than conventional TCOs.<sup>267</sup> The carrier concentration for all samples was approximately 1×10<sup>22</sup> cm<sup>-3</sup>, about a factor of two smaller than carrier concentration measured for SrVO<sub>3</sub>, but over an order of magnitude higher than conventional TCOs and UV transparent conductors in particular. For comparison, the highest carrier concentration reported for Ga<sub>2</sub>O<sub>3</sub> was on the order of low 10<sup>20</sup> cm<sup>-3</sup> with a carrier mobility of 50 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>,<sup>268,269</sup> and typical values for ZnGa<sub>2</sub>O<sub>4</sub> were similar with carrier concentrations not higher than 10<sup>20</sup> cm<sup>-3</sup> and carrier mobilities of ~80 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.<sup>270</sup> Even though the carrier mobility of SrNbO<sub>3</sub> was much lower, it was overcompensated by the high carrier concentration, giving rise to superior electrical properties compared to conventional UV transparent conductors.

# 4.4 Optical characterization

The optical properties of SrNbO<sub>3</sub> films were characterized using spectroscopic ellipsometry at room temperature by Dr. Alexej Pogrebnyakov. The complex dielectric functions measured for three SrNbO<sub>3</sub> films with thicknesses of 10, 23 and 29 nm are shown in Figure 4-4 with the dielectric function calculated from DFT shown in comparison. The dielectric function in the IR range was dominated by a Drude peak, as highlighted in Figure 4-4(a) and (c). The expected induced red-shift from the electron correlation in SrNbO<sub>3</sub> was not sufficient to push the carrier reflection edge completely into the IR range, but it did not greatly hinder the transparency at the long wavelength end of the visible spectrum. The dielectric function in the visible and UV range are highlighted in Figure 4-4(c) and (d) respectively. The main interband absorption edge was experimentally found at around 4.8 eV (~260 nm), in very good agreement with DFT predictions.

Compared to SrVO<sub>3</sub>, the interband absorption of SrNbO<sub>3</sub> was blue-shifted by over 1.5 eV into the UV range. The imaginary part of the dielectric function was small in the visible and UV range up until the absorption edge, indicating a low optical absorption coefficient and in turn high transparency. The small absorption peak at ~2.7 eV calculated by DFT calculation originated from a weak  $t_{2g}$  to  $e_g$  interband transition. A similar peak was predicted for SrVO<sub>3</sub>, but was not experimentally found in either material system. The cause for this peak's absence is not clear but we speculate that the sizeable defect concentration present in the films, which gave rise to relatively low RRR values, also affected the optical properties.



Figure 4-4: The real part of the dielectric function in the (a) infrared and (b) visible to UV ranges. The complex part of the dielectric function in the (c) infrared and (d) visible to UV ranges. The real and complex parts of the dielectric function calculated by DFT are overlaid in black. (e) Figure of merit for SrNbO<sub>3</sub> compared to other TCOs as a function of film thickness. (f) Transmission of 10-nm-thick, freestanding films of SrNbO<sub>3</sub> and SrVO<sub>3</sub> demonstrating the increased transparency at higher energies. Figure reproduced from reference.<sup>55</sup>

The performance of SrNbO<sub>3</sub> as a transparent conductor was evaluated using the Haake figure of merit ( $\Phi_{TC}$ ) as outlined in Chapter 1.3. The thickness dependence of  $\Phi_{TC}$  for SrNbO<sub>3</sub>, SrVO<sub>3</sub> and ITO was calculated in the visible range (400–700 nm), and for the UV spectrum from

260 to 320 nm, encompassing the entire UVB range (280–315 nm). The transmittance of each film was calculated from the dielectric function assuming normal incidence of light and a freestanding film including surface reflections and multiple interference effects (see Chapter 3.3.2). Since the transmittance varied with the wavelength, the transmission was averaged over each spectrum of interest. The curves for each spectrum are shown in Figure 4-4(e). In the visible spectrum, SrNbO3 was found to have a maximum  $\Phi_{TC}$  of  $5 \times 10^{-3} \Omega^{-1}$  at a film thickness of 10 nm, about a factor of two higher than SrVO<sub>3</sub> at the same thickness and a factor of three higher than the best ITO with a  $\Phi_{TC}$  of about 1.6×10<sup>-3</sup>  $\Omega^{-1}$  at a thickness of 150 nm.<sup>53</sup> The pronounced minimum in  $\Phi_{TC}$  of ITO was due to constructive interference of light reflected at both surfaces of a freestanding film. The higher  $\Phi_{TC}$  values of SrNbO<sub>3</sub> and the shift of the maximum of the  $\Phi_{TC}$  curve toward larger thickness compared to SrVO3 was indicative that the optical properties of SrNbO3 were more suitable for UV applications. Figure 4-4(f) demonstrates a direct comparison of the transmission calculated from the dielectric function for 10-nm-thick SrNbO3 and SrVO3 films. While SrNbO3 had a lower transmission in the visible spectrum at longer wavelengths, a much higher transmission in the blue spectrum led to an overall higher optical transmission in the visible range. This improvement in optical properties even compensated for the somewhat higher sheet resistance of SrNbO<sub>3</sub> (68  $\Omega$ /sq.) at a film thickness of 10 nm compared to SrVO<sub>3</sub> (45  $\Omega$ /sq.). This simple comparison demonstrates that SrNbO<sub>3</sub> is a competitive transparent conductor material in the visible range. The transmission curve further shows that SrNbO<sub>3</sub> has outstanding transmission values in the UV spectrum from 320 to 260 nm.

For the transparent conductor examined here, the UV figure of merits were smaller and the maximum of each  $\Phi_{TC}$  curve shifted towards smaller film thicknesses, indicating a reduced optical performance in the UV compared to the visible spectrum. This effect was much less pronounced for SrNbO<sub>3</sub> films, specifically the  $\Phi_{TC}$  value for 10-nm-thick films was still above  $10^{-3} \Omega^{-1}$  and thus comparable with ITO's performance in the visible. In contrast, the  $\Phi_{TC}$  for 10 nm thick SrVO<sub>3</sub> was

reduced by about two orders of magnitude, rendering it unsuitable for UV applications. ITO had a maximum UV  $\Phi_{TC}$  at a thickness of ~60 nm, albeit an order of magnitude lower than the highest  $\Phi_{TC}$  measured for SrNbO<sub>3</sub>. The figure of merit for ultrawide band gap semiconductors such as Ga<sub>2</sub>O<sub>3</sub> were estimated to be in the mid 10<sup>-7</sup>  $\Omega^{-1}$  range due to their low electrical conductivity. Large dopant concentrations in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (10% Sn) resulted in a room temperature resistivity of 10<sup>-1</sup>  $\Omega$ ·cm with carrier mobilities of ~50 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and carrier concentrations of about 10<sup>18</sup> cm<sup>-3</sup>.<sup>271</sup> Further increasing the Sn doping concentration gave rise to a red-shift of the fundamental absorption edge from 266 to 298 nm, which we attributed to a lattice expansion of the host semiconductor due to the larger size of Sn and an associated decreased band gap.

#### 4.5 Sum Rule and Extended Drude Model analysis

Certain properties of correlated metals, such as the renormalization constant  $Z_k$ , are extremely difficult to extract using traditional electronic characterization methods. Fortunately, proper analysis of the free carrier optical response can reveal otherwise unobtainable material specific information. Here, we experimentally verify the renormalization constant calculated by DFT through calculating the unscreened plasma frequency  $\omega_p$  from the measured dielectric function of SrNbO<sub>3</sub> using the Sum Rule analysis as well as the extended Drude Model.

The renormalization constant can be extracted by the ratio of carrier mass dependent quantities in the presence and absence of many-body interactions. Specifically, the renormalization constant  $Z_k$  can be estimated from the ratio of the square of the unscreened plasma frequency  $\omega_p^{Exp}$  determined experimentally by the sum rule when man-body interactions are present and the unscreened plasma frequency  $\omega_p^{DFT}$  calculated by DFT as shown in Eq. 4.3.

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$$Z_k = \frac{m_b^*}{m^*} = \left(\frac{\omega_p^{Exp}}{\omega_p^{DFT}}\right)^2$$
 Eq. 4.3

The optical conductivity  $\sigma(\omega)$  is first determined through its relation to the dielectric function  $\varepsilon(\omega)$  measured from spectroscopic ellipsometry as shown in Eq. 4.4.

$$\varepsilon(\omega) = 1 + \frac{4\pi i}{\omega}\sigma(\omega)$$
 Eq. 4.4

The experimental plasma frequency is then related to the real part of the optical conductivity shown in Eq. 4.5.<sup>272</sup> For this calculation, the integration interval was chosen to be from the smallest frequency measured ( $\omega_0$ = 0.04 eV) to a cut off frequency of  $\omega_c$ =2.25 eV. This cut-off frequency was chosen to be where the intraband and interband transition were identical ( $\varepsilon_1 = 0$ ).<sup>273</sup>

$$\frac{\omega_{pl}^2}{8} = \int_0^{\omega_c} \sigma_{Re}(\omega) \, d\omega = \int_{\omega_0}^{\omega_c} \sigma_{Re}(\omega) \, d\omega + \Delta \qquad \text{Eq. 4.5}$$

The additive constant  $\Delta$  accounts for the area not captured by integrating  $\sigma_{Re}(\omega)$ , namely the rectangular area  $\Delta_1$  in the range  $[0, \omega_0]$  on the x-axis and  $[0, \sigma_{Re}(\omega_0)]$  on the y-axis plus the area  $\Delta_2$  spanned by the three points  $[0, \sigma_{Re}(\omega_0)]$ ,  $[\omega_0, \sigma_{Re}(\omega_0)]$ , and  $[0, \sigma_{DC}]$  with  $\sigma_{DC}$  determined from the electrical resistivity converted into units of wavenumbers (cm<sup>-1</sup>). The values of each contribution to the unscreened plasma frequency are given in Table 4-1. From the sum rule, the unscreened plasma frequency was determined to be  $(3.96 \pm 0.18)$  eV.

Table 4-1: Contributions to the unscreened plasma frequency of SrNbO<sub>3</sub> thin films determined from the optical conductivity  $\sigma_{Re}(\omega)$  and electrical conductivity  $\sigma_{DC}$ .

Film thickness (nm)	$\int_{\omega_0}^{\omega_c} \sigma_{Re}(\omega)  d\omega  (\mathrm{cm}^{-1})$	$\Delta_1 (\text{cm}^{-1})$	$\Delta_2 (\text{cm}^{-1})$	$\omega_p \; (\mathrm{eV})$
10	9.62×10 <sup>7</sup>	$1.54 \times 10^{7}$	$0.41 \times 10^{7}$	3.77
23	$12.21 \times 10^{7}$	$1.55 \times 10^{7}$	$0.12 \times 10^{7}$	4.13
29	$11.23 \times 10^{7}$	$1.49 \times 10^{7}$	$0.11 \times 10^{7}$	3.97

Using the value of  $\omega_p^{DFT} = 4.93$  eV obtained from DFT calculations and the average value for the experimentally determined unscreened plasma frequency  $\omega_p^{Exp} = (3.96 \pm 0.18)$  eV, we find  $Z_k = 0.64 \pm 0.06$ . This renormalization constant contains contribution from all many-body interactions, electron-phonon and electron-electron interactions alike, which systematically overestimates the renormalization effect coming from electron-electron interactions alone, as determined by comparing the conduction band widths of SrNbO<sub>3</sub> calculated by DFT and DMFT resulting in an overall lower value.

The renormalization constant can alternatively be determined using the extended Drude model. The presence of many-body interactions, namely sizeable electron-electron and electronphonon coupling, requires an extension of the Drude model of electron conduction and its interaction with light beyond the simple assumption of an energy independent scattering time. Generalizing the scattering time to a complex and energy dependent quantity using the memory function directly reflects excitation originating from the many-body interactions, which can be mapped back onto the conventional Drude model by renormalized scattering rate  $\frac{1}{\tau^*(\omega,T)} = \frac{Z_k}{\tau(\omega,T)}$ and plasma frequency  $\omega_p^{*2} = \omega_p^2 Z_k$ .<sup>274</sup> The frequency dependent scattering rate and the mass enhancement factor can be calculated from Eq. 4.6 and Eq. 4.7 respectively.<sup>275</sup>

$$\frac{1}{\tau^*}(\omega) = -\frac{\omega_{pl}^2}{\omega} Im\left(\frac{1}{\varepsilon(\omega) - \Sigma_H}\right)$$
 Eq. 4.6

$$\frac{m^*(\omega)}{m_b} = \frac{\omega_{pl}^2}{\omega^2} Re\left(\frac{1}{\varepsilon(\omega) - \Sigma_H}\right)$$
 Eq. 4.7

Here,  $\varepsilon(\omega)$  is the complex dielectric function,  $\omega_p$  is the unscreened plasma frequency determined by Eq. 4.4, and  $\Sigma_H$  is the contribution from interband transitions, captured by the optical fitting model.



Figure 4-5: Mass enhancement (top row) and scattering rate (bottom row) for SrNbO<sub>3</sub> films. Electron-phonon coupling is the dominant many-body interaction in the blue region while electron-electron coupling is dominant in the red region. Figure reproduced from reference.<sup>55</sup>

The frequency-dependent scattering rate and mass enhancement are shown in Figure 4-5. The region highlighted in red corresponds to regions in which electron-electron interactions are dominant while the blue regions correspond to regions where electron-phonon interactions are dominant. The renormalization factor from electron-electron interactions is determined at high frequencies, i.e., much higher (5 to 10 times higher) than the highest phonon frequencies, yet small enough to avoid misinterpretation from interband transitions contributing to the optical conductivity. Here, the mass enhancement factor is expected to be frequency independent. From the phonon spectrum of SrNbO<sub>3</sub> computed by DFT, the highest phonon frequencies were found at about 18 THz (600 cm<sup>-1</sup>), thus the mass enhancement factor was expected to become frequency independent at frequencies of about 6000 cm<sup>-1</sup> or higher. The mass enhancement factor determined from the extended Drude model was found to be  $1.12\pm0.03$  resulting in a renormalization constant of  $0.89\pm0.02$ . These values were higher than the prediction from DFT and DMFT and much higher than the values calculated from the sum rule analysis. Note that the sum-rule analysis also contained contribution to the renormalization constant originating from electron-phonon coupling, which can significantly reduce  $Z_k$  if the electron-phonon coupling strength is comparable to electron-electron coupling.

The screened plasma energy ( $\hbar\omega_p$ ) extracted from the experiment at  $\varepsilon_1 = 0$  was found to be (1.98 ± 0.03) eV. This value was smaller than the reduced plasma energy of 2.15 eV found from DFT.<sup>57</sup> Taking the mass renormalization due to electron correlation effects into account from the comparison of band widths of SrNbO<sub>3</sub> calculated by DFT and DMFT, the theoretical value of the reduced plasma frequency was corrected to a smaller value of 1.82 eV. The experimental determination of the renormalization constant Z<sub>k</sub> from electron correlation effects extracted from the extended Drude model was somewhat higher (Z<sub>k</sub> = 0.89 ± 0.02) than the theoretically predicted value of 0.72. Using the experimental Z<sub>k</sub> value, a corrected reduced plasma frequency of (1.91 ± 0.04) eV was determined which was in better agreement to the measured screened plasma frequency, indicating that the calculated correlation strength might be slightly overestimated.

### 4.6 Concluding remarks

In summary, SrNbO<sub>3</sub> thin films were proposed and experimentally confirmed as highperformance UV transparent conductors with superior properties in the spectral range from 260 to 320 nm. DFT and DMFT calculations were performed, revealing that the conduction band of SrNbO<sub>3</sub> was energetically more isolated than the conduction band of SrVO<sub>3</sub>. Despite a weaker electron correlation, the reduced plasma frequency of SrNbO<sub>3</sub> was sufficiently small to open a transparent window ranging from the visible to the UV due to a considerable blueshift of the interband absorption edge to about 4.8 eV, which is comparable to those of Ga<sub>2</sub>O<sub>3</sub> and ZnGa<sub>2</sub>O<sub>4</sub>. Spectroscopic ellipsometry and transport measurements confirmed the theoretical predictions by DFT and DMFT and substantiated the potential of the correlated metal SrNbO<sub>3</sub> as highperformance transparent electrode material for UV application. The rare combination of high transmission in the UV and high electrical conductivity in SrNbO<sub>3</sub> facilitates the improvement of existing UV LEDs suffering from poor EQEs and enables energy efficient, long lasting, high performance, portable and environmentally benign solid state lighting solutions for UV sanitation, biomolecule sensing, UV phototherapy, UV curing, UV photolithography and high sensitivity solar blind detector technology.

# Chapter 5: Sputtering Sr<sub>x</sub>NbO<sub>3</sub> as an ultraviolet transparent conductor

The following section is adapted in part with permission from: Roth, et al., Sputtered Sr<sub>x</sub>NbO<sub>3</sub> as a UV-

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Following the experimental verification of SrNbO<sub>3</sub> as an effective transparent conductor in the UV and visible it was desired to further develop the deposition towards a more scalable and economically viable technique. This chapter covers the growth of Sr<sub>x</sub>NbO<sub>3</sub> films using RF sputtering. This research is focused on developing transparent, conducting correlated metals using a scalable deposition technique used in industry and details the growth on multiple substrates. This chapter details the procedure for making the target materials for sputtering as well as the growth conditions required to ensure reproducibility of the results discussed. The discussion is primarily focused on the growth of Sr<sub>x</sub>NbO<sub>3</sub> films on (La<sub>0.3</sub>Sr<sub>0.7</sub>)(Al<sub>0.65</sub>Ta<sub>0.35</sub>)O<sub>3</sub> (LSAT) substrates where the structural, optical, and electrical properties are reported as a function of film thickness. For all films, the cubic perovskite phase was maintained, although the in-plane and out-of-plane lattice parameters suggested sizeable Sr deficiencies up to 25%, which was confirmed by X-ray photoelectron spectroscopy (XPS). Despite such high levels of cation non-stoichiometry, the sheet resistance remained lower than traditional TCOs while a high optical transparency throughout the visible and into UV range was maintained. Effects arising from significant Sr vacancies on the optical properties were calculated using density functional theory (DFT) and compared to experimental values. These results demonstrate that sputter deposited  $Sr_xNbO_3$  remains an excellent candidate for UV transparent conductors even in the presence of large defect concentrations. The growth of Sr<sub>x</sub>NbO<sub>3</sub> on other substrates including SrTiO<sub>3</sub> on silicon and KTaO<sub>3</sub> is then discussed, demonstrating the ease in which Sr<sub>x</sub>NbO<sub>3</sub> can be grown on many materials.

Following the vast application space of UV transparent conductors covered in Chapter 1, it is of great importance to develop more effective materials than the traditionally used doped, widebandgap oxides such as  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, ITO, and La doped SrSnO<sub>3</sub>. The recently proposed materials design paradigm change for transparent conductors away from s-orbital based and degenerately doped wide bandgap semiconductors with high carrier mobility towards d-orbital based correlated metals with an energetically isolated conduction band offers a new avenue for the development of visible and ultraviolet TCOs.53 The presence of this isolated conduction band and strong electron correlations open an optically transparent window while maintaining a high electrical conductivity. Correlated metals such as SrVO<sub>3</sub> and SrNbO<sub>3</sub> have been grown experimentally and revealed to have high figures of merit.<sup>53,55</sup> These materials are typically grown using sophisticated film deposition techniques commonly employed at the research scale, such as hybrid molecular beam epitaxy (hMBE)<sup>53,209</sup> and pulsed laser deposition (PLD).<sup>259</sup> While there have been drastic improvements in recent years to make these methods more applicable in industrial scale applications, in order to rapidly and economically integrate these materials into current devices they must be grown using a highly scalable deposition technique that is already an industry standard, such as DC or RF sputtering.

Other perovskite based correlated metals have been grown using RF sputtering, such as SrRuO<sub>3</sub><sup>276</sup> and SrMoO<sub>3</sub>,<sup>56</sup> but few studies have evaluated the electrical and optical properties and their comparison to other deposition methods; therefore, it is unclear how significantly the electrical and optical properties are affected by using this rapid, highly energetic growth technique. Recently, the correlated metal SrVO<sub>3</sub> was sputtered and compared to films grown using other methods.<sup>277</sup> The electrical resistivity was found to be an order of magnitude higher compared to films grown by MBE; however, the optical properties were not significantly changed. Overall, this study showed that since sputtered SrVO<sub>3</sub> still had an high figure of merit, sputtering remains an effective means to grow other correlated metals.

SrNbO<sub>3</sub> films grown by PLD and evaluated as a transparent conductor material in Chapter 4 were found to be favorable due to a minimum resistivity of  $3.81 \times 10^{-5} \Omega$  cm and an interband absorption edge of 4.8 eV leading to an optical absorption coefficient smaller than  $1.0 \times 10^5$  cm<sup>-1</sup> in the visible and UVB range.<sup>55</sup> This low optical absorption in the UV pushes the boundary for UV transparent conductors, making SrNbO<sub>3</sub> the most effective UV transparent conductor to date, prompting further development of scalable thin film deposition. The growth of SrNbO<sub>3</sub> is challenging since in the SrO-Nb<sub>2</sub>O<sub>5</sub> system, the  $Sr_2Nb_2O_7$  phase is energetically favorable due to Nb preferring the 5+ oxidation state.<sup>278</sup> Therefore, highly reducing deposition conditions are required to stabilize the perovskite phase where Nb assumes the 4+ valence state. Bulk Sr<sub>x</sub>NbO<sub>3</sub> ceramics were first grown in 1955 and were identified to assume the cubic perovskite structure with a lattice parameter of 4.024 Å.<sup>252</sup> Later, more in-depth analysis has shown that the exact crystalline structure of Sr<sub>x</sub>NbO<sub>3</sub> is strongly dependent on stoichiometric ratio of Sr to Nb. A slight Sr deficiency in Sr<sub>x</sub>NbO<sub>3</sub> induces a rotation of the oxygen octahedra accompanied with an orthorhombic distortion, specifically an  $a^{-}c^{+}a^{-}$  tilt pattern of the NbO<sub>6</sub> octahedra following Glazer notation.<sup>279</sup> For larger Sr vacancies (0.6<x<0.95), Sr<sub>x</sub>NbO<sub>3</sub> returns to a cubic perovskite structure with a lattice parameter that decreases with the Sr content according to Vergard's Law.<sup>253,254</sup> SrNbO<sub>3</sub> thin films have been deposited by PLD from Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> targets in reducing atmospheres, either with N<sub>2</sub> process gas<sup>257</sup> or low oxygen partial pressure to help stabilize the Nb 4+ state.<sup>258,259</sup> The perovskite phase can be further stabilized by introducing Sr vacancies into the film that leave behind two holes that can be charge compensated by the formation of an oxygen vacancy ( $\emptyset \rightleftharpoons$  $V_{Sr}^{\prime\prime} + V_0^{\bullet\bullet}$ ) or by allowing two occupied Nb sites to assume the energetically preferred 5+ state  $(Sr_{Sr} + 2Nb_{Nb}^{x} \rightleftharpoons V_{Sr}^{\prime\prime} + 2Nb_{Nb}^{\bullet} + Sr(s))$ . Oka *et al.* reported that the Sr/Nb ratio increased with substrate temperature, suggesting that higher temperatures helped stabilize the desired perovskite phase with a reduced formation of Sr vacancies.<sup>259</sup>

# 5.1 Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> Sputtering Target

While sputtering targets are commercially available for many single component materials (Au, Fe, In, etc) and some multicomponent oxide systems (ITO, BaTiO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, etc), the majority of complex materials, especially those with multiple components, are not available and must be custom made. In order to deposit SrNbO<sub>3</sub> films using RF sputtering, a ceramic target of phase pure pyrochlore strontium niobate  $(Sr_2Nb_2O_7)$  was synthesized which had the same cation stoichiometry as the desired film. Alternatively, a SrNbO<sub>3</sub> target could have been synthesized but since  $Sr_2Nb_2O_7$ is the thermodynamically stable phase<sup>278</sup> and only the cation ratio is relevant for sputtering it was not necessary for this study. 4N SrCO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> powders were first heated to 100° C to drive out adsorbed water before combining. Stoichiometric quantities of SrCO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> were then combined and first ball milled in ethanol for 24 hours. The resulting powder was then dried at 85°C and calcined in a covered crucible in air at 1200°C for 24 hours. The calcined powder was milled for 24 hours on a vibratory mill, dried at 85°C, and formed into a green body using a 1.1-inch metal die. The green body was then sealed into a nitrile glove and was subsequently cold isostatic pressed into a 1-inch diameter target at a pressure of 200 MPa. The sputter target was removed and sintered in a covered crucible in argon at 1500°C for 12 hours. The resulting target's density was calculated using Archimedes' principle and found to have a density equal to 96% of the theoretical density (5820 kg·m<sup>-3</sup>).<sup>280</sup> Phase purity was verified using a Malvern Panalytical Empyrean X-ray diffractometer in Bragg-Brentano geometry. The XRD pattern and refinement is shown in Figure 5-1(a) where only the expected diffraction peaks from  $Sr_2Nb_2O_7$  are present. An image of the resulting target from this procedure is shown in Figure 5-1(b).

#### 5.2 Growth of Sr<sub>x</sub>NbO<sub>3</sub> films on LSAT

The Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> target was then RF sputtered using a magnetron source (Kurt J. Lesker, TORUS TM1) in a growth chamber with a base pressure of  $< 3 \times 10^{-8}$  Torr. Sr<sub>x</sub>NbO<sub>3</sub> films were grown on the (001) plane of  $10 \times 10$  mm<sup>2</sup> single crystal (La<sub>0.3</sub>Sr<sub>0.7</sub>)(Al<sub>0.65</sub>Ta<sub>0.35</sub>)O<sub>3</sub> (LSAT) substrates. Chamber pressure during sputter deposition was set to  $2.0 \times 10^{-2}$  Torr of Ar to maximize the deposition rate. A growth temperature of 700°C was used for all films. Under these conditions, the growth rate was found to be approximately 0.6 nm/min. All parameters besides growth time were maintained to achieve a thickness series of films.

# 5.2.1 Structural Characterization

The deposition system at Penn State gives a unique opportunity to record RHEED images of sputtered films by transferring the grown films from the sputter chamber into the oxide MBE chamber. Figure 5-1 shows typical reflection high energy electron diffraction (RHEED) images taken along the (d)  $\langle 100 \rangle$ , (e)  $\langle 110 \rangle$ , and (f)  $\langle 210 \rangle$  azimuths at room temperature after the films were sputtered. The main diffraction spots were streaky and sharply contrasted against the background, suggesting a highly crystalline surface. Along the  $\langle 100 \rangle$  and  $\langle 210 \rangle$  azimuths a 2× reconstruction was detected in addition to the main diffraction spots, indicated by the white arrows. Film surface morphologies were then measured ex-situ using a Bruker Dimension Icon AFM in peak force tapping mode to confirm the observations in RHEED. The AFM scan corresponding to the RHEED images here is shown in Figure 5-1(c). AFM images confirmed that the film surfaces were smooth and free of distinct features with a root mean square (RMS) roughness ranging between 0.3 to 1.0 nm.



Figure 5-1: (a) Wide angle XRD pattern for the Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> target used for deposition and for reference in XRD fitting. The pattern was refined (red line) in Jade software using JCPDF 04-006-1886 and the error for the refinement is shown in blue. (b) Image of the 1" Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> target used for deposition. (c) AFM scan of a representative film, confirming a smooth surface morphology (RMS roughness = 0.3 nm). Corresponding RHEED images for this film are shown along the (d)  $\langle 100 \rangle$ , (e)  $\langle 110 \rangle$ , and (f)  $\langle 210 \rangle$  azimuths. White arrows mark a 2× reconstruction along the  $\langle 100 \rangle$  and  $\langle 210 \rangle$  azimuths. (g) High resolution 20- $\omega$  scans of films grown as a function of thickness with GenX fits overlaid in red. Figure reproduced from reference.<sup>281</sup>

The film thicknesses and lattice parameters were determined using a Malvern Panalytical X'Pert<sup>3</sup> MRD 4-circle diffractometer using Cu-K<sub> $\alpha$ 1</sub> radiation and GenX fitting software.<sup>236</sup> High resolution 20- $\omega$  XRD scans around the 002 diffraction peak of the Sr<sub>x</sub>NbO<sub>3</sub> films discussed in this section are depicted in Figure 5-1(g) along with their corresponding GenX fit. The out of plane lattice parameters and film thicknesses were extracted from these fits. All high-resolution scans

revealed pronounced Kiessig fringes, indicating an abrupt interface and very smooth film surfaces. A wide angle  $2\theta \cdot \omega$  XRD scan of is shown in Figure 5-2(a), demonstrating that only peaks from the desired perovskite phase were present. The out-of-plane film lattice parameters, compiled in Figure 5-2(b), were found to be between 3.998 and 4.023 Å. There was no apparent correlation between film thickness and lattice parameter. With the exception of two ~29 nm thick films, all out-of-plane lattice parameters were smaller than expected for stoichiometric and fully relaxed SrNbO<sub>3</sub> films. A closeup high resolution scan is shown in Figure 5-2(c) with its corresponding rocking curve inset demonstrating the high crystallinity of the film.



Figure 5-2: (a) Wide angle  $2\theta \cdot \omega$  X-ray diffraction scan of a typical Sr<sub>x</sub>NbO<sub>3</sub> film showing only the expected diffraction peaks of the 00l oriented perovskite phase. (b) Out-of-plane lattice parameter of Sr<sub>x</sub>NbO<sub>3</sub> films extracted from high resolution  $2\theta \cdot \omega$  X-ray scans shown in Figure 5-1(g). Error bars are within the size of the squares and samples marked with a red star were examined with RSMs. (c) High resolution  $2\theta \cdot \omega$  X-ray scan of the Sr<sub>x</sub>NbO<sub>3</sub> 002 film peak showing thickness fringes confirming atomically smooth interfaces. Inset is the rocking curve ( $\omega$ -scan) of the Sr<sub>x</sub>NbO<sub>3</sub> 002 film peak with a FWHM=0.046°. (d) X-ray reciprocal space map around the -103 diffraction peak of film and substrate. The dashed and dotted line show the expected peak positions for a fully strained and fully relaxed films with varying film lattice parameter, respectively. (e) HAADF-STEM images of Sr<sub>x</sub>NbO<sub>3</sub> with three distinct regions highlighted: i) ideal perovskite, ii) areas of low order near threading dislocations, iii) nine column areas resulting from a half unit cell displacement of ideal perovskite. The intensity profile along the Sr and Nb columns is plotted to demonstrate the intensity variations on the Sr sites suggesting a high density of Sr vacancies. Figure reproduced from reference.<sup>281</sup>
The large deviations in the out of plane lattice parameter suggest that a partial film relaxation was present in addition to some level of cation stoichiometry. Therefore, to determine the level of cation stoichiometry from XRD data, the degree of strain relaxation in the films must first be assessed. For compressively strained films, the in-plane lattice parameter  $(a_{\parallel})$  is clamped to the substrate resulting in an increased out-of-plane lattice parameter  $(a_{\perp})$ . The Poisson ratio  $(\nu)$  links the strained lattice parameters to the intrinsic film lattice parameter  $(a_f)$  by:<sup>282</sup>

$$a_f = \frac{2\nu \cdot a_{\parallel} + (1 - \nu) \cdot a_{\perp}}{1 + \nu}$$
 Eq. 5.1

For a given lattice mismatch of 4.0% between a stoichiometric film with  $a_f = 4.024$  Å and LSAT substrate with  $a_s = 3.868$  Å, the critical film thickness for a coherently strained film was estimated to 0.7 nm using Freund's formulation:<sup>283,284</sup>

$$h_{c} = \frac{b}{8\pi(1+\nu) * \varepsilon_{0}\sin(\alpha)} \left[ ln\left(\frac{2h_{c}}{r_{0}}\right) - \frac{1}{2}cos(2\alpha) - \frac{(1-2\nu)}{4(1-\nu)} \right]$$
 Eq. 5.2

where *b* is the magnitude of the Burgers vector,  $\alpha$  is the angle between the dislocation and the interface,  $\nu$  is the Poisson ratio of the film,  $\varepsilon_0$  is the misfit strain,  $r_0$  is the cutoff radius for the dislocation core. For perovskite systems, it is assumed that the slip system {101}<10-1> is active;<sup>285</sup> therefore, the Burgers vector is  $\sqrt{2}a_{SrNbO_3}$  and  $\alpha$  is  $\pi/2$ . The cutoff radius and Poisson ratio are assumed to be 4 and 0.31 respectively.<sup>280</sup> Since all film thicknesses in this study exceeded the calculated critical film thickness by more than an order of magnitude, it was expected that all films were relaxed.

To accurately evaluate the intrinsic film lattice parameter, the degree of strain was determined by mapping the reciprocal space around asymmetric -103 diffraction peaks of  $Sr_xNbO_3$  and LSAT to extract  $a_{\parallel}$  and  $a_{\perp}$ , as shown in Figure 5-2(d). Note here that the relaxation line is plotted between the points in reciprocal space where the film is coherently strained and where the film is fully relaxed. The film peak was found to be quite broad in H-space, suggesting that there

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was a short in-plane coherency due to interruptions in the periodic arrangement in the plane. Assuming a Poisson ratio of 0.31,<sup>286</sup> an intrinsic film lattice parameter of 4.000±0.005 Å was extracted for the three samples marked with red stars in Figure 5-2(b). The difference between this value and that of bulk samples<sup>24,35</sup> and other thin films<sup>258,259</sup> may be attributed to Sr vacancies due to preferential resputtering of Sr atoms caused by negative ions impinging on the growing film.<sup>288</sup> Following Vegard's Law and Sr<sub>x</sub>NbO<sub>3</sub> ceramic studies,<sup>253,254</sup> a Sr concentration of x=0.8 was predicted for all films.

To further elucidate the lower-than-expected intrinsic film lattice parameter, high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) was performed to assess the structure and defect types of the sputtered  $Sr_xNbO_3$  films. This characterization was performed by Kleyser Agueda and Professor Nasim Alem. A FEI Helios Nanolab 660 focused ion beam system using Ga+ ions was used to prepare a cross-sectional sample of  $Sr_xNbO_3$  for STEM imaging. Approximately 10 µm of carbon was deposited to prevent Ga implementation to film. The initial lift-out sample was 20  $\mu$ m  $\times$  2.5  $\mu$ m. The sample was then carbon welded onto a copper V post TEM grid. The V notch was deepened to avoid copper redeposition during ion beam milling. The sample was gradually thinned, resulting in a final polishing of 2 keV and 9 pA. A doubleaberration-corrected FEI Titan<sup>3</sup> G2 STEM was used to image the sample at 300 keV. High-angle annual dark field STEM imaging was completed using Fischione detectors at a camera length of 115 mm with convergence angle of 29.98 mrad and a frame time of 20.1 seconds. Images were drift-corrected by combining two orthogonal scanned probe images into a single image using kernel density estimation and Fourier filtering to produce a combined image from all components.<sup>289</sup>

A typical HAADF-STEM image of the film-substrate interface along the (100) zone axis of  $Sr_xNbO_3$  is shown in Figure 5-2(e). An abrupt, high-quality epitaxial interface was observed. For the majority of the film, the cubic, perovskite atomic arrangement was observed, as seen in Figure 5-2(i). However, as expected from the reciprocal space maps, several types of defects were revealed within the film. Specifically, direct evidence of Sr vacancies can be seen from the peak variations in the intensity profile along the Sr columns as compared to the Nb columns which remain constant. Similar intensity profiles have been observed in the Sr columns of PLD grown  $Sr_xNbO_3$  thin films.<sup>290</sup> Misfit dislocations also were observed to occur in regular intervals of 12 nm due to the 4.0% lattice mismatch between  $Sr_xNbO_3$  and LSAT. The regions in close proximity to these misfit dislocations deviated from the regular intensity pattern (see Figure 5-2(ii)) and may be formed by the agglomeration of Sr vacancies in sufficient quantities to form a Sr-deficient phase, such as  $SrNb_2O_6$  that has been observed to exist in Sr-deficient  $Sr_xNbO_3$  films,<sup>290</sup> or even rock salt NbO.<sup>291</sup> The final defect observed was regions of nine atomic columns corresponding to an antiphase boundary with half of a unit cell shift can be resolved, shown in Figure 5-2(iii). These defects are consistent with those previously observed for SrNbO<sub>3</sub> films on SrTiO<sub>3</sub> deposited with PLD.<sup>290</sup> While many types of defects were observed in HAADF-STEM, it should be noted that  $Sr_xNbO_3$ appears to be overall very robust to defects as it primarily retains its perovskite structure.

## 5.2.2 Electrical Characterization

Since  $Sr_xNbO_3$  is primarily studied here as a transparent conductor, it is important to characterize not only its sheet resistance, but also its resistivity, carrier concentration, and mobility in order to ensure high electrical performance. Room temperature resistivity and Hall measurements were taken in the van der Pauw geometry using a Quantum Design PPMS with a source current of 500  $\mu$ A and magnetic field strengths up to 3.0 T.



Figure 5-3: Thickness dependence of (a) resistivity  $\rho$ , (b) carrier concentration n, (c) electron mobility  $\mu$ , and (d) sheet resistance  $R_s$  of sputtered  $Sr_xNbO_3$  films. For comparison, data for stoichiometric correlated metals  $SrNbO_3^{55}$  and  $SrVO_3^{53}$  doped wide band gap and ultra-wide band gap semiconductors ITO,  $^{45,292,293}$  La doped  $SrSnO_3$ ,  $^{294} \alpha$ -Ga<sub>2</sub>O<sub>3</sub>,  $^{295}$  and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub><sup>112,271</sup> are shown as well. The dashed lines in (d) serve as guides for the eye. Figure reproduced from reference.<sup>281</sup>

Despite a sizeable cation non-stoichiometry as observed from XRD and HAADF-STEM, all films were found to be highly conducting. Room temperature electrical resistivity, carrier concentration, and carrier mobility are plotted as a function of thickness and compared to other TCOs including sputtered, polycrystalline ITO,<sup>53,296</sup> SrVO<sub>3</sub>,<sup>53</sup> La-doped SrSnO<sub>3</sub>,<sup>294</sup> and Sn-doped Ga<sub>2</sub>O<sub>3</sub><sup>112,271,295</sup> in Figure 5-3. The room temperature resistivity of the sputtered Sr<sub>x</sub>NbO<sub>3</sub> films was found to be  $(3.2\pm1.5)\times10^{-4} \ \Omega \cdot \text{cm}$ , in good agreement with values of  $3.3\times10^{-4} \ \Omega \cdot \text{cm}$  measured for Sr-deficient Sr<sub>x</sub>NbO<sub>3</sub> bulk samples.<sup>255</sup> Remarkably, even though this resistivity is about one order of magnitude above that of stoichiometric SrNbO<sub>3</sub> films deposited by PLD<sup>259</sup> and SrVO<sub>3</sub> films grown by *h*MBE,<sup>53</sup> it is comparable to resistivity value of doped Ga<sub>2</sub>O<sub>3</sub>.<sup>295</sup> Hall measurements were performed to determine whether the pronounced non-stoichiometry of the sputtered films caused a resistivity increase through a decrease in carrier concentration, since Sr vacancies act as acceptors, or via enhanced carrier scattering thereby reducing the carrier mobility. Typical carrier concentration of sputtered Sr<sub>x</sub>NbO<sub>3</sub> films was found to be  $(1.3\pm0.3)\times10^{22}$  cm<sup>-3</sup>, which is comparable to stoichiometric SrVO<sub>3</sub> and SrNbO<sub>3</sub>, at least one order of magnitude higher than typical wide band gap TCO, and nearly three orders of magnitude higher than the highest carrier concentration achieved for the ultra-wide band gap semiconductor Ga<sub>2</sub>O<sub>3</sub><sup>295</sup> (see Figure 5-3(b)). The carrier mobility in Sr<sub>x</sub>NbO<sub>3</sub> was found to be significantly lower than that of cation stoichiometric correlated metals; see Figure 5-3(c). This decrease in mobility was attributed to a decreased scattering time caused by the sizeable number of point, planar, and other structural defects as seen in Figure 5-2(e) resulting from the large lattice mismatch as well as the cation nonstoichiometry. Figure 5-3(d) compares the linear trend of thickness dependent sheet resistance for sputtered  $Sr_xNbO_3$  films with SrNbO<sub>3</sub> films grown by PLD, SrVO<sub>3</sub> grown by hMBE, La doped SrSnO<sub>3</sub>, sputtered ITO, and MOCVD grown Ga2O3 films. Even the thinnest (10-nm-thick) SrxNbO3 films still had more than half an order of magnitude lower sheet resistance than the best reported ultrawide band gap semiconductors  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub><sup>295</sup> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub><sup>112,271</sup> with film thicknesses of 500 nm or more. This superior transport behavior renders the sputtered  $Sr_xNbO_3$  films highly competitive for the application as UV transparent electrodes despite the increase in the film's resistivity due to a sizeable Sr-deficiency.

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Figure 5-4: (a) Temperature dependent resistivity for sputtered  $Sr_xNbO_3$  thin films compared to PLD grown SrNbO<sub>3</sub>, reproduced from reference.<sup>281</sup>  $d\rho/dT^{3/2}$  as a function of temperature demonstrating the resistivity scaling behavior for (b) sputtered  $Sr_xNbO_3$  thin films and (c) PLD grown SrNbO<sub>3</sub>. Inset demonstrates a similar  $T^{3/2}$  scaling at low temperatures for PLD grown films.

Temperature dependent resistivity measurements were taken in a van der Pauw arrangement in a Quantum Design PPMS down to 2K, shown in Figure 5-4(a) compared to PLD grown films.<sup>55</sup> Sputtered films were found to have a higher resistivity at all temperatures, likely arising due to the significant cation nonstoichiometry.  $Sr_xNbO_3$  displayed a trend similar to that of highly defective  $SrVO_3$  films grown by *h*MBE, where the low temperature resistivity was dominated by defect and impurity scattering.<sup>177</sup> The temperature dependent scaling behavior was then determined by plotting  $dp/dT^n$  as a function of temperature. Films grown by both methods were found to display  $T^{3/2}$  scaling at temperatures above 120 K as shown in Figure 5-4(b) and (c). This scaling factor suggests that an additional scattering phenomenon was present at room temperature in addition to phonon scattering, directly indicating that the crystalline quality can be further improved to enhance the electrical performance. In addition, PLD films at low temperature

also displayed a  $T^{3/2}$  scaling which has been shown to occur in ferromagnetic materials,<sup>172</sup> prompting future investigations into the magnetization of these films.

## 5.2.3 Optical Characterization

In order to characterize the second vital property of transparent conductors, the optical constants were measured using spectroscopic ellipsometry at room temperature by Dr. Alexej Pogrebnyakov. The ellipsometric spectra were collected at room temperature at three angles of incidence (50°, 60°, and 70°) using a rotating-compensator spectroscopic ellipsometer (J. A. Woollam, M2000) over the spectral range from 1.24 to 6.46 eV (0.194 – 1.000  $\mu$ m). Spectra in *n* and microstructural parameters were extracted using a least-squares regression analysis and an unweighted error function to fit the experimental ellipsometric spectra based on an optical model consisting of a semi-infinite LSAT substrate, Sr<sub>x</sub>NbO<sub>3</sub> film, and surface roughness. The model for LSAT was obtained by measuring the ellipsometric spectra of a bare LSAT substrate from the same batch used for film growth. The surface roughness was represented by a Bruggeman effective medium approximation of 0.5 void + 0.5 film material fractions. Oscillator parameters as well as thicknesses of the Sr<sub>x</sub>NbO<sub>3</sub> film and the surface roughness layer were used as fitting parameters and are shown in Table 5-1.

Nominal	Optical		Surface
Thickness (nm)	Thickness (nm)	Eoffset	Roughness (nm)
$57.5\pm0.5$	$58.23\pm0.135$	$2.103 \pm 0.0363$	0
Oscillator	ρ (μΩ. cm)	τ (fs)	
Drude	$211.37\pm0.149$	$1.786 \pm 0.0115$	

Table 5-1: Oscillators used in fitting  $Sr_xNbO_3$  thin films on LSAT with optically determined thickness and surface roughness in the spectral range from 1.24 eV to 6.46 eV.

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Oscillator	$E_{\theta}$ (eV)	Α	Γ (eV)	$E_g$ (eV)
UV Pole	$7.394 \pm 0.0782$	$23.4567 \pm 2.0735$		
Lorentz	$6.143\pm0.0171$	$1.7312 \pm 0.1302$	$1.4807 \pm 0.0565$	
Lorentz	$2.385\pm0.0221$	$0.1071 \pm 0.0046$	$1.1306 \pm 0.0841$	
Lorentz	$4.002 \pm 0.0182$	$0.2141 \pm 0.0194$	$0.3939 \pm 0.0084$	
Lorentz	$4.527 \pm 0.0683$	$0.2417 \pm 0.0384$	$0.3562 \pm 0.0047$	
Cody-Lorentz	$5.272 \pm 0.0105$	$17.836 \pm 0.676$	$1.745\pm0.050$	$4.167\pm0.011$

The complex dielectric function extracted from these measurements is shown in Figure 5-5. Free carrier reflection at energies below the visible range gives rise to  $\varepsilon_2 \ge 2$ , indicating low optical transmission in this region. The imaginary part of the dielectric function  $\varepsilon_2$  remained low throughout the entire visible spectrum and into the UV range, indicating a high optical transmission across the entire visible spectrum and into the UV spectrum until approximately 4.5 eV. At higher photon energies a sharp increase in  $\varepsilon_2$  occurred due to interband transitions between the O 2p band and the Nb 4d band.<sup>55</sup> The slight variation in the optical properties overall all samples was likely due to the different degrees of non-stoichiometry and strain relaxation in the films.



Figure 5-5: The (a) real and (b) imaginary parts of the complex dielectric function for  $Sr_xNbO_3$  with the visible spectra and 280 nm highlighted. Figure reproduced from reference.<sup>281</sup>

Although the amount of Sr deficiencies was sizeable according to the XRD analysis, the optical properties were found to be largely unaffected. The real and imaginary parts of the complex refractive index, *n* and *k*, are shown in Figure 5-6(a) and (b) respectively. The overall trends follow those seen in the complex dielectric function. Most importantly, k < 0.5 throughout the visible spectra into the UV, suggesting a high transmission over this large region. Figure 5-6(c) shows the absorption coefficient calculated from *k*, confirming the very low optical absorption present in Sr<sub>x</sub>NbO<sub>3</sub> in the spectral range from 2 eV to 4.5 eV. The optical transmission ( $T = e^{-\alpha t}$ ) for all samples grown in the series with different thicknesses is shown in Figure 5-6(d). Over 90% optical transmission was achieved for most of the visible spectra for films with thicknesses less than 25 nm. The maximum optical transmission at a wavelength of 280 nm of 86% was achieved for a 10-nm-thick Sr<sub>x</sub>NbO<sub>3</sub> film, which in combination with the favorable sheet resistance makes sputtered Sr<sub>x</sub>NbO<sub>3</sub> a promising candidate for a UV transparent conductor despite the lack of cation stoichiometry.



Figure 5-6: (a) Refractive index n, (b) extinction coefficient k, (c) absorption coefficient  $\alpha$ , and (d) optical transmission Sr<sub>x</sub>NbO<sub>3</sub> films of various thicknesses from the near IR to the deep UV. The photon energy for light with a wavelength of 280 nm is highlighted by a vertical purple line. (e) UV transmission at a wavelength of 280 nm as a function of sheet resistance of sputtered Sr<sub>x</sub>NbO<sub>3</sub> films compared to the best values found for  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub>,<sup>295</sup>  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>,<sup>112,271</sup> ITO,<sup>39,40</sup> La doped SrSnO<sub>3</sub>,<sup>294</sup> SrVO<sub>3</sub>,<sup>53</sup> and PLD grown SrNbO<sub>3</sub>.<sup>55</sup> The constant figure of merit  $\sigma/\alpha$  lines in units of  $\Omega^{-1}$  are shown as dotted lines. Samples used in the XPS analysis shown in Figure 5-7 are marked with a star. Figure reproduced from reference.<sup>281</sup>

In this study, the performance of  $Sr_xNbO_3$  as a UV transparent conductor was evaluated using the simple 'intrinsic' figure of merit (FOM): the ratio of the electrical conductivity  $\sigma = \rho^{-1}$ and absorption coefficient  $\alpha$  which has been widely used to quantify the performance of transparent conductor materials as it provides a thickness independent comparison of the material dependent properties.<sup>45-47</sup> A wavelength of 280 nm was chosen to compare the UV effectiveness as it is the upper boundary of the UVC range, indicating an equal or greater transmission at higher wavelengths in the UV spectrum in addition to remaining effective in disinfection applications.<sup>300</sup> Figure 5-6(e) shows the optical transmission at 280 nm as a function of sheet resistance for all Sr<sub>x</sub>NbO<sub>3</sub> films grown. ITO, Ga<sub>2</sub>O<sub>3</sub>, La doped SrSnO<sub>3</sub>, SrVO<sub>3</sub>, and PLD grown SrNbO<sub>3</sub> are shown for comparison with constant FOM lines indicated as well. This method of TCO comparison is ideal for selecting the right material for a specific application of interest requiring a particular sheet resistance or optical transmission. The sputtered Sr<sub>x</sub>NbO<sub>3</sub> films had varying sheet resistances between 20 to 200  $\Omega$ /sq. and transmission at 280 nm between 53% and 86%. Despite the high degree of Sr deficiencies, the  $Sr_xNbO_3$  films still have competitive FOMs ranging from 0.01 to 0.06  $\Omega^{-1}$ , although these values were somewhat smaller than the FOM values of (0.28±0.10)  $\Omega^{-1}$  reported for stoichiometric SrNbO<sub>3</sub> films grown by PLD in Chapter 4. In this region, both ITO and SrVO<sub>3</sub> exhibit limited transmission, not exceeding 80% due to a sizeable absorption coefficient present at UV wavelengths. From this plot, the limitations of the conventional design for transparent conductors utilizing degenerately doped ultra-wide band gap semiconductors are also apparent. Though  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> is optically transparent, it has very large sheet resistances arising from difficulties activating dopants. For  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, both the sheet resistance and transmission are insufficient, resulting in a figure of merit more than two orders of magnitude below that of Sr<sub>x</sub>NbO<sub>3</sub> films. While the sputtering process induced a high level of Sr deficiencies, electrical conductivity and optical transmission remained very robust. Although both properties degraded somewhat compared to stoichiometric SrNbO<sub>3</sub>, sputtered Sr<sub>x</sub>NbO<sub>3</sub> films were found to be highly competitive when compared to ultra-wide band gap semiconductor Ga<sub>2</sub>O<sub>3</sub>.

## 5.2.4 Stoichiometry and cation valance states

The presence of a sizeable Sr deficiency, as determined from XRD and STEM images and the distribution of the figure of merit for the sample series suggests a systematic trend between cation non-stoichiometry and performance. In order to establish such a relation, X-ray photoelectron spectroscopy (XPS) experiments were performed on the film with the lowest FOM and the two films with the highest FOM. These samples have been marked in Figure 5-6(e).

XPS measurements and subsequent fitting were performed by Jeff Shallenberger of the Penn State Material Characterization Lab using a Physical Electronics VersaProbe II instrument equipped with a monochromatic Al K<sub>a</sub> X-ray source (hv = 1486.7 eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (<5 eV) and argon ions. The binding energy axis was calibrated using sputter cleaned Cu (Cu  $2p_{3/2} = 932.62$  eV, Cu  $3p_{3/2} = 75.1$  eV) and Au foils (Au  $4f_{7/2} = 83.96$  eV).<sup>301</sup> Peaks were charge referenced to Sr<sup>2+</sup> band in the Sr 3d spectra at 133.2 eV. Measurements were taken at a takeoff angle of 85° with respect to the sample surface plane. This resulted in a typical sampling depth of 4-7 nm (95% of the signal originated from this depth or shallower). As the sputter target had the desired Sr/Nb ratio of the films, it was used as a standard reference material. Therefore, relative sensitivity factors acquired from XPS measurements of an air-cleaved Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> target prior to any deposition were used to determine the Sr and Nb composition of the sputter deposited films. The survey scans for each sample are shown in Figure 5-7(a). The spectra of the most intense peaks, namely the O 1s, Sr 3d, and Nb 3d core level peaks were examined and are shown in Figure 5-7(bf). The total integrated intensity of the Sr 3d and Nb 3d core level peaks were quantified after background subtraction using relative sensitivity factors derived from high resolution XPS scans of the Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> sputter target to verify the Sr/Nb ratio. The details of the elemental composition in the measured films are given in Table 5-2.



Figure 5-7: (a) Survey scans of  $Sr_xNbO_3$  for three different film thicknesses. High resolution scans of the Nb 3*d* peak for (b) 23.2 nm, (c) 54.4 nm, and (d) 55.7 nm films containing doublets for each Nb valence state. Symmetric doublets split by 2.72 eV with identical FWHM and an area ratio of 3/2 were fit to each peak. (e) High resolution scans of the Sr 3*d* peak for each sample including the SrCO<sub>3</sub> doublet from surface carbonates. (f) High resolution scans of the O 1*s* peak for each sample with a slight edge due to an adsorbate layer containing hydroxides and carbon at the film surface. Figure reproduced from reference.<sup>281</sup>

High resolution scans around the Nb 3*d* peak was found to be relatively complex as shown in Figure 5-7(b-d). As Nb can assume different valence states resulting in chemical shifts, the Nb 3*d* spectra can contain contributions from Nb<sup>5+</sup>, Nb<sup>4+</sup>, Nb<sup>3+</sup>, and Nb<sup>2+</sup>. Previous investigations on Sr<sub>x</sub>NbO<sub>3</sub> ceramics assumed that the Nb 3*d* spectra in Sr<sub>x</sub>NbO<sub>3</sub> were only composed of Nb<sup>5+</sup> and Nb<sup>4+</sup>;<sup>302</sup> however, the edge at ~204 eV cannot be fit by these two valence states. To achieve an acceptable fit of the entire high resolution Nb 3*d* XPS spectra, the contribution from the Nb<sup>3+</sup> peak was added as suggested by Demirer *et al.*,<sup>303</sup> as well as a contribution from Nb<sup>2+</sup>. The presence of Nb<sup>2+</sup> is unexpected since extremely reducing conditions would be required to reach this valence state. One possible explanation relates to the formation of NbO in a rock salt phase due to high degree of Sr-deficiency.<sup>291</sup> While no NbO phases were directly resolved in STEM imaging, it is possible that some NbO was formed near misfit dislocations instead of SrNb<sub>2</sub>O<sub>6</sub>. Nb<sup>2+</sup> may also arise from unexpected bonding relations with the absorbate layer at the surface. A similar Nb<sup>2+</sup> peak was observed in PLD grown films and was simply attributed to the presence of oxygen vacancies.<sup>304</sup> The ratio of O/Nb  $\approx$  3 for each film calculated from Table 5-2 suggests that Sr vacancies are compensated by changes of the Nb valence state.

Table 5-2: Stoichiometry of the sputtering target and the  $Sr_xNbO_3$  films with the lowest and highest FOM. All units are in atom percent.

Sample	σ/α	O Content	Sr Content	Nb Content	Sr/Nb Ratio
Sr <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub> Target	N/A	$61.7\pm0.5$	$18.9\pm0.5$	$18.9\pm0.5$	$1.00\pm0.03$
Sr <sub>x</sub> NbO <sub>3</sub> : 23.2 nm	0.013	$61.8\pm0.5$	$16.8\pm0.5$	$21.5\pm0.5$	$0.78\pm0.03$
Sr <sub>x</sub> NbO <sub>3</sub> : 54.4 nm	0.060	$61.8\pm0.5$	$14.8\pm0.5$	$23.4\pm0.5$	$0.63\pm0.03$
Sr <sub>x</sub> NbO <sub>3</sub> : 55.7 nm	0.063	$62.2\pm0.5$	$17.4\pm0.5$	$20.7\pm0.5$	$0.84\pm0.03$

High-resolution scans of the Sr 3*d* peaks shown in Figure 5-7(f) for each sample primarily consisted of the Sr 3*d* doublet expected for SrO with a small doublet arising from SrCO<sub>3</sub> formed by the an absorbate layer on the surface. Finally, the scans of the O 1*s* peak for each sample is shown in Figure 5-7(e). This peak was observed at a binding energy of 530 eV for all samples with a slight asymmetry at the higher binding energy side attributed to the presence of carbon-oxygen bonds and hydroxyl groups that were expected to originate from the adsorbate layer present due to exposure of the films to atmosphere before XPS.

The films with the highest and lowest FOM had Sr/Nb ratios of  $0.84 \pm 0.03$  and  $0.78 \pm 0.03$  respectively which is consistent with the expected stoichiometry of 0.8 interpolated from the unstrained lattice parameter extracted from XRD. However, the film with the second highest FOM had a significantly smaller Sr/Nb ratio of  $0.63 \pm 0.03$ . This significant difference suggests that a higher Sr vacancy concentration cannot directly be correlated with improved optical and electrical performance.

## 5.2.5 Theoretical calculations

Following the theoretical calculations of stoichiometric SrNbO<sub>3</sub> deposited by PLD in Chapter 4, DFT was further performed on Sr deficient SrNbO<sub>3</sub> by Dr. Arpita Paul and Prof. Turan Birol of the University of Minnesota. This work was performed based on density functional theory within full-potential projected augmented wave (FP-LAPW) with the localized orbitals method as implemented in the Wien2k package.<sup>260</sup> DFT calculations were implemented using a 2×2×2 supercell of SrNbO<sub>3</sub> with 1, 2, and 3 Sr atoms removed, reflecting a Sr content of x=0.875, 0.75, and 0.625, to clarify how Sr vacancies in Sr<sub>x</sub>NbO<sub>3</sub> affect the optical properties. Muffin tin radii of Nb, Sr, and O were chosen to be 1.98, 2.50, and 1.80 Bohr respectively. In the interstitial region, plane wave expansion of the wavefunction was truncated at  $R_{MT}^{min}K_{max} = 7$  to ensure convergence of energy eigenvalues, where  $R_{MT}^{min}$  is the smallest atomic sphere radius and  $K_{max}$  is the cutoff on the wave vector of a plane wave. Local density approximation was used to treat the exchangecorrelation functional. The complex dielectric function was then computed within random phase approximation using 30,000 k-points.<sup>55,56</sup>



Figure 5-8: Band diagrams and density of states (DOS) for  $Sr_xNbO_3$  where (a) x = 1, (b) x = 0.875, (c) x = 0.75, and (d) x = 0.625. The level of Sr deficiency was modeled in a 2×2×2 supercell removing 1 (x=.0875), 2 (x=.075), and 3 (x=0.625) Sr atoms. Figure reproduced from reference.<sup>281</sup>

The band diagrams and the corresponding density of states for x = 1, x = 0.875, x = 0.75, and x = 0.625 are shown in Figure 5-8(a-d) respectively. Note that the band structure in Figure 5-8(a) is more complex than the one shown in Figure 4-1(a) since it was calculated on a supercell to capture randomly placed Sr vacancies in subsequent calculations. As Sr vacancies increased, the energy separation between the valance and the conduction band decreased. It can also be noted that the overall widths of the bands making up the Sr *d*, Nb  $e_g$ , and Nb  $t_{2g}$  decreased as Sr vacancies increased. Note that in the case where two Sr atoms were removed from the supercell (x = 0.75), the cell no longer had cubic symmetry and was reduced to either Im-3m or P4/mmm depending on the position of the vacancies (Im-3m is shown here).



Figure 5-9: (a) The refractive index n and (b) the extinction coefficient k for  $Sr_xNbO_3$  samples of various thicknesses. (c) The averaged refractive index n and (d) extinction coefficient k for the experimental values compared to DFT calculations for various Sr concentrations x in  $Sr_xNbO_3$ . The shift of the Nb  $t_{2g}$  to Nb  $e_g$  absorption peak from 2.6 eV to higher energies as x increases is highlighted. Figure reproduced from reference.<sup>281</sup>

To better quantify the effects of introducing Sr vacancies, the optical constants were calculated from the corresponding band diagrams. Figure 5-9(c) and (d) demonstrate the trends of n and k calculated by DFT with increasing level of Sr deficiency compared to the averaged experimental n and k. Three distinct trends were observed in k with increasing Sr deficiency: (1) the Drude tail shifted towards lower energies into the IR, (2) the interband absorption edge shifted to lower energies, and (3) the interband transition at 2.6 eV disappeared. Each trend is detailed as follows.

1. The shift in the Drude tail was due to the decreased DC conductivity as the Sr deficiency decreased the free carrier density, i.e., the occupation of the  $t_{2g}$  state (see Figure 5-8). The Drude tail of the measured *k* was well-aligned with the calculated curve for x=0.75 which closely matched the experimentally measured x of 0.63 to 0.84.

- 2. The absorption peak composed of O 2p to Sr 4d and O 2p to Nb  $e_g$  interband transitions calculated at about 6 eV for stoichiometric films showed an even larger red shift by over 1 eV. The large amount of Sr vacancies caused an electronic imbalance which resulted in an up-shift of the O 2p valence bands to higher energy (see Figure 5-8). The reduction of the O 2p Nb 4d (Sr 4d) gap qualitatively explained the red shifting of the interband absorption peak. Considering the effects of lattice relaxations, electronic correlations, and disorder into the DFT calculations quantitively alter the p d gap with the red shift of the absorption peak. It should be noted that since band gaps are underestimated in DFT, it is reasonable that the experimentally measured absorption edge is at higher energies.<sup>306</sup>
- 3. Finally, the Nb  $t_{2g}$  to Nb  $e_g$  interband transition theoretically predicted at ~2.6 eV for stoichiometric films by DFT was found to decrease with increasing Sr deficiency, which indeed was absent in the experiments. It is remarkable that the localized trap states of Sr vacancies suppressed the interband transition at 2.6 eV because typically trap states typically give rise to a larger absorption coefficient at lower energies, resulting in a higher *k* and lower optical transmission.

These calculations support the presence of a sizeable concentration of Sr point defects in the films. The small interband transition peak at ~2.6 eV for stoichiometric films (x=1) was not found experimentally; however, a transition around ~4 eV can clearly be resolved for three Sr<sub>x</sub>NbO<sub>3</sub> films as seen in the absorption coefficient in Figure 5-6(c). It is likely that the interband transition at ~2.6 eV for x = 1 continues to move to higher energies as the Sr vacancy concentration increases but is hidden behind the large O 2p to Sr 4d and O 2p to Nb  $e_g$  interband transition peak that was red-shifted and widened due to a higher degree of Sr deficiency. The position of this interband transition could potentially be used as a metric for the cation stoichiometry in Sr<sub>x</sub>NbO<sub>3</sub>. This absorption peak likely arises due to a transition below the Fermi energy in the Nb  $t_{2g}$  band to the bottom of the Nb  $e_g$  band between the  $\Gamma$  and X points. The combination of these effects provides

another avenue to further optimize the optical transparency of  $Sr_xNbO_3$  without sacrificing electrical conductivity simply by adjusting the level of Sr vacancies in the film.

# 5.3 Growth of epitaxially strained Sr<sub>x</sub>NbO<sub>3</sub> on KTaO<sub>3</sub>

Following the growth of  $Sr_xNbO_3$  on LSAT using RF sputtering, growth on other substrates was investigated to verify its integration with other materials. First, to form a better comparison with the coherently strained films investigated in Chapter 4,  $Sr_xNbO_3$  was deposited on KTaO<sub>3</sub>. Deposition conditions were identical to those on LSAT; therefore, the stoichiometry was expected to be the same. Assuming an intrinsic lattice parameter of  $4.000\pm0.005$  Å arising from 20% Sr vacancies as characterized in Chapter 5.2.1 for  $Sr_xNbO_3$  on LSAT, epitaxial deposition on KTaO<sub>3</sub> (a=3.989 Å) was expected to result in a 0.27% compressive strain.



Figure 5-10: RHEED images of  $Sr_xNbO_3$  on KTaO\_3 along the (a) (100), (b) (110), and (c) (210) azimuths. (d) AFM micrograph of  $Sr_xNbO_3$  on KTaO\_3 with an RMS roughness 0.47 nm. (e) High resolution  $2\theta - \omega$  X-ray scan of the  $Sr_xNbO_3$  002 film peak with thickness fringes confirming the atomically smooth interfaces. (f) X-ray reciprocal space map around the -103 diffraction peak, showing the coherently strained film peak.

Post-growth RHEED images at room temperature are shown in Figure 5-10(a)-(c). Overall, the RHEED patterns for Sr<sub>x</sub>NbO<sub>3</sub> on KTaO<sub>3</sub> were much sharper and more well defined than films grown on LSAT, indicating an increased crystallinity and lateral coherency of the film surface. This increased lateral coherency was attributed to an absence of threading dislocation due to the minimal lattice mismatch between KTaO<sub>3</sub> and Sr<sub>x</sub>NbO<sub>3</sub>. Similar to films grown on LSAT, a 2× reconstruction was observed along the (100); however, the reconstruction on the (210) azimuth was not observed here. The surface morphology was further characterized using AFM, as shown in Figure 5-10(d). The RMS roughness was found to be 0.47 nm, similar to films grown on LSAT. A high resolution  $2\theta$ - $\omega$  XRD scan around the 002 diffraction peak of the KTaO<sub>3</sub> substrate is depicted in Figure 5-10(e). Here, the Sr<sub>x</sub>NbO<sub>3</sub> film peak was observed to form the shoulder on the side of the substrate peak. Even in the presence of strong Kiessig fringes which indicated atomically smooth interfaces, no reasonable fit could be made using GenX. Instead, the thickness of the film was estimated to be 22 nm using the growth rate of films on LSAT as well as the distance between adjacent Kiessig fringes. The coherent epitaxial arrangement was further verified by measuring a RSM around the asymmetric KTaO<sub>3</sub> -103 diffraction peak which is shown in Figure 5-10(f).

The performance as a transparent conductor was then verified by characterizing the electrical resistivity and optical constants. The resistivity was measured to be  $2.36 \times 10^{-4} \Omega$ cm corresponding to a sheet resistance of 107.1  $\Omega$ /sq. An additional, thicker film (54 nm) was found to have a resistivity of  $1.98 \times 10^{-4} \Omega$ cm and an R<sub>s</sub> of 36.5  $\Omega$ /sq. Example fitting parameters for the measured ellipsometric spectra of these films are shown in Table 5-3. Note that the optical fitting resulted in an estimated film thickness of 16.5 nm; however, a film thickness of 22 nm was used for all comparisons.

Nominal	Optical		Surface	
Thickness (nm)	Thickness (nm)	<b>E</b> offset	Roughness (nm)	
$22.0\pm0.5$	$16.47\pm0.104$	$2.285\pm0.0312$	$0.53\pm0.159$	
Oscillator	ρ (μΩcm)	τ (fs)		
Drude	$258.70\pm0.05$	$1.379\pm0.019$		
Oscillator	$E_{\theta}$ (eV)	Α	Γ (eV)	$E_g$ (eV)
UV Pole	$6.928\pm0.068$	$6.9090 \pm 1.0041$		
Lorentz	$2.2800 \pm 0.0052$	$0.72624 \pm 0.02250$	$0.5618 \pm 0.0243$	
Lorentz	$4.379\pm0.0590$	$0.50426 \pm 0.02777$	$1.4076 \pm 0.10878$	
Cody-Lorentz	$4.961\pm0.0194$	$34.714 \pm 0.5904$	$2.131\pm0.0188$	$4.322\pm0.007$

Table 5-3: Oscillators for fitting  $Sr_xNbO_3$  on KTaO<sub>3</sub> substrates with optically determined thickness and surface roughness in the spectral range from 1.24 eV to 6.46 eV.

The optical constants, n and k, for films with comparable sheet resistances grown on LSAT and KTaO<sub>3</sub> are compared in Figure 5-11(a) and (b) respectively. Films grown on both substrates had nominally the same n; however, k for the film grown on KTaO<sub>3</sub> was found to extend further into the UV, suggesting an improved optical transmission. This improvement is further observed in the optical absorption shown in Figure 5-11(c) as well as the optical transmission in Figure 5-11(d).



Figure 5-11: The optical constants (a) n and (b) k, (c) the absorption coefficient  $\alpha$ , and (d) the optical transmission for Sr<sub>x</sub>NbO<sub>3</sub> films with comparable  $R_s$  grown on LSAT and KTaO<sub>3</sub>. (e) UV transmission at a wavelength of 280 nm as a function of sheet resistance of sputtered Sr<sub>x</sub>NbO<sub>3</sub> films compared to other transparent conductors. The dotted lines are constant figure of merit  $\sigma/\alpha$  lines in units of  $\Omega^{-1}$ .

The films grown on KTaO<sub>3</sub> were then added to the FOM comparison plot shown in Figure 5-6(e), updated here in Figure 5-11(e). Films grown on KTaO<sub>3</sub> were found to have considerably higher optical transmission at 280 nm compared to  $Sr_xNbO_3$  grown on LSAT, SrVO<sub>3</sub>, and ITO films with comparable sheet resistances. This large improvement was attributed to the increased crystallinity enabled by the favorable epitaxial arrangement on KTaO<sub>3</sub>, minimizing defects other than those from the expected nonstoichiometry. This improvement placed the films grown by RF sputtering in line with those grown by PLD, suggesting that either films grown by PLD were Sr deficient or Sr deficiencies alone do not significantly reduce the performance of SrNbO<sub>3</sub> as a transparent conductor.

#### 5.4 Sr<sub>x</sub>NbO<sub>3</sub> as a bottom electrode for SrTiO<sub>3</sub>/Si based structures

In addition to applications as a transparent conductor, Sr<sub>x</sub>NbO<sub>3</sub> offers many opportunities as a highly conductive bottom electrode for a host of electronic devices such as capacitors, fieldeffect transistors, and piezoelectric devices. While conducting, single crystal substrates such as Nb doped  $SrTiO_3$  exist, they are not scalable to large size wafers. In industrial applications, Pt (111) is widely used as a bottom electrode material due to its low resistivity and straightforward integration with silicon wafers using either a TiO<sub>2</sub> buffer layer or a thermally grown native oxide layer.<sup>307–309</sup> Unfortunately, the orientation and lattice parameter of Pt (111) is not suitable for epitaxial growth of most perovskite materials. Recently, it was shown that SrTiO<sub>3</sub> could be epitaxially integrated on large scale silicon wafers at high growth rates using hMBE.<sup>222,310</sup> This development offers a platform for integrating conducting perovskite materials into silicon based devices. While the lattice mismatch between  $SrTiO_3/Si$  substrates (a=3.93 Å) and  $Sr_xNbO_3$  (a=4.00 Å for x=0.8) results in a compressive strain of 1.7%, films grown on LSAT (3.4% tensile strain) remained highly conductive. The tunability of  $Sr_xNbO_3$ 's lattice parameter by changing the Sr vacancy concentration is an added benefit for engineering epitaxially matched substrates. This effect could further be developed by using a solid solution of SrTiO<sub>3</sub> and CaTiO<sub>3</sub> or BaTiO<sub>3</sub> as a buffer layer to the silicon wafer.



Figure 5-12: RHEED images of a SrTiO<sub>3</sub>/Si substrate and a Sr<sub>x</sub>NbO<sub>3</sub> film along the (a)  $\langle 100 \rangle$ , (b)  $\langle 110 \rangle$ , and (c)  $\langle 210 \rangle$  azimuths. (d) Wide angle 20- $\omega$  X-ray scan of the Sr<sub>x</sub>NbO<sub>3</sub> and SrTiO<sub>3</sub> film peaks in comparison to the Si substrate 004 peak. Inset is a high-resolution scan demonstrating the presence of thickness fringes confirming the atomically smooth interface between SrTiO<sub>3</sub> and Sr<sub>x</sub>NbO<sub>3</sub>. (e) AFM micrograph of the Sr<sub>x</sub>NbO<sub>3</sub> film with an RMS roughness 1.3 nm.

In this study, a 40-nm-thick Sr<sub>x</sub>NbO<sub>3</sub> film was deposited on a 50-nm-thick SrTiO<sub>3</sub>/Si substrate using the same experimental conditions outlined in Section 5.2; therefore, an intrinsic lattice parameter of 4.00 Å was expected. RHEED images of the substrate are shown in comparison to the as grown film along the (100), (110), and (210) azimuths in Figure 5-12(a)-(c). The Sr<sub>x</sub>NbO<sub>3</sub> film was observed to have a spotty RHEED pattern with some small polycrystalline rings indicating domains were present in the film. The film was then structurally characterized using XRD. A wide angle 20- $\omega$  X-ray scan of the Sr<sub>x</sub>NbO<sub>3</sub> and SrTiO<sub>3</sub> film peaks in comparison to the Si substrate 004 peak is shown in Figure 5-12(d) where only the expected diffraction peaks were present. A high-resolution scan around the 002 peaks of Sr<sub>x</sub>NbO<sub>3</sub> and SrTiO<sub>3</sub> is inset where Kiessig fringes around the Sr<sub>x</sub>NbO<sub>3</sub> film peak indicated that the film had high quality interfaces. Finally, the surface morphology determined using AFM as shown in Figure 5-12(e) where an RMS roughness of 1.3 nm was extracted. The electrical resistivity was then determined to be 7.8×10<sup>-4</sup>  $\Omega$ cm, corresponding to an R<sub>s</sub> of 195  $\Omega$ /sq. Even though the electrical properties were found to be lacking

compared to films grown on LSAT and KTaO<sub>3</sub>, bottom electrodes do not face the same thickness limitations as transparent conductors; therefore, the sheet resistance can be further decreased simply by growing thicker films. In addition, further optimization could be done to improve the crystalline quality of films grown on  $SrTiO_3/Si$ . For example,  $SrTiO_3/Si$  substrates could be transferred in-situ immediately after growth to prevent any degradation of the growth surface. In addition, the epitaxial mismatch could potentially be reduced by increasing the Sr vacancy concentration in  $Sr_xNbO_3$ .

# 5.5 Concluding Remarks

In summary,  $Sr_xNbO_3$  thin films were grown by RF sputtering and were found to assume the perovskite phase. The presence of various defects observed in STEM had surprisingly little impact on the room temperature resistivity and optical properties. Films grown on KTaO<sub>3</sub> were found to have comparable properties to those grown by PLD, demonstrating a maximum transmission of 94% at a wavelength of 280 nm with a resistivity of  $2.36 \times 10^{-4} \Omega \text{cm}$ . Films grown on LSAT were found to have a slightly lower performance with a transmission of 86% at a wavelength of 280 nm with a resistivity of  $3.2 \times 10^{-4} \Omega \text{cm}$ . The favorable electrical and optical properties were barely degraded compared to PLD grown films and were found to be very robust against large amounts of A-site vacancies. First-principles DFT calculations revealed that large amounts of Sr vacancies caused a red shift of the O 2p to Nb  $e_g$  absorption peak and decreased the intensity of the Nb  $t_{2g}$  to  $e_g$  absorption peak, in excellent agreement with the experimentally observed trends in Sr deficient Sr<sub>x</sub>NbO<sub>3</sub>. This work demonstrates the technologically vital ability to sputter deposit correlated transparent conductors ideally suited for UV applications and opens opportunities for increasing the scalability of these materials and potentially enable increased output efficiency of UV LEDs.

# Chapter 6: Interplay between disorder and electronic transport in SrVO<sub>3</sub>

The following section is adapted from work in preparation for journal submission by Roth, et al.

The sensitivity of electron interactions to defects, chemical composition, and external stimuli makes it challenging to experimentally verify theoretical models and predictions of correlated oxides. This sensitivity necessitates highly crystalline, stoichiometric films for the study of intrinsic effects arising from electron correlation. Unfortunately, this is easier said than done. The growth of complex, multicomponent correlated materials is inherently problematic, making it difficult to minimize defect concentrations. In particular, even though SrVO<sub>3</sub> has long been a testbed material to refine theoretical frameworks and develop numerical techniques, traditional material synthesis techniques have not yielded samples of sufficient quality to verify predictions. SrVO<sub>3</sub> has been grown using bulk synthesis,<sup>311,312</sup> RF sputtering,<sup>277</sup> Pulsed Laser Deposition (PLD),  ${}^{313-317}$  and hMBE.  ${}^{10,177}$  Thin films using traditional thin film growth methods have only attained a maximum residual resistivity ratio (RRR) of  $\sim 11$ ,<sup>315,318</sup> likely due to the high energy nature of PLD and sputter deposition or due to lower purity precursors, while bulk materials have reached RRR values of ~56.226 These traditional techniques have recently been superseded by the development of hybrid molecular beam epitaxy which has enabled the growth of SrVO<sub>3</sub> films with RRRs in excess of 200 largely owed to the precise control of stoichiometry through a self-regulated growth mode.<sup>10</sup>

Here *h*MBE was utilized to synthesize a wide range of SrVO<sub>3</sub> thin films with RRR values stepping from the ultraclean to the disordered limit to investigate the effect of disorder and anisotropic, k-dependent scattering times on the transport properties of itinerant carriers with sizeable electron interaction. An electronic phase diagram of SrVO<sub>3</sub> was experimentally determined from films with a wide range of defect concentrations by extracting the exponent *n* of the temperature dependent resistivity. Aside from hopping transport in the highly disordered limit, a robust T<sup>2</sup> dependence - an indicator that itinerant carrier scattering is dominated by electronelectron interactions - was found at low temperatures up to 20 K irrespective of the degree of disorder. The resistivity scaling at room temperature was found to vary with defect concentration, ranging from nearly n=2 in the ultraclean limit to n=3/2 in the highly disordered limit. Comprehensive Hall analysis unveiled a slight nonlinearity, attributed to a multicarrier transport behavior present in the films. The transport channel carrying the characteristics of a Fermi liquid behavior at low temperature has been identified along with a transient regime between 20 K and 100 K with exponents n>2. Correlating the temperature dependent Hall coefficient and prefactor  $A_{ee}$  of the low temperature T<sup>2</sup> transport regime provides new insights into the role of anisotropic scattering and disorder in correlated electron systems by offering a simple interpretation of the prefactor  $A_{ee}$  over the entire range of carrier densities in correlated electron systems and unveiling that not only disorder and carrier density, but also anisotropic scattering time strongly affects the prefactor.

# 6.1 Temperature Dependent Resistivity Scaling in SrVO<sub>3</sub>

To investigate the scaling mechanisms in SrVO<sub>3</sub>, it was first vital to examine the temperature dependent resistivity for samples with varying levels of disorder. This necessitated unambiguous fitting of the temperature dependent resistivity parameters, namely the scaling factor n of the temperature dependent resistivity and the temperature dependent scaling prefactor  $A_n$  given by  $\rho(T) = \rho_0 + A_n T^n$ . Simple polynomial fits are commonly employed to extract n and  $A_n$ ; however, this fitting requires the primary scattering mechanism to be dominant over a wide range of temperatures, ideally over several hundred degrees, to obtain a robust fit and minimize ambiguity

in the interpretation of results. In cases where a specific transport regime dominates in a smaller temperature interval, resistivity scaling behavior can be identified more robustly by plotting  $\frac{d\rho}{dT^n}$  as a function of T and modulating the exponent *n* such that a temperature region with constant  $\frac{d\rho}{dT^n}$  is found. This method deconvolutes the scaling regime determination by eliminating the dependence on the temperature independent residual resistivity  $\rho_0$  and provides a highly sensitive determination of the exponent *n*.



Figure 6-1:  $d\rho/dT^n$  vs T plots for an ultraclean sample (RRR=187), an intermediate sample (RRR=57) and a disordered sample (RRR=4) with different scaling factors, n, demonstrating the distinct deviation from  $T^2$  scaling at high temperature for all samples investigated and this method's sensitivity to determine the proper scaling factor n.

The fitting of the high temperature resistivity for three respective  $SrVO_3$  samples is shown in Figure 6-1 for n=2.0, 1.8, and 1.5. The cleanest sample, RRR=187, displayed a reasonable agreement for n=2.0 in the temperature range of around 150K-200K; however, the tendency to decrease at higher temperatures and the formation of an arc-like deviation from a constant line indicate that the choice of 2.0 for the exponent was too high. Scaling factors of n=1.9 or 1.8, as shown in Figure 6-1, had a much better agreement over a wider range of temperatures. Choosing an exponent that is too small, such as n=1.5, resulted in a much smaller linear region. Similar trends were found for the sample with RRR=56 and the highly disordered sample (RRR=4). While n=2.0 provided a relatively poor agreement to a constant resistivity slope  $\frac{dp}{dT^n}$ , exponents of n=1.8 and n=1.5 yielded regions with constant slope in the same temperature interval of T>150 K seen for the cleanest sample. This fitting procedure was completed on all 26 samples in the disorder series, as shown in Figure 6-2.



Figure 6-2:  $d\rho/dT^n$  vs T plots for the high temperature region of all samples. Note the change in y-axis scale as n decreases.

While n=2.0 scaling at high temperatures has previously been reported for  $SrVO_3$ , albeit using the less suitable polynomial fit, all samples in this study were found to have n<2.0.<sup>242</sup> Ultraclean samples revelated the largest exponent of n=1.9, which was somewhat reduced to n=1.8 at around a RRR of 56, which further reduced to n=1.5 in the disordered limit.



Figure 6-3:  $d\rho/dT^n$  vs T plots for the low temperature region of all samples. All samples were found to have linear regions at temperatures below 25K with the exception of the most disordered sample.

In addition to the high temperature limit, the resistivity scaling behavior at low temperatures was also investigated to confirm the presence of a low temperature Fermi liquid phase with a T<sup>2</sup> scaling. The scaling for all samples is shown in Figure 6-3. All SrVO<sub>3</sub> films investigated

here showed the expected n=2 scaling law dependence at low temperature up to  $\sim 20$  K with the exception of the most disordered sample with RRR=4 where no uniform scaling could be resolved.

While this derivative fitting is the ideal method for analyzing temperature dependent resistivity, it is highly susceptible to noise; even careful experimental measurements can lead to an amplification of noise in the data. To further confirm the results extracted from derivative fitting,  $A_{ee}$  and *n* for the Fermi liquid phase were determined using Random Sample Consensus (RANSAC) fitting of  $\Delta \rho$  as a function of  $T^2$ , shown in Figure 6-4.<sup>319</sup> Using the previously determined regions as starting points, linear regions below 100 K were determined using the RANSAC algorithm with a residual threshold of  $5 \times 10^{-10}$  and 10000 trials. This fitting allowed an unambiguous determination of the endpoints of the Fermi liquid phase when increased resistivity due to localization set in at low temperatures.



Figure 6-4: Plots of  $\Delta \rho$  as a function of  $T^2$  where linear regimes designate where the resistivity follows a  $T^2$  dependence. Linear regions were determined using the Random Sample Consensus (RANSAC) algorithm using a residual threshold of  $5 \times 10^{-10}$  and 10000 trials. Points that lay in the  $T^2$  region are labeled in blue while outliers are red.

Finally, polynomial fits of the temperature dependent resistivity for eight respective samples were performed as a comparison to the derivative fitting and are shown in Figure 6-5. These simple polynomial fits were limited to the regions determined from the derivative fitting to prevent any inclusion of the higher order scaling regime at intermediate temperatures. The disparity between both fitting methods is shown in Figure 6-5(i) where the derivative fits consistently yielded slightly lower values of  $A_{ee}$ .



Figure 6-5: (a)-(h)  $\rho$  vs *T* plots for the eight respective films with corresponding polynomial fits for the high and low temperature  $T^2$  regions. (i) Comparison of the scattering prefactor  $A_{ee}$  fit using derivative and polynomial fitting.

The different types of temperature dependent resistivity fits were then combined to generate a temperature-disorder scaling phase diagram for SrVO<sub>3</sub>, shown in Figure 6-6. All samples were found to have a robust  $T^2$  dependence at temperatures up to ~20 K, irrespective of the level of disorder. While previous studies employing the simply polynomial fit on SrVO<sub>3</sub> thin films with RRR<12, categorized here as highly disordered, demonstrated a  $T^2$  dependence up to 300 K,<sup>318,320,321</sup> the improved method employed here enabled the identification of a  $T^2$  dependence

between 10-20 K for samples with RRR<20 before it was fully obscured by the onset of localization and increase of the resistivity at low temperatures due to the elevated level of disorder, likely due to Anderson localization.<sup>322</sup> This clear T<sup>2</sup> scaling at these low temperatures is indicative of Fermi liquid behavior similar to that seen in many transition metals and other complex oxide systems such as  $SrTiO_3^{165}$  and  $La_{2-x}Sr_xCuO_4$ ,<sup>323</sup> where some combination of Umklapp and Baber scattering were the dominant relaxation mechanisms for inelastic electron-electron scattering at low temperatures.



Figure 6-6: Phase diagram outlining the resistivity scaling regions for  $SrVO_3$  as a function of RRR and temperature. The scaling for the high temperature strange metal phase is indicated by a gradient from n=1.5 (purple) to n=1.9 (blue). Orange indicates the low temperature fermi liquid phase and green indicates the onset of localized transport behavior.

At temperatures exceeding 20 K, the  $T^2$  resistivity behavior of all films changed to a larger exponent before re-entering into the constant resistivity slopes with different exponents at T>150 K, termed the 'transient regime.' In this temperature regime from about 20 K to 150 K, no resistivity scaling law could be identified using the fitting methods described above, signifying that multiple different momentum relaxation mechanisms concurrently contributed to the resistivity and no particular contribution dominated at these temperatures. Above 150 K, all samples resumed displaying distinct scaling regimes with exponents ranging from 1.9 in the ultraclean limit to 1.5 in the disordered limit. The transition from the n=1.8 to the n=1.5 scaling law occurred at a RRR of 10, aligning with the onset of the localized transport behavior at low temperatures. As the Debye temperature in SrVO<sub>3</sub> is 350 K,<sup>324,325</sup> it is to be expected that the resistivity shows a linear temperature dependence ( $\rho$ -T) since phonon scattering is expected to be the dominant contribution. Instead, the observed scaling appeared to be a combination of two comparable contributions, from electron-phonon scattering as well as electron-electron scattering with T and T<sup>2</sup> dependences respectively. The fact that phonon scattering did not dominate the transport characteristics at room temperature not only indicates that a sizeable electron-electron interaction still persists at these temperatures, but also that  $SrVO_3$  has abnormally high  $A_{ee}$ . In this regard, the change of the exponent from n=1.9 in the ultraclean limit to smaller values with decreasing RRR values is an indication that disorder reduces the magnitude of  $A_{ee}$  by directly reducing the likelihood of momentum relaxing scattering phenomena, or by weakening the electron-electron interaction strength and therefore reducing the number of quasiparticles present in the system. This observation that quasi-particles are still present at such high temperatures conflicts with the expectation that the electron quasiparticles become ill-defined at high temperatures; therefore, we only indicate that an additional higher order scattering was present at elevated temperatures which is not understood at this point. While a  $T^2$  resistivity scaling law is commonly used as a hallmark of Fermi liquid phases, different transport mechanisms and phenomena not considered can also display similar, indistinguishable resistivity scaling. Due to these observations, we classify the room temperature transport of SrVO<sub>3</sub> as that of a strange metal while a robust Fermi liquid phase can be identified at

low temperatures.

## 6.2 Origin of the transient resistivity scaling behavior

To investigate the role of carriers on each scaling regime, in-depth Hall effect analysis was performed on eight respective samples with different degrees of disorder. The measured Hall resistance,  $R_{xy}$ , as a function of transverse magnetic field and temperature is shown in Figure 6-7(a)-(c) for an ultraclean, an intermediate, and a disordered sample, respectively. The presence of multiple carrier transport was immediately evident from the nonlinearities observed in all samples, which can be best seen by plotting  $dR_{xy}/dB$ , shown in Figure 6-7(d)-(f). All samples exhibited a negative slope in  $R_{xy}$ , indicating that the primary carriers were electrons at all temperatures. The slope of  $R_{xy}$  was found to have a significant temperature dependence for all samples with RRR greater than 27.



Figure 6-7: Temperature dependent transverse Hall resistance and first derivative density plots as a function of temperature and disorder for (a,d) ultraclean SrVO<sub>3</sub>, (b,e) intermediate SrVO<sub>3</sub>, and (c,f) highly disordered SrVO<sub>3</sub>.
At temperatures exceeding 100 K,  $dR_{xy}/dB$  was linear for all samples, indicating that the electric conduction was dominated by a single transport channel. Below this temperature, all films were observed to have distinct nonlinearities arising from multiple carrier channels. These nonlinearities were highly dependent on temperature and disorder, indicating variations in each carrier channel's contributions to the electronic transport. For the ultraclean samples, a flattening of the Hall slope around 0 B-field between 100 K and 30 K evolved, which became more pronounced with decreasing temperatures, indicating a sizeable contribution of a hole channel to the total electrical conductivity. This flattening resulted in the formation of a peak in the  $dR_{xy}/dB$  plot shown in Figure 6-7(d). Below 30 K this peak split, creating a minimum at 0 B-field, signifying the emergence of an additional electron channel. While the presence of three carrier channels has previously been observed for ultraclean samples,<sup>242</sup> it was found here that these multicarrier transport features can be observed in SrVO<sub>3</sub> with RRR values as low as 50. These nonlinearities were quantified here by separating the contributions from three noninteracting carrier channels using multicarrier fitting as detailed in Appendix B and extracting each channel's carrier concentration and mobility, shown in Figure 6-8.



Figure 6-8: The carrier concentration n for (a) the primary electron channel  $e_1$ , (b) the secondary electron channel  $e_2$ , and (c) the hole channel p. Carrier mobility for (a) the primary electron channel  $e_1$ , (b) the secondary electron channel  $e_2$ , and (c) the hole channel p. Resistivity scaling regions outlined in Figure 6-6 are overlaid.

At temperatures above ~120 K, the electronic transport was entirely driven by the primary electron carrier,  $e_l$ , shown in Figure 6-8(a). The carrier concentration of this primary carrier,  $n_{el}$ , was observed to reach a maximum of  $3.5 \times 10^{22}$  cm<sup>-3</sup> in the ultraclean limit of the strange metal region and decrease to  $2.5 \times 10^{22}$  cm<sup>-3</sup> in the disordered limit. Depending on the degree of disorder, very different temperature dependent behaviors were found for  $n_{el}$ . For films with RRR>25, a strong temperature dependence was found with  $n_{el}$  decreasing to a minimum value of  $7 \times 10^{21}$  cm<sup>-3</sup> while those films with RRR<25,  $n_{el}$  had a minimal temperature dependence. This temperature independent region was well aligned with the onset of the low temperature insulating region in Figure 6-6. The mobility for the  $e_l$  channel, shown in Figure 6-8(d), was found to be ~10 cm<sup>2</sup>V<sup>-1</sup>s<sup>-</sup>

The secondary electron channel  $e_2$  became apparent at temperatures below 50 K for films with RRR>40, aligning with the Fermi liquid regime as shown in Figure 6-8(b) and (e). The carrier concentration of this channel was found to be roughly a factor of three smaller than the primary electron channel. Conversely, the mobility was considerably larger, reaching up to ~12200 cm<sup>2</sup>V<sup>-</sup> <sup>1</sup>s<sup>-1</sup> in the ultraclean limit. Finally, the hole channel *p* shown in Figure 6-8(c) and (f), was observed to be present in all samples with RRR>50 up to a maximum temperature of ~150 K. The carrier concentration for this channel was found to be nearly two orders of magnitude less than the primary electron channel,  $n_1$ . In addition, the mobility for samples with RRR>75 followed the same trend as the primary electron channel. The mobility for samples with RRR>75 followed the same trend as the primary electron channel, increasing at low temperatures to a maximum value of 3300 cm<sup>2</sup>V<sup>-</sup> <sup>1</sup>s<sup>-1</sup>. Three key results were drawn from this multicarrier fitting:

- The strange metal phase is associated with the primary electron channel while the transient and Fermi liquid phases arise from contributions from multiple carrier channels.
- All three channels were present inside the Fermi liquid regime, signifying that there was strong anisotropic scattering which enabled a significant momentum relaxation from Baber scattering. For each sample, the relative contributions from each channel remained constant until the disappearance of the second electron channel, marking the transition from the Fermi liquid region to the transient region. This suggested that the T<sup>2</sup> resistivity dependence from Baber scattering coincided with the existence of two well-defined electron channels whose components were constant. These observations further suggested that the secondary electron channel should have persisted to lower RRR values, but became indistinguishable from the primary electron channel in the disordered limit.

• In the transient regime the carrier concentrations and mobilities of each channel rapidly changed with respect to each other as the temperature increased. These drastic relative changes altered the scattering cross section as a function of temperature, disallowing any region of constant scaling to be resolved. The scaling in this region was further complicated by a linear contribution from phonon scattering closer to the Debye temperature.

The robust existence of a Fermi liquid phase at low temperature, its dissipation at temperatures exceeding 20 K, and the stabilization of an anomalous scaling region at high temperature were all expected to arise from the intricate multicarrier transport stemming from SrVO<sub>3</sub>'s complex multi-sheet Fermi surface shown in Figure 6-9. The complex Fermi surface of SrVO<sub>3</sub> is made up of three, non-intersecting Fermi surface sheets derived from the  $t_{2g}$  orbital manifold. The outer sheet has a 'jungle gym' type structure formed by the intersection of three perpendicular cylindrical surfaces. The middle and innermost surfaces lie entirely within the first Brillouin zone and can be approximated by cubes with 'faceted' and 'rounded' edges, respectively. These surfaces and their *k*-dependent Fermi velocities were calculated using DFT by Prof. Turan Birol. Fermi velocities for the 'jungle gym' surface were in the range of  $3.7 \times 10^7$  m/s to  $5.1 \times 10^7$  m/s, while somewhat larger velocities ranging up to  $5.4 \times 10^7$  m/s were calculated for the two inner Fermi surface sheets. The lowest velocities were found for Fermi wave vectors pointing along the (111) direction.



Figure 6-9: (a) Schematic of the first Brillouin zone containing SrVO<sub>3</sub>'s three Fermi surface sheets. Each Fermi surface sheet mapped with (b) the *k* dependent Fermi velocity and (c) the Fermi surface curvature for constant  $k_z$  values. Reproduced from reference.<sup>242</sup>

In addition to the trends determined from the multicarrier fitting in the temperature range from 20 K to 150 K, additional noteworthy observations were made for the temperature/disorder phase diagram of SrVO<sub>3</sub>. The resistivity, shown in Figure 6-10(a), was observed to remain the same order of magnitude across the strange metal phase and into the insulating regime at low temperatures. The degree of nonlinearity of the Hall resistance  $R_{xy}$ , quantified by the ratio of the Hall resistance slopes at high and zero magnetic field shown in Figure 6-10(b), remained unity above 100 K, indicating that a single charrier channel dominated transport in the strange metal phase. In the transient regime, the degree of nonlinearity was larger than one, signifying the onset of multicarrier transport, specifically the emergence of a hole transport channel. Below 20 K, the nonlinearity remained above unity in the disordered limit but transitioned to values below unity in the ultraclean limit, marking the formation of a secondary, high mobility electron channel that was otherwise suppressed by disorder scattering.



Figure 6-10: (a) The logarithm of resistivity, (b) nonlinearity of  $R_{xy}$  given as the ratio of the slope at high and low field, and (c) scattering anisotropy given as the value of the inverse Hall coefficient ( $eR_H$ )<sup>-1</sup> at low field normalized to the value at room temperature as a function of temperature and RRR. Resistivity scaling regions outlined in Figure 6-6 are overlaid.

In the case of strong anisotropic scattering such as that arising from multiple carrier channels, the normal relation of the Hall coefficient to the carrier concentration is no longer valid  $[(eR_H)^{-1} \neq n]$ . In addition, the effective mass of the individual carriers cannot be distinguished from their *k*-dependent scattering time; therefore, we relate the general, sample dependent scattering anisotropy to the inverse Hall coefficient. Using the 2D geometrical interpretation, the 2D Hall coefficient is entirely dependent on the scattering path length vector  $l(k) = \tau_k \cdot v_{F_i}$  and the shape of the Fermi surface where *S* is the circumference of the Fermi surface slice and *A* is the area traced by l(k) as outlined in Section 3.2.4.<sup>245</sup> Expanding this expression to three dimensions by integrating over all 2D slices gives:

$$(eR_H)^{-1} = \frac{1}{8\pi^2} \cdot \frac{\left[\sum_j \int l_{av,k_z,j} \cdot S_{k_z,j} dk_{z,j}\right]^2}{\sum_j \int A_{l,k_z,j} dk_{z,j}} \propto \frac{\langle \tau \rangle^2}{\langle \tau^2 \rangle}$$
Eq. 6.1

Combining all sample independent quantities arising from the Fermi surface geometry into the constant term C, the Hall coefficient is shown to depend only on the ratio of the average scattering time squared over the average of the scattering time squared. If the scattering time varies on the Fermi surface, this ratio deviates from unity, making the temperature dependence of the Hall coefficient in metals a direct measure of the degree of anisotropic scattering in the system. Note that for Baber scattering to occur, the type of anisotropic scattering does not matter, only the amount. In the high temperature limit, isotropic phonon scattering evenly redistributes the scattering time providing a baseline isotropic value of the Hall coefficient. Therefore, the temperature dependent inverse Hall coefficient,  $(eR_{\rm H})^{-1}$ , for each sample was normalized to the room temperature value as shown in Figure 6-10(c). At high temperatures, near the strange metal phase, carrier scattering was found to be entirely isotropic. In the disordered limit, the Hall coefficient was not affected by temperature as it transitioned cleanly from isotropic phonon scattering smoothing out any anisotropic scattering from the Fermi surface to isotropic defect scattering at low temperatures. In the ultraclean limit, the Hall coefficient decreased with temperature, signaling a transition to anisotropic scattering in the presence of dominant electronelectron scattering. At low temperatures, the level of anisotropic scattering increased nearly linearly with increasing RRR, allowing RRR to be used as a measure of anisotropic scattering for the complete sample set. The robust nature of the low temperature Fermi liquid phase in addition to the emergence of anisotropic scattering times with increasing RRR offers a unique opportunity to study how anisotropic scattering and disorder affect the temperature independent scaling parameter  $A_{ee}$ .

#### 6.3 The effect of anisotropic scattering on the scattering prefactor $A_{ee}$

This measure of anisotropy coupled with a large sample set and a robust low temperature Fermi liquid phase offers a unique opportunity to study how anisotropic scattering affects the electron-electron scattering prefactor  $A_{ee}$ . This relation is shown in Figure 6-11(a) where ultraclean samples with a high degree of anisotropic scattering were found to have  $A_{ee}$  on the order of ~7×10<sup>-11</sup>  $\Omega$ cmK<sup>-2</sup> while those in the disordered, isotropic limit were lowered to ~2×10<sup>-11</sup>  $\Omega$ cmK<sup>-2</sup>. This large sample dependence of  $A_{ee}$  was primarily caused by anisotropic scattering due to the complex Fermi surface geometry in SrVO<sub>3</sub>. While normal electron-electron scattering (NEES) events normally do not contribute to the resistivity, if the scattering time is *k*-dependent, NEES redistributes electrons into regions of stronger electron scattering and effectively contributes to the resistivity, enabling a large enhancement in  $A_{ee}$ .<sup>163</sup> Once the impurity concentration reached a level in which isotropic scattering was dominant, NEES events no longer contributed to the resistivity and  $A_{ee}$  decreased. In the ultraclean limit, significant uncertainties were present in  $A_{ee}$ . Even though ultraclean samples were expected to be highly stoichiometric due to the self-regulated growth, the remaining defects were so sparse that the type of defect may have drastically altered the amount of anisotropic scattering, be it Sr, V, or O vacancies, leading to large deviations in  $A_{ee}$ .



Figure 6-11: (a) Sample dependence of the scattering prefactor  $A_{ee}$  as a function of RRR. The blue line serves as a guide for the eye. (b) The scattering prefactor  $A_{ee}$  normalized to  $A_{ee}$  in the isotropic limit as a function of

the ratio of the resistance arising from impurities to resistivity arising from anisotropic scattering. The red line follows Eq. 6.2.

The trend of the scattering prefactor was further compared to anisotropic scattering following the procedure used for simple metals such as copper, silver, and potassium.<sup>163</sup> The scattering prefactor was first normalized to the experimental  $A_{ee}$  in the isotropic, or most disordered limit,  $A_{iso}$ . The ratio of scattering prefactor values then follow Eq. 6.2, where  $\rho_{imp}$  and  $\rho_{ani}$  are the resistivities arising from isotropic and anisotropic scatterers respectively.<sup>163</sup>

$$\frac{A_{ee}}{A_{iso}} = 1 + \frac{3.5}{1 + \rho_{imp}/\rho_{ani}}$$
 Eq. 6.2

For SrVO<sub>3</sub>, resistivity arising from anisotropic scattering was assumed to be the same for all samples since it was expected to arise from the Fermi surface shape and was therefore set to  $\rho_0$ for the most disordered sample. Resistivity arising from impurities was then defined to be the residual resistivity for each sample. These adjustments are shown in Figure 6-11(b) with Eq. 6.2 plotted as a guide. The most disordered samples were found to be in the isotropic limit and to closely followed Eq. 6.2 into the anisotropic limit where increased uncertainties in  $A_{ee}$  were introduced. Even though ultraclean samples were expected to be highly stoichiometric due to the self-regulated growth, small nonstoichiometries could exist which strongly altered the redistribution of electron scattering on the Fermi surface.



Figure 6-12: (a) The scaling prefactor  $A_{ee}$  as a function of carrier concentration for typical perovskite oxide materials including SrVO<sub>3</sub> from this work, SrTiO<sub>3</sub>,<sup>165</sup> SrMoO<sub>3</sub>,<sup>326</sup> SrNbO<sub>3</sub>,<sup>259</sup> CaSrVO<sub>3</sub>,<sup>327</sup> CaYTiO<sub>3</sub>,<sup>328</sup> SrLaTiO<sub>3</sub>,<sup>329</sup> and SrTiNbO<sub>3</sub><sup>166</sup> where single crystals are given as squares while thin films are presented as circles. Dashed lines serve as a guide to the eye for the scattering regimes in the disordered and ultraclean limits. (b) Electron-electron scattering strength  $\alpha$  as a function of the residual resistivity ratio for the same materials. The dotted line serves as a guide to where non-electron-electron scattering must be considered.

 $A_{ee}$  was then compared to other complex oxide materials. To form a reasonable comparison to the literature where polynomial fits of the temperature dependent resistivity are commonplace instead of the more robust derivative fits, the representative SrVO<sub>3</sub> samples were refit using a polynomial where the high temperature strange metal phase also displayed T<sup>2</sup> scaling (shown in Figure 6-5). These values are shown in comparison to various perovskite oxides including SrTiO<sub>3</sub>,<sup>165,166,329</sup> YCaTiO<sub>3</sub>,<sup>328</sup> CaSrVO<sub>3</sub>,<sup>330</sup> and SrMoO<sub>3</sub><sup>326</sup> single crystals as well as SrTiO<sub>3</sub>,<sup>9,331,332</sup> SrNbO<sub>3</sub>,<sup>259</sup> SrMoO<sub>3</sub>,<sup>64</sup> CaMoO<sub>3</sub>,<sup>64</sup> and CaVO<sub>3</sub><sup>218</sup> thin films as in Figure 6-12. Note that while  $A_{ee}$ values have been reported for other SrVO<sub>3</sub> thin films, their T<sup>2</sup> dependence was fit over the entire temperature range, resulting in unrealistically high values compared to those reported here.<sup>318,320,321,333</sup>

Several different phenomena can contribute to the magnitude of inelastic electron-electron scattering and lead to the sample dependence of  $A_{ee}$ . Following Eq. 1.14,  $A_{ee}$  is proportional to the scattering cross section divided by the carrier concentration. Umklapp and Baber scattering arise from intrinsic effects and their scattering cross sections should not be sample dependent, allowing for linear regions with  $A \sim n^{-1}$ . Deviations from this trend must arise from contributions from additional scattering effects such as phonon scattering. This can be observed in Figure 6-11(a) where two distinct linear regions with  $A \sim n^{-1}$  were present, defined as the ultraclean limit where electron-electron scattering was dominant and the disordered limit where additional scattering contributed to the temperature dependent resistivity. The ultraclean limit consisted of materials with low defect concentrations, hMBE grown and single crystal SrTiO<sub>3</sub> in the low carrier limit and the low temperature SrVO<sub>3</sub> in the high carrier limit. As additional scattering mechanisms were introduced, whether it be ionized impurity scattering in the case of doped SrTiO<sub>3</sub> or phonon scattering, Aee values increased, deviating from the values predicted from the ultraclean limit, eventually forming the parasitic limit. The transition between these regimes has previously been explained in the case of SrTiO<sub>3</sub> by a Lifshitz transition of the Fermi surface as it evolved and became more complex.<sup>165</sup> Our insights offer an alternative explanation; however, it can also be explained by the addition of ionized impurity scattering which parasitically adds what was assumed to be pure electron-electron scattering. Samples can also lie in this high temperature limit due to contributions from other, non-electron-electron scattering events. For example, the high temperature region of SrVO<sub>3</sub> (HT) was observed to have a significantly larger A<sub>ee</sub> than the low temperature Fermi liquid phase (LT) due to the addition of phonon scattering contributions.

The transition between these limits can be deconvoluted from the dependence on the carrier concentration by defining  $\alpha = A_{ee}/n$  which is plotted in Figure 6-12(b) for all samples. The transition can then be described using the case of SrTiO<sub>3</sub>. The lowest carrier samples have few oxygen vacancies or defects in general; therefore, the carrier scattering is entirely anisotropic,

resulting in the maximum value of  $A_{ee}$  for pure electron-electron scattering. As the carrier concentration started to increase, the level of dopants increased, smoothing out any existing anisotropy and lowering  $A_{ee}$  to a constant, isotropic region. At carrier concentrations exceeding  $\sim 4 \times 10^{18}$  cm<sup>-3</sup>, ionized impurity scattering began to increase the carrier scattering cross section causing  $A_{ee}$  to rise into the disordered limit. All samples in this limit were affected by additional scattering that prevented accurate measurements of the intrinsic  $A_{ee}$  for electron-electron scattering.

Similar to dilute SrTiO<sub>3</sub>, ultraclean SrVO<sub>3</sub> has significant contributions to  $A_{ee}$ , and therefore  $\alpha$ , from anisotropic scattering sites. As disorder is added, the anisotropies are smoothed out and  $\alpha$  decreases while the carrier concentration remains mostly constant. This demonstrates the importance of synthesizing materials with crystalline quality high enough to observe intrinsic electron interactions that are unobscured by additional scattering effects.

### 6.4 Concluding Remarks

In summary, the electronic transport of SrVO<sub>3</sub> was mapped as a function of disorder and temperature through modulating the crystalline quality using *h*MBE. The resistivity scaling factors were unambiguously determined to construct a phase diagram for the resistivity scaling of SrVO<sub>3</sub> where strange metal, Fermi liquid, transient, and insulating phases were revealed. Comprehensive Hall measurements were then performed along with multicarrier fitting to map the carrier concentrations and mobilities of three carrier channels in relation to the scaling phase diagram. These comparisons revealed that the Fermi liquid phase was enabled by the uniform scaling of the three carrier channels below 20 K. Finally, the effect of anisotropic and isotropic scattering was discussed to diagonalize the impact of other scattering mechanisms to  $A_{ee}$ . Scattering prefactor values were further compared to other complex oxides, demonstrating a distinction between pure electron-electron scattering and other scattering mechanisms. These results offer a basis for how

the electrical properties in strongly correlated metals evolve as a function of temperature and disorder. In addition, this work provides a fundamental distinction of the potential contributions to  $A_{ee}$  and outlines the dramatic effects of anisotropic scattering in oxide materials which leads to a sample dependent inclusion of NEES events.

# Chapter 7: Synthesis of [111]-oriented SrVO<sub>3</sub> by hMBE

The following section is reproduced in part from: Roth, *et al.*, Self-regulated growth of [111]-oriented perovskite oxide films using hybrid molecular beam epitaxy. *APL Materials* 9, 021114 (2021) with the

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As discussed in the introduction, [111]-oriented perovskite films and superlattices offer many opportunities to enable a wide variety of technologically valuable properties including nontrivial band topologies,<sup>121,122</sup> ferroelectricity,<sup>123,124</sup> Dirac semimetal phases,<sup>125</sup> spin-nematic phases,<sup>121</sup> the quantum spin Hall effect,<sup>126,127</sup> and the quantum anomalous Hall effect.<sup>128–131</sup> While many of these effects have been predicted, few have been experimentally realized due to the inherent difficulties in growing [111]-oriented perovskite films and superlattices. Unlike [001]oriented perovskites, such as SrTiO<sub>3</sub>, that have alternating charge neutral  $Sr^{2+}O^{2-}/Ti^{4+}O_2^{4-}$  layers, [111]-oriented SrTiO<sub>3</sub> has alternating  $Sr^{2+}O_3^{6-}/Ti^{4+}$  layers creating a stacking sequence with highly charged atomic planes. The polar stacking sequence gives rise to the emergence of electric dipoles energetically destabilizing the growth front thus detrimentally affecting film growth, potentially driving the formation of unexpected phases, undesired orientations, and unwanted exposed facets as the film attempts to minimize its surface energy.<sup>119,120</sup> Typically, this is counteracted by utilizing a high energy growth technique operating far from thermodynamic equilibrium, such as pulsed laser deposition (PLD) which has been used for the growth of SrRuO<sub>3</sub>,<sup>134-136</sup> SrFeO<sub>3</sub>,<sup>137</sup> La0.7Sr0.3MnO3,138 AlFeO3,139 NdNiO3,140 SrIrO3,141 LaFeO3,142 BaTiO3,142 LaAlO3,143 PbTiO3,144 and Ba<sub>0.94</sub>La<sub>0.04</sub>SnO<sub>3</sub><sup>145</sup> or such as sputtering for the growth of SrTiO<sub>3</sub>,<sup>119,146</sup> NdNiO<sub>3</sub>,<sup>147</sup> and GdMnO3148.

While [111]-oriented perovskites have been successfully synthesized using these methods, it is highly desirable to establish growth using a low energy deposition technique, such as molecular beam epitaxy (MBE), where unintentional defect concentrations can be minimized. Currently, homoepitaxial growth of SrTiO<sub>3</sub> is the only reported successful growth of [111]-oriented perovskites by MBE.<sup>334</sup> The highly desirable heteroepitaxial growth, which is required to take advantage of materials design degrees of freedom in thin film growth, specifically, epitaxial strain, atomically abrupt interfaces and layer thickness, and layering sequence has remained largely elusive. The inherent difficulties of utilizing MBE for heteroepitaxial growth along unfavorable directions has been observed for the growth of [111]-oriented rocksalt MgO<sup>335</sup> and CaO<sup>336</sup> on GaN. Under regular conditions, where the cations were supplied by evaporation and subsequently oxidized on the growth front, octupolar surface reconstructions were found to serve as nucleation points for lower energy {100} facets which resulted in undesirable 3D film growth after just a few monolayers. In contrast, the co-exposure of the surface to water vapor enabled continuous layerby-layer heteroepitaxial growth of [111]-oriented rocksalt films. During growth, hydroxyl groups bonded to the positively charged cations on the surface, thereby reducing the polar character of the surface, and thus stabilizing the growth front. This effect was further confirmed through density functional theory calculations.<sup>336</sup> The situation for the growth of [111]-oriented perovskites is similar, and it is therefore hypothesized that agents aiding the charge reduction of the interface are beneficial to the growth. This effect might also be achieved through the use of other chemical groups such as polar ligands liberated by the thermolysis of the metalorganic precursors used in hybrid MBE (hMBE),<sup>209,337</sup> thus enabling the growth of perovskites along highly polar directions with high crystalline quality.

This hypothesis has been tested here for the heteroepitaxial growth of the correlated metal SrVO<sub>3</sub> which has been extensively studied lately<sup>315,318,338–340</sup> due to its potential use as transparent electrode material.<sup>53</sup> Since SrVO<sub>3</sub> is a metal, the material quality can be determined by the simple,

widely used metric of the residual resistivity ratio (RRR) which is defined as the ratio of the room temperature and low temperature (2 K) resistivities, thus making SrVO<sub>3</sub> an ideal material choice to determine the effectiveness of [111]-oriented growth using *h*MBE. PLD grown [111]-oriented SrVO<sub>3</sub> has been reported but the low RRR of 5 confirmed a high defect concentration.<sup>341</sup> Recently it was shown that *h*MBE, which exploits a self-regulated growth mode to achieve stoichiometric films, is ideally suited to grow ultraclean SrVO<sub>3</sub> thin films where, in the [001]-orientation.<sup>10,177</sup> In this chapter, a detailed growth study of [111]-oriented SrVO<sub>3</sub> thin films by *h*MBE is presented. A self-regulated growth window was discovered for [111]-oriented growth where films inside had atomically abrupt surface and interfaces. The RRR value of 21 for *h*MBE grown films inside the growth window significantly exceeded the RRR quality metric of previously grown [111]-oriented SrVO<sub>3</sub> by PLD by a factor of four.

## 7.1 Growth of [111]-oriented SrVO<sub>3</sub> thin films

Thin films of SrVO<sub>3</sub>(111) were grown using a DCA M600 *h*MBE equipped with a Sr thermal effusion cell and a molecular oxygen plasma source. Vanadium was supplied in the form of the metalorganic vanadium oxytriisopropoxide (VTIP) using a heated gas injector connected to a heated gas inlet system. The VTIP flux was controlled by maintaining a constant gas inlet pressure,  $P_{VTIP}$ . Growth was performed on the closest lattice matched substrate, [111]-oriented (La<sub>0.3</sub>Sr<sub>0.7</sub>)(Al<sub>0.65</sub>Ta<sub>0.35</sub>)O<sub>3</sub> (LSAT), giving rise to a 0.67% tensile strain. Stoichiometric growth conditions were mapped by choosing a fixed Sr flux of 2.50×10<sup>13</sup> cm<sup>-2</sup>s<sup>-1</sup> using a quartz crystal microbalance and growing a series of samples using different  $P_{VTIP}$  pressures. LSAT substrates were prepared by sonication in acetone and isopropyl alcohol followed by a five-minute UV/ozone clean. Prior to film growth, substrates were heated to a temperature of 900°C and exposed for 15 minutes to an oxygen plasma supplied from an RF plasma source (Oxford Applied Research)

operated at 250 W resulting in a background pressure of  $\sim 5 \times 10^{-7}$  Torr. Prior to growth, no surface reconstructions were observed on the LSAT substrates. SrVO<sub>3</sub> films were grown under the same conditions for approximately 1 hour, resulting in film thicknesses of about 50 nm.



Figure 7-1: RHEED images along the (a)  $\langle 10-1 \rangle$  and (b)  $\langle 11-2 \rangle$  azimuths of [111]-oriented LSAT and SrVO<sub>3</sub> films grown at different VTIP pressures. Films grown outside the growth window can be identified by changes in surface reconstructions and intensity modulations on the second order diffraction rod. Figure reproduced from reference.<sup>342</sup>

Immediately after growth, films were cooled in vacuum to 100°C and RHEED images were taken along the  $\langle 10-1 \rangle$  and  $\langle 11-2 \rangle$  azimuths to examine the surface morphology as a function of VTIP gas inlet pressure,  $P_{VTIP}$ , as shown in Figure 7-1. For VTIP inlet pressures between 78 and 84 mTorr the RHEED intensity spots were confined to the Laue circles and the Kikuchi lines were sharp, both signifying a smooth highly crystalline film surface similar to what has been observed for [001]-oriented SrVO<sub>3</sub> films.<sup>177</sup> RHEED taken from SrVO<sub>3</sub> films grown outside this region exhibited a more streaky RHEED pattern with intensity modulations along the 2<sup>nd</sup> order diffraction rods, indicative of a slightly more corrugated growth front, yet still two-dimensional. While not immediately obvious, the occurrence of these RHEED features marked the boundaries of the self-regulated growth window, which ranged from 78 mTorr to 84 mTorr, as will be discussed below. Reconstructions of the polar (111) perovskite surface are known to be complex, and diverse atomic arrangements have been observed depending on cation termination and oxidation conditions.<sup>343</sup> For

example, [111]-oriented SrTiO<sub>3</sub> has been observed to form reconstructions including  $n \times n$  where n = 1-6,  $\sqrt{7} \times \sqrt{7} R19.1^\circ$ , and  $\sqrt{13} \times \sqrt{13} R13.9^\circ$  depending on surface termination, oxidation conditions, annealing temperature and time.<sup>343–345</sup> For SrVO<sub>3</sub> films grown here, surface reconstructions were found along both azimuths but were sometimes difficult to index. For example, along the (10-1) azimuth additional reflections from surface reconstructions appeared somewhat blurred suggesting that the surface did not assume a singular, specific reconstruction. Instead, multiple surface reconstructions coexisted. Remarkably it was observed that an odd numbered reconstruction, referred to as (2n+1)×, was present for all Sr-rich films grown with a gas inlet pressure  $P_{VTIP} \leq 78$ mTorr while an even reconstructions along the (11-2) azimuth were more sharply defined and followed a similar trend, going from a 7× reconstruction on the Sr-rich side to a 6× reconstruction inside the growth window. RHEED features arising from surface reconstructions vanished with increasing  $P_{VTIP}$  to become exceptionally blurry, likely due to a superposition of odd and even surface reconstructions, and finally vanished for V-rich films ( $P_{VTIP} > 84$  mTorr).

### 7.2 Growth window determination using XRD and AFM

Films were further characterized using X-ray diffraction to verify the structure and film orientation. High resolution  $2\theta$ - $\omega$  scans around the [111]-diffraction peak of LSAT and SrVO<sub>3</sub> are shown in Figure 7-2(a). Unlike the case of commensurately strained SrVO<sub>3</sub>(001) films where the film peak position reflected the films' cation stoichiometry due to the associated lattice parameter expansion,<sup>177,220</sup> the film peak position for [111]-oriented films did not change as a function of VTIP pressure. Only interface and surface quality of the films seemed to be affected by the growth conditions, as evidenced from the presence of Kiessig fringes around the [111] film peaks. X-ray

scans taken from films grown at VTIP foreline pressures in the range of 78 mTorr to 84 mTorr (labeled in orange) had pronounced Kiessig fringes indicating abrupt film surfaces, which faded away for larger ( $P_{VTIP} = 86$  mTorr) and smaller ( $P_{VTIP} = 74,76$  mTorr) VTIP foreline pressures (labeled in blue). A reciprocal space map taken around the 303 asymmetric diffraction peak of the SrVO<sub>3</sub>(111) film grown at  $P_{VTIP} = 81$  mTorr revealed that the films inside the growth window were coherently strained, as shown in Figure 7-2(b). Films grown outside the growth window were found to partially relax. Each high-resolution X-ray  $2\theta$ - $\omega$  scan was fit using GenX<sup>236</sup> to determine the film thickness and the interplanar spacing  $d_{111}$ . The interplanar spacing was directly compared to those of [001]-oriented SrVO<sub>3</sub> films which were grown immediately after the [111]-oriented growth series. The trends of  $d_{111}$  and  $d_{001}$  are shown as a function of  $P_{VTIP}$  in Figure 7-2(c). The interplanar spacings extracted for both [111]-oriented and [001]-oriented films were also compared to the calculated lattice parameter of strained SrVO3 using the experimentally determined Poisson ratio of 0.24 for SrVO<sub>3</sub>.<sup>10,324</sup> For [001]-oriented films, a clear growth window was observed as d<sub>001</sub> reached a minimum out-of-plane interplanar spacing for  $P_{VTIP}$  values from 78 mTorr to 83 mTorr, similar to previous studies and near the calculated lattice parameter of 3.824 Å for strained SrVO<sub>3</sub>(001).<sup>10,177</sup> On the other hand, the out-of-plane interplanar spacing of [111]-oriented films near the calculated value of  $d_{111}=2.209$  Å remained relatively unchanged as a function of VTIP pressure, suggesting that defect accommodation mechanisms incorporating excess Sr and V into the films were present in [111]-oriented  $SrVO_3$  that did not increase the out-of-plane lattice parameter and that were unavailable for [001]-oriented films.



Figure 7-2: (a) High resolution  $2\theta - \omega$  XRD scans around the 111 diffraction peaks of LSAT and SrVO<sub>3</sub> as a function of  $P_{VTIP}$ . (b) X-ray reciprocal space map around the 303-diffraction peak of a SrVO<sub>3</sub>(111) film grown at 81mT. (c) Interplanar spacing of [001]- and [111]-oriented SrVO<sub>3</sub> films extracted from high resolution  $2\theta - \omega$  XRD scans using GenX. Calculated interplanar spacings are shown as dotted lines for each orientation. (d) Root mean square roughness extracted from AFM micrographs as a function of  $P_{VTIP}$  outlining the growth window for [111]-oriented SrVO<sub>3</sub>. (e) Corresponding AFM micrographs of films grown at different  $P_{VTIP}$ . Surface height profiles are shown for characteristic Sr-rich, stoichiometric, and V-rich films where height is given in nanometers. Figure reproduced from reference.<sup>342</sup>

To obtain further insights into why the out-of-plane interplanar spacing remained unchanged for such a wide range of growth parameters, atomic force microscopy (AFM) images were taken to map the film surface morphology as a function of  $P_{VTIP}$ . The RMS roughness values as a function of  $P_{VTIP}$  along with representative AFM images are shown in Figure 7-2(d) and (e), respectively. Films grown at VTIP pressures between 78 mTorr and 84 mTorr had an atomic terrace morphology with a RMS surface roughness of about (0.2±0.1) nm. It is remarkable that this favorable surface morphology was aligned with the SrVO<sub>3</sub> growth window for [001]-oriented films.

 $SrVO_3(111)$  films grown outside the  $SrVO_3(001)$  growth window revealed regularly shaped, rather deep holes with lateral dimensions on the order of several tens of nanometers. These holes were separated by otherwise atomically smooth film areas laterally expanding over hundreds of nanometers. Theses regularly shaped holes were primarily oriented in the same direction, suggesting that specific crystallographic directions gave rise to the facets defining the holes' circumference. Films grown under Sr-rich conditions had hexagonal shaped holes, while films grown under V-rich conditions had primarily triangular shaped holes which were about half the lateral size compared to those found in Sr-rich films. These holes allowed films grown under Srrich and V-rich conditions another avenue to release stress induced by increased levels of cation nonstoichiometry in the film plane rather than by increasing the out-of-plane interplanar spacing. Therefore, the formation of these holes rendered the out-of-plane interplanar spacing irrelevant for the determination of stoichiometric growth conditions for [111]-oriented SrVO<sub>3</sub> films. Instead, the pronounced increase in film roughness due to the hole formation gave rise to a growth-window like relation, as shown in Figure 7-2(d). The growth window from surface roughness data of SrVO<sub>3</sub>(111) films closely matched the width and position of the growth window found for  $SrVO_3(001)$  films using the interplanar spacing in the out-of-plane direction  $d_{001}$  (see Figure 7-2(c)). The close resemblance of the growth windows for  $SrVO_3(111)$  and  $SrVO_3(001)$  films suggested that the kinetic processes at play were not affected by the film surface orientation.

While at first it seemed strange that a surface sensitive technique such as RHEED was not able to identify a film surface with nanometer deep corrugations, the specific, rather seldom film surface morphology found for SrVO<sub>3</sub>(111) grown under non-stoichiometric conditions, namely holes formed from inward oriented facets with lateral dimension on the order of tens of nanometers and hundreds of nanometers apart can indeed give the false sense of a smooth, coalesced film via RHEED. Streaky RHEED patterns occurred since the surface was quite smooth overall. Spotty RHEED patterns typically arise if electrons transmit through the crystal, e.g. when protrusions are present or the film growth occurs in island mode. If holes are present in the film the majority of the electrons get diffracted on the overall smooth surface and only a small portion transmits through the edges of the hole that are sufficiently electron transparent. The contribution of these electrons gave rise to the intensity modulation along the diffraction rods, which occurred in the  $2^{nd}$  order diffraction rod in RHEED pattern for Sr-rich and V-rich growth conditions along both azimuths. Therefore, stoichiometric growth can still be monitored using this in-situ technique, the Sr-rich growth window edge is found by a change in surface reconstruction from 6-fold to 7-fold along the  $\langle 11-2 \rangle$  azimuth accompanied with a pronounced intensity modulation along the diffraction rods, while at the V-rich growth window edge the intensity modulations emerged in addition to the blurred surface reconstructions.

## 7.3 Structural characterization of [111]-oriented SrVO<sub>3</sub> using STEM

To gain further insights into the accommodation of defects in SrVO<sub>3</sub>(111) films with large non-stoichiometries, a Sr-rich, stoichiometric, and V-rich film were imaged in cross section using HAADF-STEM performed in a ThermoFisher Titan<sup>3</sup> S/TEM by Leixin Miao and Professor Nasim Alem. For this imaging, the operating voltage was 300 kV with a beam current of 0.1 nA and the probe convergence angle was 30 mrad. The aberration correctors were tuned to achieve a spatial resolution of about 70 pm.

Low magnification survey scans of the Sr-rich, stoichiometric, and V-rich film are shown in Figure 7-3(a-c) and higher magnification images are shown in Figure 7-3(d-e). Low magnification images of the Sr-rich film revealed large regions of uniformly spaced Ruddlesden-Popper (RP)-like stacking faults that are known to occur in Sr-rich SrVO<sub>3</sub>(001) films. This phase appeared to be similar to those observed in  $Sr_3V_2O_7$ ;<sup>346,347</sup> however, in this case the orientation of the stacking faults were along the [111] direction. Rock salt like AO stacking faults oriented along the [111] direction in ABX<sub>3</sub> perovskites have been previously observed in halide perovskites, such as Cs<sub>3</sub>B<sub>2</sub>X<sub>9</sub> (B=Sb, In, Bi and X=Cl, Br, I),<sup>348–350</sup> as well as organic perovskites such as [NH(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>Sb<sub>2</sub>Cl<sub>9</sub>,<sup>351,352</sup> whereby long-range vacancy order and sizeable bond distortion were observed in the former case, and where the local degrees of freedom of organic molecules allowed to stabilize the layered structure in the latter case. Given the nominal stacking sequence of the Srrich phase, namely two perovskite blocks with layers B-AX<sub>3</sub>-B-AX<sub>3</sub> followed by the stacking fault AX<sub>3</sub>, the general chemical formula of A<sub>3</sub>B<sub>2</sub>X<sub>9</sub> is expected; however unlike in the two cases of halide and organic perovskites, the X anion is doubly charged for the oxide case suggesting the presence of an oxygen vacancy ordered phase of either Sr<sub>3</sub>V<sub>2</sub>O<sub>8</sub> with vanadium assuming a highest possible oxidation state 5+, or Sr<sub>3</sub>V<sub>2</sub>O<sub>7</sub> with V<sup>4+</sup> on the B-site. As RP stacking faults have been observed for oxide films, it is much more likely that this phase is simply vanadium orthovanadate.

STEM images taken from stoichiometric SrVO<sub>3</sub>(111) films are shown in Figure 7-3(b), (e), and (h). The stoichiometric films were found to have the expected cubic perovskite structure and no large-scale defects or structural domains were observed. The higher magnification image revealed virtually no defects, indicating a phase-pure, stoichiometric, and high-quality film. The interface between the film and substrate was observed to be abrupt due to the sharp Z-contrast within one unit cell. Stoichiometric films were further examined using annular bright field (ABF) STEM to investigate the arrangement of the oxygen anions. No displacements or octahedral rotations were observed as shown in Figure 7-3(h).



Figure 7-3: Low magnification STEM images of (a) Sr-rich, (b) stoichiometric, and (c) V-rich thin films grown on LSAT along the (10-1) zone axis. (d) High magnification image of the Sr-rich film where the Ruddlesden-Popper faults in the layered Sr-rich phase were normal to the [111]-direction. Inset shows the orientation of the stacking fault layers. (e) Stoichiometric SrVO<sub>3</sub> forming an atomically sharp interface with the substrate. The inset shows the orientation of the SrVO<sub>3</sub>. (f) Wedge-shaped holes found in V-rich SrVO<sub>3</sub> where the crystalline facets contain (101) and (010) directions as highlighted. (g) High magnification image of the Sr-rich film away from large scale defects demonstrating a high-quality interface. (h) ABF-STEM image of the V-rich film away from large scale defects demonstrating a high-quality interface. Figure reproduced from reference.<sup>342</sup>

Films grown under V-rich conditions were found to exhibit wedge-shaped holes lined with amorphous material, as shown in Figure 7-3(c). The higher magnification image shown in Figure 7-3(f) revealed crystalline facets that contained <010> and <101> directions. The triangular shape of the holes seen in AFM suggested that a specific family of planes formed the facets. It was suspected that the crystal facets formed are {001} as they are the lowest energy facets in perovskites; however, more in-depth analysis is required to unambiguously determine the geometry of the wedge-shaped holes. Aside from these two prominent features in Sr-rich and V-rich films, no other extended defects were observed. Away from these large-scale defects, nonstoichiometric films had abrupt interfaces with the substrate, as shown in Figure 7-3(g) and (i), indicating that an increasing degree of non-stoichiometry was accumulated on the growth front first before it was incorporated into the film. The STEM results suggested that Sr-rich films accommodated excess Sr into RP-like phases while V-rich films incorporated excess V into amorphous regions forming {001} facetted growth, giving rise to an out-of-plane interplanar spacing that did not vary as a function of  $P_{VTIP}$  as was observed in XRD measurements in Figure 7-2(c).



Figure 7-4: EDS measurements of the Sr-rich, stoichiometric, and V-rich [111]-oriented SrVO<sub>3</sub> films for Sr, V, O, La, and Ta. Figure reproduced from reference.<sup>342</sup>

Composition mapping of each film was then completed using energy dispersive X-ray spectroscopy (EDS). The EDS mapping was acquired with a beam current of 0.09 nA and a dwell time of 0.1  $\mu$ s over 256×256 pixels in each map. Each map was acquired with the automatic drift-correction turned on in the Bruker software and the acquisition time for each map was between 8

The transition between the perovskite region and the layered Sr-rich phase was most prominent in the distribution of V as it was more spaced out due to the formation of the SrO stacking faults in the Sr-rich phase. The Sr-rich and stoichiometric films had a film/substrate interface that was sharply defined by the V, La, and Ta distributions. The small amounts of V in the substrate and La and Ta in the film are expected from the FIB preparation. Instead of displaying the V-rich film/substrate interface which was also sharply defined, the elemental makeup of the amorphous region around the holes is shown. The amorphous material covering the facets primarily consisted of V, which was suspected to act as an amorphizing agent forming a cap, which prevented the advancement of epitaxial growth along the out-of-plane direction and instead gave rise to faceted growth.

# 7.4 Optical properties and RRR quality of [111]-oriented SrVO<sub>3</sub>

Following the successful growth and identification of high quality, stoichiometric [111]oriented SrVO<sub>3</sub> films, the optical and electronic properties were investigated and compared to those of [001]-oriented films. The refractive index and extinction coefficient for [111]- and [001]oriented SrVO<sub>3</sub> thin films grown by *h*MBE, shown in Figure 7-5(a) and (b), respectively, were characterized using spectroscopic ellipsometry performed by Dr. Alexej Pogrebnyakov. Two samples of equivalent thickness (47 nm and 46 nm, determined by X-ray diffraction) and a significantly thinner SrVO<sub>3</sub> (111) film (17 nm) were compared to a 20-nm-thick SrVO<sub>3</sub>(001) film. No significant sample to sample variations were found for the refractive index or the extinction coefficient in the wavelength interval from 200 nm to 1700 nm. As expected from the isotropy of the cubic system, the extinction coefficient followed the same trend as [001]-oriented SrVO<sub>3</sub> where a region with low *k* was confined by substantially larger values of the extinction coefficient in the infrared region due to the free carrier reflection response, and in the ultraviolet range from optical absorption due to interband transitions, leaving a spectral window of high optical transparency in the visible range.<sup>53</sup> The extinction coefficient for [111]-oriented samples was significantly lower in the visible range from 450 nm to 750 nm suggesting a higher optical transmission. This effect was likely due to different strain states of the films. The corresponding optical absorption coefficient *a* and optical transmission coefficient ( $T = e^{-\alpha t}$ ) are shown in Figure 7-5(c) and (d), respectively. Here, [111]-oriented SrVO<sub>3</sub> is shown to have a higher optical transmission in the visible range coupled with nearly the same room temperature resistivity indicate that SrVO<sub>3</sub> retains a high performance as a transparent conductor irrespective of the film orientation.



Figure 7-5: The optical constants (a) *n* and (b) *k*, (c) the absorption coefficient  $\alpha$ , and (d) the optical transmission for [111]- and [001]-oriented SrVO<sub>3</sub> thin films grown inside the growth window. (e) Temperature dependent resistivity of *h*MBE grown [111]-oriented SrVO<sub>3</sub> compared to the best [001]-oriented SrVO<sub>3</sub> grown by other methods. (f) Comparison of residual resistivity ratios for SrVO<sub>3</sub>(111) grown by *h*MBE and PLD<sup>341</sup> as well as SrVO<sub>3</sub>(001) grown by *h*MBE,<sup>10</sup> MBE,<sup>318</sup> and PLD.<sup>315</sup> Figure reproduced from reference.<sup>342</sup>

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While it has been shown that films grown inside the growth window had no visible defects in STEM, the material quality was further verified by measuring the temperature dependent resistivity to determine the RRR. The dominant scattering mechanism at low temperature arises from defects in the film while phonon scattering limits the carrier mobility at room temperature; therefore, the RRR is an ideal metric for determining material quality. The temperature dependent resistivity of the [111]-oriented SrVO<sub>3</sub> grown at  $P_{VTIP}$ =81 mTorr is shown in Figure 7-5(e) in comparison to highest quality [001]-oriented SrVO<sub>3</sub> grown by MBE<sup>318</sup> and PLD.<sup>315</sup> The resistivity of [111]-oriented SrVO<sub>3</sub> was found to be lower at all temperatures, ranging from a room temperature resistivity of 2.8×10<sup>-5</sup>  $\Omega$  cm to a residual resistivity of 1.3×10<sup>-6</sup>  $\Omega$  cm resulting in a RRR of 21. The RRR of [111]-oriented SrVO<sub>3</sub> is shown in comparison to [111]-oriented SrVO<sub>3</sub> grown by PLD,<sup>341</sup> the highest quality 001-oriented SrVO<sub>3</sub> grown by MBE<sup>318</sup> and PLD,<sup>315</sup> and ultraclean SrVO<sub>3</sub> grown by *h*MBE<sup>10</sup> in Figure 7-5(f). The [111]-oriented SrVO<sub>3</sub> grown in this study was found to have a significantly higher quality than any film grown in any orientation by PLD and MBE, signifying that even in an unfavorable growth direction, *h*MBE remains an ideal growth method.

## 7.5 Temperature dependent of electonic transport of [111]-oriented SrVO<sub>3</sub>

In order to determine the effects of film orientation, the temperature dependent electronic properties of [111]- and [001]-oriented  $SrVO_3$  films grown by *h*MBE were compared in detail. The temperature dependent resistivity for films with both orientations is shown in Figure 7-6(a). The resistivity of [001]-oriented  $SrVO_3$  was consistently below that of [111]-oriented films, suggesting that additional scattering sites were present at all temperatures in [111]-oriented films. In both cases, the resistivity was found to saturate at low temperature to a constant value and did not show any upturn from localization effects. The temperature dependent resistivities were further analyzed

by plotting  $\frac{d\rho}{dT^2}$  as a function of T, fully eliminating the dependence of the residual resistivity and allowing the extraction of the Fermi liquid like regimes which have been shown to exist in SrVO<sub>3</sub> in Chapter 6. Both films revealed the presence of a Fermi liquid like regime at low temperatures extending to about 20 K, followed by a transient regime with no consistent resistivity scaling. At higher temperatures, both films resumed a T<sup>2</sup> dependence; however, [111]-oriented SrVO<sub>3</sub> reentered into a regime revealing a dominant scattering mechanism at approximately 40 K compared to around 120 K for [001]-oriented SrVO<sub>3</sub>, adding further uncertainty to this high temperature scaling region's origin.



Figure 7-6: (a) Temperature dependent resistivity of [111]- and [001]-oriented SrVO<sub>3</sub> grown by *h*MBE. (b) First derivative of resistivity with respect to  $T^2$  where constant regions indicate Fermi liquid like  $T^2$  resistivity scaling.

Temperature dependent Hall measurements were performed to extract the transverse Hall resistance  $R_{xy}$  and the longitudinal resistance  $R_{xx}$ . The longitudinal resistance is shown in Figure 7-7 for films of both orientations in terms of the magnetoresistance:  $MR = (R_{xx}(B) - R_{xx}(0))/R_{xx}(0) * 100\%)$ . At 2 K, [001]-oriented SrVO<sub>3</sub> reached a MR of nearly 300% at 8 T while [111]-oriented films barely exceeded 40%. In addition, [111]-oriented films were observed to have a negative magnetoresistance at low fields, similar to that arising from weak localization. Weak localization typically arises from the interference of carriers traveling in self-intersecting paths.<sup>353</sup> It is peculiar to observe such a weak-localization effect in a three-dimensional metallic system as

they are typically only observed in 2D materials. For weak localization to occur in a 3D system, carriers would need to be restricted to primarily travel in a plane as the additional dimension reduces the number of potential self-intersecting pathways.



Figure 7-7: Temperature dependent magnetoresistance for (a) [111]-oriented and [001]-oriented SrVO<sub>3</sub>. Low field magnetoresistance for (a) [111]-oriented SrVO<sub>3</sub> demonstrating the onset of weak localization and (b) [001]-oriented SrVO<sub>3</sub> with no localization.

The Hall resistance for [111]- and [001]-oriented SrVO<sub>3</sub> is shown in Figure 7-8(a) and (b) respectively. Films of both orientations were found to display distinct nonlinearities at temperatures below 100 K. While [001]-oriented SrVO<sub>3</sub> has previously been shown to have nonlinearities in  $R_{xy}$ , see Chapter 6, [111] films had significantly more pronounced nonlinearities at higher magnetic field strengths. Irrespective of film orientation, a linear transverse resistance was observed at room temperature corresponding to carrier concentrations of  $2.0 \times 10^{22}$  cm<sup>-3</sup> and  $2.5 \times 10^{22}$  cm<sup>-3</sup> and mobilities of 8.9 and 7.1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for [001]- and [111]-oriented films, respectively. As temperature

decreased, the slope for [111] films decreased, transitioning cleanly into an anomalous Hall effect like shape while the slope for [001] films increased.



Figure 7-8: Temperature dependence of the transverse Hall resistance  $R_{xy}$  for (a) [111]- and (b) [001]-oriented SrVO<sub>3</sub>.

Distinct nonlinearities in the Hall resistance, such as those shown here, are known to arise from two effects: the anomalous Hall effect (AHE) due to broken time-reversal symmetry and multicarrier transport. A theory of AHE was developed by Karplus and Luttinger who demonstrated that the additional Hall current perpendicular to the electric field was a result of spin-orbit interactions.<sup>354</sup> These interactions can arise from side jump scattering from impurity atoms, intrinsic deflections due to crystalline potentials from Berry curvatures, or skew scattering.<sup>355</sup> While the first two interactions require the presences of magnetic moments and are typically observed in ferromagnetic materials, skew scattering can arise due to spin orbit coupling of magnetic or nonmagnetic impurities. The contributions of each effect are unfortunately difficult to separate in experimental measurements. Traditionally, the contribution for skew scattering is argued to be linear with  $\sigma_{xx}$  while the other two contributions are linear with  $\sigma_{xx}^{2}$ .<sup>357</sup>

The AHE component of the transverse Hall resistance is captured by the anomalous Hall resistance  $R_{xy}^{AHE}$  shown in Eq. 7.1.

$$R_{xy}(B) = \frac{B}{ne} + R_{xy}^{AHE} * Tanh(\frac{B}{B_c})$$
 Eq. 7.1

The experimental, temperature dependent Hall resistance of [111]-oriented SrVO<sub>3</sub> was fit using Eq. 7.1 where the traditional Hall effect was assumed to arise from a single electron carrier channel. The extracted values of  $R_{xy}^{AHE}$  were then converted into the anomalous Hall conductivity  $\sigma_{AHE}$  using the resistivity tensor relationship and plotted as a function of  $\sigma_{xx}^2$  in Figure 7-9(a). [111]oriented SrVO<sub>3</sub> was observed to demonstrate the expected linear relationship between the anomalous Hall conductivity and  $\sigma_{xx}^2$ ; however, when compared to other materials in Figure 7-9(b), it was found to have higher values of  $\sigma_{AHE}$  than any other material system.<sup>358</sup> This completely unexpected result seems to indicate that the nonlinearities in  $R_{xy}$  do not arise from the AHE as none of the contributing factors are expected to arise in SrVO<sub>3</sub>.



Figure 7-9: (a) The anomalous Hall conductivity  $\sigma_{AHE}$  as a function of  $\sigma_{xx}^2$  demonstrating a linear relationship. (b)  $\sigma_{AHE}$  as a function of  $\sigma_{xx}$  comparing [111]-oriented SrVO<sub>3</sub> with other materials. Reproduced from reference.<sup>358</sup>

To further investigate the potential contributions of magnetism to the AHE in SrVO<sub>3</sub>, samples of both orientations were characterized using X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) at the  $L_{2,3}$  edges (2p core levels) which provide an element-specific probe for the ionic valence state and magnetic moment, respectively.<sup>359,360</sup>

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Measurements were performed by Professor T. Hesjedal and Professor G. van der Laan using the portable octupole magnet system (POMS) on beamline I10 at the Diamond Light Source (Didcot, UK) using luminescence yield (LY) detection. In LY mode, transmitted X-rays that are not absorbed in the thin film sample give rise to X-ray-excited optical luminescence in an appropriate substrate, such as MgO or LSAT. The emitted optical photons, which exit through a hole in the back of the sample holder, are detected by a photodiode behind the sample. Like transmission, LY probes the X-ray absorption over the entire depth of the thin film sample. This detection mode of XAS is advantageous compared to total-electron yield (TEY) detection, which only has a sampling depth of 3-5 nm.<sup>359</sup> For these measurements, the sample surface was normal to incident X-ray beam and along the applied magnetic field direction. The X-rays were 100% circularly polarized and the measurements were completed between 20 and 90 K where the nonlinearities in the Hall resistance were observed.

The XAS was recorded across the V  $L_3$  (~516 eV) and  $L_2$  (~523 eV) absorption edges, directly probing the unoccupied 3*d* states of the vanadium. The XMCD spectrum was then obtained as the difference between the two XAS spectra with the circular polarization vector parallel and antiparallel to the external magnetic field direction. To reduce the experimental asymmetries for the 80 K data, the XMCD was obtained using the four different XAS spectra with circular positive and negative polarization and with positive and negative magnetization direction.

Samples of SrVO<sub>3</sub> grown on (001) and (111) LSAT substrates were measured in LY mode. As a reference sample for the energy calibration, a fresh batch of  $V_2O_5$  powder was used, which was mixed with graphite powder and then pressed in the form of a disc. This sample was measured in TEY mode with the assumption that the surface composition of  $V_2O_5$  was similar to the bulk.



Figure 7-10: Normalized V  $L_{2,3}$  XAS spectra for [111]- and [001]-oriented SrVO<sub>3</sub> thin films in comparison to a V<sub>2</sub>O<sub>5</sub> reference sample. Arrows indicate additional shoulders of the V  $L_{2,3}$  peaks.

The V  $L_{2,3}$  XAS spectra for all three samples were normalized to the V  $L_3$  peak height and are shown in Figure 7-10. The spectra for films of both orientations were very similar but differ from the V<sub>2</sub>O<sub>5</sub> reference spectrum. The peak maxima were almost at the same photon energy indicating the chemical shift between V<sub>2</sub>O<sub>5</sub> and SrVO<sub>3</sub> was negligible; however, the films displayed additional shoulders at lower energies (marked by arrows in the plot). A comparison of reference oxides measured using electron energy loss spectroscopy can be found in Figure 1 of Gloter *et al.*,<sup>361</sup> which shows a shift to lower photon energy of 0.1 eV for VO<sub>2</sub> and 1.2 eV for V<sub>2</sub>O<sub>3</sub> with respect to the peak maximum in V<sub>2</sub>O<sub>5</sub>; however, subtle changes in the structure and crystal-field parameters can lead to larger photon energy shifts than 0.1 eV.<sup>362,363</sup> The SrVO<sub>3</sub> spectral shape was rather similar to that reported for VO<sub>2</sub>,<sup>364</sup> with V<sup>4+</sup> 3*d*<sup>1</sup>. Small differences in spectral shape were inevitably present due to a different degree of hybridization. From this analysis, the vanadium valence state in the SrVO<sub>3</sub> films was somewhere between 4+ and 5+.



Figure 7-11: XAS spectra of (a) [001]-oriented SrVO<sub>3</sub> and (b) [111]-oriented SrVO<sub>3</sub> for parallel and antiparallel alignment of circular polarization and magnetization direction under 500 mT applied field from 20 K to 90 K. The XMCD, or difference spectrum, of (c) [001]-oriented SrVO<sub>3</sub> and (d) [111]-oriented SrVO<sub>3</sub> which is seen to be zero within the detected limit.

The XAS spectra of [001]- and [111]-oriented SrVO<sub>3</sub> films are shown in Figure 7-11(a) and (b) respectively for parallel and antiparallel alignment of circular polarization and magnetization direction, measured between 20 and 90 K under 500 mT applied field after field cooling the sample from 120 K. The XAS spectra were obtained using  $-\ln(I_{LY}/I_0)$ , where  $I_{LY}$  is the luminescence yield and  $I_0$  is the incident X-ray beam intensity. The spectrum at 20 K was obtained by averaging over 24 repeats while the rest were averaged over 5 repeats. The curve was normalised to the off-edge slope (500-505 eV, not shown). A remaining signal in the difference spectrum between the two dichroic spectra across the  $L_{2,3}$  edges is shown in the XMCD spectra for [001]-and [111]-oriented SrVO<sub>3</sub> in Figure 7-11(c) and (d), respectively. Over the entire temperature range of

20-90 K, the upper limit of the spin moment extracted from the XMCD data was below the experimental detection limit which is  $m_{\rm S} < 0.01 \ \mu_{\rm B}/V$  atom. The vanishingly small value of the measured spin moment confirms the absence of any ferromagnetic order in SrVO<sub>3</sub>.

The absence of a magnetic moment in  $SrVO_3$  eliminates many of the potential contributions from the AHE; however, it does not preclude them entirely. As the anomalous Hall conductivity in Figure 7-9(b) is in the intrinsic region, the AHE may arise directly from a non-zero Berry curvature unaccompanied by a non-zero magnetic moment. Therefore, studies are currently ongoing to calculate the Berry curvature of  $SrVO_3$  to fully probe the potential contributions of the AHE in  $SrVO_3$ . While the contributions from the AHE are not yet fully conclusive, we will demonstrate that the significant changes and nonlinearities in  $R_{xy}$  can be entirely explained using multicarrier transport arising from a tilting in the Fermi surface orientation.

#### 7.6 Multicarrier fitting in [111]-oriented SrVO<sub>3</sub>

Multicarrier fitting of the Hall coefficient in [111]-oriented SrVO<sub>3</sub> was performed following the considerations used in the fitting of [001]-oriented SrVO<sub>3</sub> detailed in Chapter 6. In the case of [001]-oriented SrVO<sub>3</sub>, nonlinearities in the low temperature limit were explained using two electron channels and one hole channel. Identical multicarrier fitting procedures were applied here for [111]-oriented SrVO<sub>3</sub>. To demonstrate the robustness of these fits, the Hall resistance is shown for [111]-oriented SrVO<sub>3</sub> at 2 K up to  $\pm 14$  T with its corresponding fit in Figure 7-12(a).


Figure 7-12: (a) The transverse Hall resistance Rxy for [111]-oriented SrVO<sub>3</sub> at 2 K with the corresponding three carrier fit. A schematic of the Hall bar setup is inset. (b) Carrier mobility and (c) carrier concentration extracted for each carrier channel as a function of temperature.

Above 100 K, films of both orientations were fit using a single electron channel. At lower temperatures, [001] films only required the addition of a hole channel between 30 and 100 K while [111] films immediately required all three channels at 100 K. The extracted carrier concentrations and mobilities for the primary electron channel ( $n_1$ ), the secondary electron channel ( $n_2$ ), and the hole channel (p) are shown for films with both orientations in Figure 7-12(b) and (c) respectively. The primary electron channel for both channels was approximately  $2 \times 10^{22}$  cm<sup>-3</sup> at all temperatures but the mobility was nearly two orders of magnitude higher for [001]-oriented films. The major disparity between the two orientation arose from contributions of the two minor carriers. For [001]-oriented SrVO<sub>3</sub>, the secondary electron channel at low temperatures. This relation was almost exactly reversed for [111]-oriented SrVO<sub>3</sub>. Such a dramatic alteration was attributed to the change of the Fermi surface orientation with respect to the transport plane.

### 7.7 Orientation dependence of SrVO<sub>3</sub>'s Fermi surface

To investigate the effects of orientation on the transport properties of SrVO<sub>3</sub>, the Fermi surface was first calculated by Amartyajyoti Saha and Professor Turan Birol. The three sheets were calculated using a  $100 \times 100 \times 100$  grid of energy eigenvalues across the Brillouin zone. This grid was then interpolated to generate functions for the extraction of the energy and its gradient at all points on the Fermi surface. A zero-energy 3D mesh was then generated to represent the Fermi surface on which Fermi velocities and Fermi surface curvatures were calculated. The 2D Fermi surface curvature was calculated along slices of the Fermi surface parallel to the transport plane such that  $k_x$  and  $k_y$  were traced at constant  $k_z$  values. For each slice, a circle was fit to each point's neighbors. This radius vector of this circle along with the gradient function were then used to obtain the magnitude and sign of the 2D curvature at each point. While the determination of electron and hole like character requires a combination of the Fermi velocity and the Fermi surface curvature, only the curvature is dependent on the orientation; therefore, the curvature alone can be used to draw important observations of the orientation dependent transport.

The *k*-dependent 2D Fermi surface curvature for the individual sheets of [001]- and [111]oriented SrVO<sub>3</sub> are shown in Figure 7-13. The outermost 'jungle gym' and inner 'faceted' cube surfaces contained positive and negative curvatures leading to a potential mixture of electron and hole like character. For [001]-SrVO<sub>3</sub>, the vertical cylinder of the 'jungle gym' only contributed electrons to transport while the horizontal cylinders only contributed a few positive curvature orbits. Orbits containing negative curvatures were restricted to the intersections of the cylinders. The 'faceted' cube surface was primarily made up of electron orbits at the edges while only a few orbits contained negative curvature. The rough locations of orbits were similar for [111]-oriented SrVO<sub>3</sub>, albeit more evenly distributed across the surfaces. For example, all three cylinders for the outermost surface had an even distribution of positive curvature orbits. The innermost, 'rounded' cube surface had an entirely positive curvature for both orientations, solely contributing electrons to transport.



Figure 7-13: 2D Fermi surface curvature for (a) the outer 'jungle gym' surface, (b) the 'faceted' cube surface, and the (c) the 'rounded' cube surface for [001]-oriented SrVO<sub>3</sub> and (d-f) [111]-oriented SrVO<sub>3</sub>.

The analysis of the Fermi surface curvature shows that the simple tilting of complex Fermi surfaces can result in a striking differences of multi-carrier contributions to transport, resulting in a higher contribution of holes in [111]-oriented SrVO<sub>3</sub>. To quantify the contribution of this curvature redistribution, the inverse Hall coefficient was calculated using Ong's geometrical interpretation<sup>245</sup> as outlined in Section 3.2.4. Using the theoretical values calculated from DFT, the inverse Hall coefficient was calculated for films of both orientations using Eq. 3.38 with a constant relaxation time. The contributions to the numerator and denominator of Eq. 3.38 from each Fermi surface sheet for [001]- and [111]-oriented SrVO<sub>3</sub> are shown in Table 7-1 and Table 7-2 respectively.

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Fermi Surface Index	Numerator (cm <sup>-1</sup> )	Denominator (cm)
i – 'rounded' cube	$0.98 \times 10^{23}$	4.84×10 <sup>22</sup>
ii – 'faceted' cube	$1.18 \times 10^{23}$	4.89×10 <sup>22</sup>
iii – 'jungle gym'	$2.67 \times 10^{23}$	$3.69 \times 10^{22}$

Table 7-1: Contributions of each Fermi surface sheet shown in Figure 6-9 to the inverse Hall coefficient for [001]-oriented SrVO<sub>3</sub>.

Table 7-2: Contributions of each Fermi surface sheet shown in Figure 6-9 to the inverse Hall coefficient for [111]-oriented SrVO<sub>3</sub>.

Fermi Surface Index	Numerator (cm <sup>-1</sup> )	Denominator (cm)
i – 'rounded' cube	$1.94 \times 10^{23}$	$1.04 \times 10^{22}$
ii – 'faceted' cube	$2.37 \times 10^{23}$	$1.03 \times 10^{22}$
iii – 'jungle gym'	5.79×10 <sup>23</sup>	$8.45 \times 10^{22}$

These contributions resulted in a calculated inverse Hall coefficient of  $2.2 \times 10^{23}$  cm<sup>-3</sup> for [001]-oriented SrVO<sub>3</sub> and  $4.44 \times 10^{23}$  cm<sup>-3</sup> for [001]-oriented SrVO<sub>3</sub>. This difference arises only from geometric effects due to the difference in orientation of the Fermi surface with respect to the transport plane. This adjustment changes the scattering space trajectories, making them vary considerably between [001]- and [111]-oriented films, resulting in an orientation dependent inverse Hall coefficient. Further, in depth calculations of the *k*-dependent relaxation time would further verify the experimental trends shown in Section 7.6.

## 7.8 Concluding Remarks

In conclusion, we have demonstrated that [111]-SrVO<sub>3</sub> can be grown in a self-regulated growth regime for a wide range of VTIP pressures using hMBE. The growth window was found to be independent of the growth direction, indicating that the growth kinetics were largely unchanged. The formation of large-scale defects such as holes and layered Sr-rich phases under non-stoichiometric growth conditions rendered the out-of-plane lattice parameter to be an ineffective measure to determine the growth window position; therefore, the growth window boundaries were instead identified by RHEED and AFM measurements. Stoichiometric films inside the growth

window were found to be virtually defect-free in STEM and to have a high RRR of 21. The optical properties of [111]-SrVO<sub>3</sub> were found to be mostly independent of orientation albeit with a slightly reduced extinction coefficient in the visible range compared to  $SrVO_3(001)$ . Finally, [111]-oriented films were found to display intense nonlinearities in  $R_{xy}$  which were explained using an alteration in the multicarrier transport arising from orientation dependent Fermi surface curvature. This work demonstrates the ability to deposit highly crystalline perovskite materials along an unfavorable growth direction using a self-regulated, low energy growth technique which opens up opportunities to investigate the electronic, magnetic, and topological properties of [111]-oriented perovskites and heterostructures without obstructions from defects.

## **Chapter 8: Future Work**

Over the years of research conducted and described in this thesis, observations, trends, and conclusions have opened up new research avenues and have identified very promising opportunities that simply could not be pursued due to the limited time available for a single Ph.D. thesis. This chapter outlines some of the many new directions that have arisen from this work. This discussion is limited to the next steps of material integration into devices. First, the determination of the work function of SrNbO<sub>3</sub> will be covered. Then integration of TCOs into light emitting and photovoltaic devices will be discussed with a focus on GaN based LEDs and BaTiO<sub>3</sub> ferroelectric solar cells.

#### 8.1 Work function of SrNbO<sub>3</sub>

While the work in this thesis has demonstrated SrNbO<sub>3</sub>'s high figure of merit as a UV transparent conductor, over an order of magnitude higher than any competing UV transparent conductor, integration with UV LED devices requires additional levels of performance. For instance, the transparent conducting electrode's work function must be greater than that of the device material to prevent the formation of a large Schottky barrier. This becomes increasingly difficult for AlGaN based LEDs which have a bandgap ranging from 3.44 eV for pure GaN and 6.28 eV for pure AlN.<sup>365</sup>

Determination of a metal contact's work function is typically done measuring the C-V characteristics of a Schottky junction. The capacitance, C, arising from the depletion region formed in the semiconductor can first be related to the built-in potential at zero bias,  $V_{bi}$ , using Eq. 8.1 where  $N_D$  is the doping concertation of the semiconductor,  $\varepsilon_r$  is the dielectric constant of the doped semiconductor,  $\varepsilon_0$  is the vacuum permittivity, and V is the applied DC voltage.

$$\frac{1}{C^2} = \frac{2}{qN_D\varepsilon_r\varepsilon_0} (V_{bi} - V)$$
 Eq. 8.1

The work function of the metal contact,  $\phi_{metal}$ , can then be determined by correcting the built-in potential with the energy difference between the conduction band minimum and Fermi level of the semiconductor given by  $\xi$  as well as the electron affinity of the semiconductor,  $\chi$ , according to Eq. 8.2.

$$\phi_{metal} = V_{bi} + \chi + \xi \qquad \qquad \text{Eq. 8.2}$$

To determine the work function of SrNbO<sub>3</sub>, Schottky barrier structures were constructed by depositing 20-nm-thick SrNbO<sub>3</sub> on Nb-doped SrTiO<sub>3</sub> substrates with dopant levels ranging from 0.05% to 0.7%. Depositions followed the same conditions as outlined in Section 5.2, therefore the unstrained lattice parameter and Sr vacancy concentration was assumed to be similar. RHEED for each film is shown along the (100), (110), and (210) azimuths in Figure 8-1(a-d). While films grown on highly doped SrTiO<sub>3</sub> had high quality RHEED, similar to that observed in LSAT depositions, films grown on the lower doped SrTiO<sub>3</sub> had some 3D nature. Corresponding high resolution  $2\theta$ - $\omega$  XRD scans around the 002 SrTiO<sub>3</sub> substrate peak are shown in Figure 8-1(e). All films had out-of-plane lattice parameters of  $4.020\pm0.005$  Å and demonstrated pronounced thickness fringes indicating smooth interfaces and high-quality films.



Figure 8-1: RHEED images along the (100), (110), and (210) azimuths of  $Sr_xNbO_3$  grown on (a) 0.7%, (b) 0.5%, (c) 0.1%, and (d) 0.05% Nb doped SrTiO<sub>3</sub> substrates. (e) High resolution  $2\theta$ - $\omega$  X-ray scans of the 002 peaks of  $Sr_xNbO_3$  and Nb:SrTiO<sub>3</sub>.

While the films have been successfully deposited and structurally characterized, the final device patterning and electrical measurements have not yet been carried out. The remaining experimental procedure is as follows. Ohmic TiN contacts must be deposited on the SrNbO<sub>3</sub> films followed by patterning into 100 µm circular devices. A tri-layer Al/Ni/Au ohmic contact for Nb doped SrTiO<sub>3</sub> must then be deposited to form the diode.<sup>366,367</sup> The Schottky barrier height must then be extracted from the C-V characteristics as discussed above. Further verification of the work function could then be performed using XPS measurements.<sup>368</sup> While verification of a contact material's work function is important, it is sometimes more efficient to examine its effectiveness of a contact material on the desired structure as unexpected Fermi level pinning can drastically alter the expected performance.

### 8.2 Integration of correlated metals into devices

As many current UV LEDs are based on AlGaN structures, it is important to demonstrate the compatibility of the UV transparent conductor SrNbO<sub>3</sub> with these hexagonal nitrides. Preliminary tests were completed by using RF sputtering to deposit Sr<sub>x</sub>NbO<sub>3</sub> on thick GaN films. GaN has a hexagonal crystal structure with a=3.16 Å and c=5.125 Å;<sup>369</sup> therefore, SrNbO<sub>3</sub> would optimally arrange in the [111]-orientation even with the large lattice mismatch. While this thesis has previously demonstrated high quality growth of [111]-oriented SrVO<sub>3</sub>, the lattice mismatch here is large enough to lead to poor nucleation and growth, potentially leading to misoriented or polycrystalline growth.<sup>142</sup> In addition to these difficulties, the temperature of SrNbO<sub>3</sub> must be lower than the optimal conditions as the AlGaN buffer layer begins to degrade above 700°C, potentially compromising the GaN layer.<sup>370</sup>

RF sputtering was used to deposit a 40 nm Sr<sub>x</sub>NbO<sub>3</sub> film on a GaN film grown on a Si (111) wafer through the use of AlN/AlGaN buffer layers. Deposition was done at a substrate temperature of 700°C to preserve the integrity of the GaN structure, otherwise deposition conditions followed the procedures outlined in Section 5.2. A wide angle  $2\theta$ - $\omega$  XRD scan around the Si 111 peak, shown in Figure 8-2(a), includes the expected 0002 peaks for the GaN film and AlN/AlGaN buffer layers as well as 111 peak of Sr<sub>x</sub>NbO<sub>3</sub>. An additional Sr<sub>x</sub>NbO<sub>3</sub> 011 peak was observed, indicating some misorientation in the film as expected from the large lattice mismatch. An additional scan around the 0004 peaks of the GaN structure is shown in Figure 8-2(b) where the Sr<sub>x</sub>NbO<sub>3</sub> 222 peak was well defined. No other unexpected peaks were observed in wider range scans. RHEED for the GaN substrate and Sr<sub>x</sub>NbO<sub>3</sub> film is shown in along the (10-1) and (11-2), azimuths in Figure 8-2(c-d). The GaN surface was relatively hazy indicating a potential partial oxidation of the surface due to atmospheric exposure. The resulting Sr<sub>x</sub>NbO<sub>3</sub> film had a 3D pattern potentially arising from the large lattice mismatch and in part from the presence of (011) domains as indicated from XRD. These 3D reconstructions may have also been the result of nucleation issues from the contaminated

GaN surface as seen in RHEED. Since the typical cleaning using an oxygen plasma would be detrimental to the GaN surface, minimal cleaning was done to these substrates.



Figure 8-2: High resolution  $2\theta \cdot \omega$  X-ray scans around the (a) 0002 peaks of the GaN structures including the Si and Sr<sub>x</sub>NbO<sub>3</sub> 111 peaks and the (b) 0004 peaks of the GaN structures including the Sr<sub>x</sub>NbO<sub>3</sub> 222 peak. RHEED images along the (c) (10-1) and (d) (11-2) azimuths of Sr<sub>x</sub>NbO<sub>3</sub> grown on GaN. (e) AFM micrograph of the corresponding film with an RMS roughness of 0.84 nm. (f) Schematic of the structure (not to scale).

While this initial deposition was not ideal, many improvements can be made to enable a higher quality film. First, future substrates should be cleaned of any potential contaminants using either an HF etch or in-situ N<sub>2</sub> plasma cleaning. Next, low temperature nucleation could be used to promote a better epitaxial relationship.<sup>371</sup> Once the deposition conditions are optimized and high-quality growth with low contact resistance is achieved, a shift could be made to deposit Sr<sub>x</sub>NbO<sub>3</sub> as a contact material for deep UV AlGaN LED devices to determine the light extraction efficiency.

## 8.3 Perovskite based solar cells

While many LED structures are based on hexagonal materials, many solar cell structures are perovskite based. Many of these solar cell structures are based on halide perovskites such as CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub> which could potentially utilize SrNbO<sub>3</sub> or SrVO<sub>3</sub> as a bottom electrode even with their large lattice mismatch.<sup>372</sup> However, the most straightforward integration of these materials would be with ferroelectric based solar cells such as BaTiO<sub>3</sub> and LiNbO<sub>3</sub>.<sup>373</sup> While traditional solar cells use p-n junctions to generate electron/hole pairs, their generation is somewhat different in ferroelectric materials which utilize the bulk photovoltaic effect. These materials, which have a spontaneous polarization arising from the non-centrosymmetric displacement of the positive and negative charges in a unit cell, have been shown to generate photovoltages greater than their bandgaps. This has been attributed to an asymmetric momentum distribution of nonthermalized carriers. As these photoexcited carriers lose their energy, they uniformly 'shift' in the crystal resulting in a net photocurrent.<sup>374</sup>

This type of solar cell has an added benefit of being transparent in the visible range, BaTiO<sub>3</sub> for instance has a bandgap of 3.2 eV.<sup>375</sup> Combing this with the transparent conductors discussed in this work would enable a fully transparent solar cell which could be invisibly integrated into windows and other surfaces. BaTiO<sub>3</sub> has a perovskite structure with a tetragonal distortion having lattice parameters a=3.994 Å and c=4.034 Å, rendering it almost perfectly lattice matched with the Sr deficient SrNbO<sub>3</sub> discussed in this work. The straightforward synthesis of BaTiO<sub>3</sub> using either hMBE<sup>216</sup> or sputtering<sup>376</sup> makes these devices well suited to be synthesized in the MBE/sputter growth cluster at Penn State.

# References

- 1. Chen, C.-W., Choe, J. & Morosan, E. Charge density waves in strongly correlated electron systems. *Reports Prog. Phys.* **79**, 084505 (2016).
- Rau, J. G., Lee, E. K.-H. & Kee, H.-Y. Spin-Orbit Physics Giving Rise to Novel Phases in Correlated Systems: Iridates and Related Materials. *Annu. Rev. Condens. Matter Phys.* 7, 195–221 (2016).
- 3. Alloul, H., Bobroff, J., Gabay, M. & Hirschfeld, P. J. Defects in correlated metals and superconductors. *Rev. Mod. Phys.* **81**, 45–108 (2009).
- 4. Wan, X., Turner, A. M., Vishwanath, A. & Savrasov, S. Y. Topological semimetal and Fermi-arc surface states in the electronic structure of pyrochlore iridates. *Phys. Rev. B Condens. Matter Mater. Phys.* **83**, 205101 (2011).
- 5. Picozzi, S. & Ederer, C. First principles studies of multiferroic materials. *J. Phys. Condens. Matter* **21**, 303201 (2009).
- 6. Wang, Z. *et al.* Fermi liquid behavior and colossal magnetoresistance in layered MoOCl<sub>2</sub>. *Phys. Rev. Mater.* **4**, 041001 (2020).
- Kobayashi, R. *et al.* Dimer-Mott and charge-ordered insulating states in the quasi-onedimensional organic conductors δp' - And δc' -(BPDT-TTF)<sub>2</sub>ICl<sub>2</sub>. *Phys. Rev. B* 96, 115112 (2017).
- 8. Schlom, D. G., Chen, L.-Q., Pan, X., Schmehl, A. & Zurbuchen, M. A. A Thin Film Approach to Engineering Functionality into Oxides. *J. Am. Ceram. Soc.* **91**, 2429–2454 (2008).
- 9. Jalan, B., Allen, S. J., Beltz, G. E., Moetakef, P. & Stemmer, S. Enhancing the electron mobility of SrTiO<sub>3</sub> with strain. *Appl. Phys. Lett.* **98**, 132102 (2011).
- 10. Moyer, J. A., Eaton, C. & Engel-Herbert, R. Highly Conductive SrVO<sub>3</sub> as a Bottom Electrode for Functional Perovskite Oxides. *Adv. Mater.* **25**, 3578–3582 (2013).
- 11. Kotliar, G. & Vollhardt, D. Strongly Correlated Materials: Insights From Dynamical Mean-Field Theory. *Physics Today* vol. 57 53–59 (2004).
- 12. De Boer, J. H. & Verwey, E. J. W. Semi-conductors with partially and with completely filled 3d-lattice bands. *Proc. Phys. Soc.* **49**, 59–71 (1937).
- 13. Mott, N. F. The basis of the electron theory of metals, with special reference to the transition metals. *Proc. Phys. Soc. Sect. A* **62**, 416–422 (1949).
- 14. Maldague, P. F. Optical spectrum of a Hubbard chain. *Phys. Rev. B* 16, 2437–2446 (1977).
- 15. Damascelli, A., Hussain, Z. & Shen, Z. X. Angle-resolved photoemission studies of the cuprate superconductors. *Reviews of Modern Physics* vol. 75 473–541 (2003).
- 16. Cuk, T. *et al.* A review of electron-phonon coupling seen in the high-T<sub>c</sub> superconductors by angle-resolved photoemission studies (ARPES). *Phys. status solidi* **242**, 11–29 (2005).
- 17. Yang, Z., Ko, C. & Ramanathan, S. Oxide Electronics Utilizing Ultrafast Metal-Insulator Transitions. *Annu. Rev. Mater. Res.* **41**, 337–367 (2011).
- 18. Zhou, Y. & Ramanathan, S. Mott Memory and Neuromorphic Devices. *Proceedings of the IEEE* vol. 103 1289–1310 (2015).
- 19. Haule, K. & Birol, T. Free Energy from Stationary Implementation of the DFT+DMFT Functional. *Phys. Rev. Lett.* **115**, 256402 (2015).

- 20. Park, H., Millis, A. J. & Marianetti, C. A. Computing total energies in complex materials using charge self-consistent DFT+DMFT. *Phys. Rev. B* **90**, 235103 (2014).
- Haule, K., Yee, C. H. & Kim, K. Dynamical mean-field theory within the full-potential methods: Electronic structure of CeIrIn<sub>5</sub>, CeCoIn<sub>5</sub>, and CeRhIn<sub>5</sub>. *Phys. Rev. B - Condens. Matter Mater. Phys.* 81, 195107 (2010).
- 22. Parcollet, O. *et al.* TRIQS: A toolbox for research on interacting quantum systems. *Comput. Phys. Commun.* **196**, 398–415 (2015).
- 23. Adler, R., Kang, C.-J., Yee, C.-H. & Kotliar, G. Correlated materials design: prospects and challenges. *Reports Prog. Phys.* 82, 012504 (2018).
- 24. Badeker, K. Concerning the electricity conductibility and the thermoelectric energy of several heavy metal bonds. *Ann. Phys.* **22**, 749 (1907).
- 25. Grundmann, M. Karl Bädeker (1877-1914) and the discovery of transparent conductive materials. *Phys. status solidi* **212**, 1409–1426 (2015).
- 26. Holland, L. & Siddall, G. The properties of some reactively sputtered metal oxide films. *Vacuum* **3**, 375–391 (1953).
- 27. McMaster, H. A. Electrically conducting films and method of application. (1947).
- 28. Mattox, D. M. & Mattox, V. H. 50 years of vacuum coating technology and the growth of the Society of Vacuum Coaters. (Society of Vacuum Coaters, 2007).
- 29. Reilly, J. F. U.S. Geological Survey, Mineral commodity summaries. (2019).
- 30. Graedel, T. E. *et al.* Criticality of metals and metalloids. *Proc. Natl. Acad. Sci.* **112**, 4257–4262 (2015).
- 31. Granqvist, C. G. Transparent conductors as solar energy materials: A panoramic review. *Sol. Energy Mater. Sol. Cells* **91**, 1529–1598 (2007).
- 32. Guillén, C. & Herrero, J. Transparent conductive ITO/Ag/ITO multilayer electrodes deposited by sputtering at room temperature. *Opt. Commun.* **282**, 574–578 (2009).
- 33. Wang, W. *et al.* Fabrication and thermo stability of the SnO<sub>2</sub>/Ag/SnO<sub>2</sub> tri-layer transparent conductor deposited by magnetic sputtering. *Ceram. Int.* **47**, 3548–3552 (2020).
- 34. Castillo, R. H. *et al.* Electrical percolation threshold evaluation of silver thin films for multilayer WO<sub>3</sub>/Ag/WO<sub>3</sub> transparent conductive oxide. *Mater. Lett.* **260**, 126913 (2020).
- 35. Ohara, M. *et al.* Characterization of Ag/ZnS/Ag multilayered film as transparent electrode for organic light-emitting diode. *Thin Solid Films* **704**, 137999 (2020).
- 36. Cho, E., Cha, S., Kim, Y. & Kim, C. Transparent and flexible electrode composed of a graphene multilayer interlayer-doped with MoO<sub>3</sub>. *Org. Electron.* **77**, 105437 (2019).
- Adamska, L., Sadasivam, S., Foley, J. J., Darancet, P. & Sharifzadeh, S. First-Principles Investigation of Borophene as a Monolayer Transparent Conductor. J. Phys. Chem. C 122, 4037–4045 (2018).
- 38. Wassei, J. K. & Kaner, R. B. Graphene, a promising transparent conductor. *Materials Today* vol. 13 52–59 (2010).
- 39. Liu, Y. *et al.* High-yield and rapid synthesis of ultrathin silver nanowires for low-haze transparent conductors. *RSC Adv.* 7, 4891–4895 (2017).
- 40. Niu, Z. *et al.* Ultrathin Epitaxial Cu@Au Core-Shell Nanowires for Stable Transparent Conductors. *J. Am. Chem. Soc.* **139**, 7348–7354 (2017).
- 41. Teo, M. Y. *et al.* Highly stretchable and highly conductive PEDOT:PSS/Ionic liquid composite transparent electrodes for solution-processed stretchable electronics. *ACS Appl. Mater. Interfaces* **9**, 819–826 (2017).

- 42. Wang, Y. *et al.* Properties of graphene-thermoplastic polyurethane flexible conductive film. *Coatings* **10**, 400 (2020).
- 43. Gueye, M. N., Carella, A., Faure-Vincent, J., Demadrille, R. & Simonato, J. P. Progress in understanding structure and transport properties of PEDOT-based materials: A critical review. *Progress in Materials Science* vol. 108 100616 (2020).
- McLellan, K., Yoon, Y., Leung, S. N. & Ko, S. H. Recent Progress in Transparent Conductors Based on Nanomaterials: Advancements and Challenges. *Adv. Mater. Technol.* 5, 1900939 (2020).
- 45. Ellmer, K. Past Achievements and Future Challenges in the Development of Optically Transparent Electrodes. *Nat. Photonics* **6**, 808–816 (2012).
- Preissler, N., Bierwagen, O., Ramu, A. T. & Speck, J. S. Electrical transport, electrothermal transport, and effective electron mass in single-crystalline In<sub>2</sub>O<sub>3</sub> films. *Phys. Rev. B - Condens. Matter Mater. Phys.* 88, 085305 (2013).
- 47. Elangovan, E. & Ramamurthi, K. Studies on optical properties of polycrystalline SnO<sub>2</sub>:Sb thin films prepared using SnCl<sub>2</sub> precursor. *Cryst. Res. Technol.* **38**, 779–784 (2003).
- 48. Esro, M. *et al.* Solution processed SnO<sub>2</sub>:Sb transparent conductive oxide as an alternative to indium tin oxide for applications in organic light emitting diodes. *J. Mater. Chem. C* **4**, 3563–3570 (2016).
- 49. Igasaki, Y. & Saito, H. The effects of deposition rate on the structural and electrical properties of ZnO:Al films deposited on (1120) oriented sapphire substrates. *J. Appl. Phys.* **70**, 3613–3619 (1991).
- 50. Lin, M. L. *et al.* High mobility transparent conductive Al-doped ZnO thin films by atomic layer deposition. *J. Alloys Compd.* **727**, 565–571 (2017).
- 51. Serway, R. A. *Principles of physics*. (Saunders College Pub, 1998).
- 52. Kasap, S. O. *Principles of Electronic Materials and Devices*. (McGraw-Hill Publishing Company, 2002).
- 53. Zhang, L. *et al.* Correlated Metals as Transparent Conductors. *Nat. Mater.* **15**, 204–210 (2016).
- 54. Chen, W., Thoreson, M. D., Ishii, S., Kildishev, A. V. & Shalaev, V. M. Ultra-thin ultrasmooth and low-loss silver films on a germanium wetting layer. *Opt. Express* 18, 5124– 5134 (2010).
- 55. Park, Y. *et al.* SrNbO<sub>3</sub> as Transparent Conductor in the Visible and Ultraviolet Spectrum. *Commun. Phys.* **3**, 102 (2020).
- 56. Mizoguchi, H. *et al.* Optical Properties of SrMoO<sub>3</sub> Thin Film. *J. Appl. Phys.* **87**, 4617–4619 (2000).
- 57. Paul, A. & Birol, T. Strain tuning of plasma frequency in vanadate, niobate, and molybdate perovskite oxides. *Phys. Rev. Mater.* **3**, 085001 (2019).
- 58. Stewart, M. K. *et al.* Optical study of strained ultrathin films of strongly correlated LaNiO<sub>3</sub>. *Phys. Rev. B* **83**, 75125 (2011).
- 59. Eguchi, R. *et al.* Fermi surfaces, electron-hole asymmetry, and correlation kink in a threedimensional Fermi liquid LaNiO<sub>3</sub>. *Phys. Rev. B - Condens. Matter Mater. Phys.* **79**, 115122 (2009).
- 60. Zabolotnyy, V. B. *et al.* Renormalized band structure of Sr<sub>2</sub>RuO<sub>4</sub>: A quasiparticle tightbinding approach. *J. Electron Spectros. Relat. Phenomena* **191**, 48–53 (2013).
- 61. Lichtenberg, F., Catana, A., Mannhart, J. & Schlom, D. G. Sr<sub>2</sub>RuO<sub>4</sub>: A metallic substrate

for the epitaxial growth of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>-δ. *Appl. Phys. Lett.* **60**, 1138–1140 (1992).

- 62. Koster, G. *et al.* Structure, physical properties, and applications of SrRuO<sub>3</sub> thin films. *Rev. Mod. Phys.* **84**, 253–298 (2012).
- 63. Allen, P. B. *et al.* Transport properties, thermodynamic properties, and electronic structure of SrRuO<sub>3</sub>. *Phys. Rev. B* **53**, (1996).
- 64. Stoner, J. L. *et al.* Chemical Control of Correlated Metals as Transparent Conductors. *Adv. Funct. Mater.* **29**, 1808609 (2019).
- 65. Fraser, D. B. & Cook, H. D. Highly Conductive, Transparent Films of Sputtered In<sub>2-x</sub>Sn<sub>x</sub>O<sub>3-y</sub>. *J. Electrochem. Soc.* **119**, 1368 (1972).
- 66. Haacke, G. New figure of merit for transparent conductors. J. Appl. Phys. 471, 41109–1048 (1976).
- 67. Zhang, X., Bradley, A. & Thibos, L. Achromatizing the human eye: the problem of chromatic parallax. *J. Opt. Soc. Am. A* **8**, 686–691 (1991).
- 68. Furubayashi, Y. *et al.* A transparent metal: Nb-doped anatase TiO<sub>2</sub>. *Appl. Phys. Lett.* **86**, 1–3 (2005).
- 69. Wang, H. F. *et al.* Transparent and conductive oxide films with the perovskite structure: La- and Sb-doped BaSnO<sub>3</sub>. *J. Appl. Phys.* **101**, 106105 (2007).
- Tashman, J. W. *et al.* Epitaxial growth of VO<sub>2</sub> by periodic annealing. *Appl. Phys. Lett.* 104, 063104 (2014).
- 71. Lee, H. N. S., McKinzie, H., Tannhauser, D. S. & Wold, A. The low-temperature transport properties of NbSe<sub>2</sub>. *J. Appl. Phys.* **40**, 602–604 (1969).
- 72. Myers, G. E. & Montet, G. L. Optical properties of single crystals of NbSe<sub>2</sub> and Nb<sub>1.04</sub>Se<sub>2</sub>. *J. Appl. Phys.* **41**, 4642–4649 (1970).
- 73. Thompson, A. H., Pisharody, K. R. & Koehler, R. F. Experimental study of the solid solutions Ti<sub>x</sub>Ta<sub>1-x</sub>S<sub>2</sub>. *Phys. Rev. Lett.* **29**, 163–166 (1972).
- 74. Schleife, A., Rinke, P., Bechstedt, F. & Van De Walle, C. G. Enhanced optical absorption due to symmetry breaking in TiO<sub>2(1-x)</sub>S<sub>2x</sub> alloys. *J. Phys. Chem. C* **117**, 4189–4193 (2013).
- 75. Levy, F. Electrical resistivity and Hall effect in TiSe<sub>2</sub> containing vanadium impurities. *J. Phys. C Solid State Phys.* **12**, 3725–3732 (1979).
- 76. Buslaps, T., Johnson, R. L. & Jungk, G. Spectroscopic ellipsometry on 1T-TiSe<sub>2</sub>. *Thin Solid Films* **234**, 549–552 (1993).
- Železný, V., Chvostová, D., Tarasenko, A., Klein, N. & Xi, X. X. Anisotropy in the optical response of superconducting MgB<sub>2</sub> films. *Thin Solid Films* 516, 7758–7763 (2008).
- Van Der Heide, P. A. M., Baelde, W., De Groot, R. A., De Vroomen, A. R. & Mattocks, P. G. Optical properties of ZrZn<sub>2</sub> from 0.6 to 3.8 eV. J. Phys. F Met. Phys. 14, 1745–1750 (1984).
- 79. Nakajima, M. *et al.* Unprecedented anisotropic metallic state in undoped iron arsenide BaFe<sub>2</sub>As<sub>2</sub> revealed by optical spectroscopy. *Proc. Natl. Acad. Sci. U. S. A.* **108**, 12238–12242 (2011).
- Hsu, L. S. & Wang, Y. K. Optical properties of Ni<sub>3</sub>Al, Ni<sub>3</sub>Ga, and Ni<sub>3</sub>In. J. Alloys Compd. 377, 29–33 (2004).
- 81. Fluitman, J. H. J. *et al.* Possible explanations for the low temperature resistivities of Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga alloys in terms of spin density fluctuation theories. *J. Phys. F Met. Phys.* **3**, 109–117 (1973).

- 82. Diffey, B. L. Solar ultraviolet radiation effects on biological systems. *Phys. Med. Biol.* **36**, 299–328 (1991).
- 83. ASTM E490 00a(2019) Standard Solar Constant and Zero Air Mass Solar Spectral Irradiance Tables. *ASTM International* https://www.astm.org/Standards/E490.htm (2021).
- 84. ASTM G173 03(2020) Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface. *ASTM International* https://www.astm.org/Standards/G173.htm.
- 85. Krutmann, J. & Morita, A. Mechanisms of Ultraviolet (UV) B and UVA Phototherapy. J. Investig. Dermatology Symp. Proc. 4, 70–72 (1999).
- 86. Singh, R. K. *et al.* The Patient's Guide to Psoriasis Treatment. Part 1: UVB Phototherapy. *Dermatology and Therapy* vol. 6 307–313 (2016).
- 87. Dalla Via, L. & Magno, S. M. *Photochemotherapy in the Treatment of Cancer. Current Medicinal Chemistry* vol. 8 (2001).
- 88. Schreiner, M. *et al.* UV-B-Induced Secondary Plant Metabolites Potential Benefits for Plant and Human Health. *CRC. Crit. Rev. Plant Sci.* **31**, 229–240 (2012).
- 89. Layani, M., Wang, X. & Magdassi, S. Novel Materials for 3D Printing by Photopolymerization. *Adv. Mater.* **30**, 1706344 (2018).
- 90. Nilsen, L. T. N., Hannevik, M. & Veierød, M. B. Ultraviolet exposure from indoor tanning devices: a systematic review. *Br. J. Dermatol.* **174**, 730–740 (2016).
- 91. Abe, S. *et al.* Master Recording for High-Density Disk Using 248 nm Laser Beam Recorder. *Jpn. J. Appl. Phys.* **41**, 1704–1708 (2002).
- 92. Dobbs, M., Kelsoe, J. & Haas, D. UV counterfeit currency detector. (2006).
- 93. Cruikshank, D., Merry, T. & Suzzarini, L. Security document with ultraviolet authentication security feature. (2010).
- 94. Downes, A. & Blunt, T. P. The Influence of Light upon the Development of Bacteria 1. *Nature* **16**, 218–218 (1877).
- 95. Douki, T. The variety of UV-induced pyrimidine dimeric photoproducts in DNA as shown by chromatographic quantification methods. *Photochemical and Photobiological Sciences* vol. 12 1286–1302 (2013).
- 96. Quek, P. H. & Hu, J. Indicators for photoreactivation and dark repair studies following ultraviolet disinfection. *J. Ind. Microbiol. Biotechnol.* **35**, 533–541 (2008).
- 97. Gates, F. L. A Study of the Bactericidal Action of Ultra Violet Light: I. The Reaction to Monochromatic Radiations. *J. Gen. Physiol.* **13**, 231–248 (1929).
- 98. *Guidelines for drinking-water quality, 4th edition, incorporating the 1st addendum.* https://www.who.int/publications/i/item/9789241549950 (2017).
- 99. Nieuwenhuijsen, M. J., Toledano, M. B., Eaton, N. E., Fawell, J. & Elliott, P. Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: A review. *Occupational and Environmental Medicine* vol. 57 73–85 (2000).
- 100. Gerchman, Y., Mamane, H., Friedman, N. & Mandelboim, M. UV-LED disinfection of Coronavirus: Wavelength effect. *J. Photochem. Photobiol. B Biol.* **212**, 112044 (2020).
- Heßling, M., Hönes, K., Vatter, P. & Lingenfelder, C. Ultraviolet irradiation doses for coronavirus inactivation - review and analysis of coronavirus photoinactivation studies. *GMS Hyg. Infect. Control* 15, (2020).
- 102. Gómez-López, V. M., Koutchma, T. & Linden, K. Ultraviolet and Pulsed Light Processing of Fluid Foods. in *Novel Thermal And Non-Thermal Technologies For Fluid*

Foods 185-223 (Elsevier Inc., 2012). doi:10.1016/B978-0-12-381470-8.00008-6.

- 103. Chen, J., Loeb, S. & Kim, J.-H. LED revolution: fundamentals and prospects for UV disinfection applications. *Cite this Environ. Sci. Water Res. Technol* **3**, 188 (2014).
- 104. Nagasawa, Y. & Hirano, A. A Review of AlGaN-Based Deep-Ultraviolet Light-Emitting Diodes on Sapphire. *Appl. Sci.* **8**, 1264 (2018).
- Hirayama, H. Recent Progress in AlGaN Deep-UV LEDs. in Light-Emitting Diode An Outlook On the Empirical Features and Its Recent Technological Advancements (InTech, 2018). doi:10.5772/intechopen.79936.
- 106. III-Nitride Ultraviolet Emitters. vol. 227 (Springer International Publishing, 2016).
- Balasubramanian, N. & Subrahmanyam, A. Electrical and Optical Properties of Reactively Evaporated Indium Tin Oxide (ITO) Films-Dependence on Substrate Temperature and Tin Concentration. J. Phys. D. Appl. Phys. 22, 206–209 (1989).
- 108. Lu, J. G. *et al.* Carrier Concentration Dependence of Band Gap Shift in n-Type ZnO:Al Films. *J. Appl. Phys.* **101**, (2007).
- 109. Refractive Index of ITO, Indium Tin Oxide. http://www.filmetrics.com/refractive-index-database/ITO/Indium-Tin-%0AOxide-InSnO.
- Shinohara, D. & Fujita, S. Heteroepitaxy of Corundum-Structured α-Ga<sub>2</sub>O<sub>3</sub> Thin Films on α-Al<sub>2</sub>O<sub>3</sub> Substrates by Ultrasonic Mist Chemical Vapor Deposition. *Jpn. J. Appl. Phys.* 47, 7311–7313 (2008).
- 111. Tsao, J. Y. *et al.* Ultrawide-Bandgap Semiconductors: Research Opportunities and Challenges. *Adv. Electron. Mater.* **4**, 1600501 (2018).
- Mi, W., Du, X., Luan, C., Xiao, H. & Ma, J. Electrical and Optical Characterizations of β-Ga<sub>2</sub>O<sub>3</sub> :Sn Films Deposited on MgO (110) Substrate by MOCVD. *RSC Adv.* 4, 30579 (2014).
- Chikoidze, E. *et al.* Electrical, Optical, and Magnetic Properties of Sn Doped α-Ga<sub>2</sub>O<sub>3</sub> Thin Films. *J. Appl. Phys.* **120**, 025109 (2016).
- 114. Poklonskii, N. A. & Vyrko, S. A. Electrostatic Model of Edge Luminescence of Heavily Doped Degenerate Semiconductors. *J. Appl. Spectrosc.* **69**, 434–443 (2002).
- 115. Pernot, C. *et al.* Development of High Efficiency 255-355 nm AlGaN-Based Light-Emitting Diodes. *Phys. status solidi* **208**, 1594–1596 (2011).
- Liu, M., Zhou, S., Liu, X., Gao, Y. & Ding, X. Comparative experimental and simulation studies of high-power AlGaN-based 353 nm ultraviolet flip-chip and top-emitting LEDs. *Jpn. J. Appl. Phys.* 57, 031001 (2018).
- 117. Mordor Intelligence. UV LED Market | Growth, Trends, and Forecasts (2020 2025). https://www.mordorintelligence.com/industry-reports/uv-led-market (2020).
- 118. Jain, A. *et al.* Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Mater.* **1**, 011002 (2013).
- 119. Schmidt, S. *et al.* Microstructure of epitaxial SrTiO<sub>3</sub>/Pt/Ti/sapphire heterostructures. *J. Mater. Res.* **20**, 2261–2265 (2005).
- Chakraverty, S., Ohtomo, A., Okude, M., Ueno, K. & Kawasaki, M. Epitaxial structure of (001)- and (111)-oriented perovskite ferrate films grown by pulsed-laser deposition. *Cryst. Growth Des.* 10, 1725–1729 (2010).
- Rüegg, A. & Fiete, G. A. Topological insulators from complex orbital order in transitionmetal oxides heterostructures. *Phys. Rev. B - Condens. Matter Mater. Phys.* 84, 201103 (2011).

- 122. Liang, Q.-F., Wu, L.-H. & Hu, X. Electrically tunable topological state in [111] perovskite materials with an antiferromagnetic exchange field. *New J. Phys.* **15**, 063031 (2013).
- 123. Tagantsev, A. K., Pertsev, N. A., Muralt, P. & Setter, N. Strain-induced diffuse dielectric anomaly and critical point in perovskite ferroelectric thin films. *Phys. Rev. B - Condens. Matter Mater. Phys.* 65, 121041–121044 (2002).
- 124. Reyes-Lillo, S. E., Rabe, K. M. & Neaton, J. B. Ferroelectricity in [111]-oriented epitaxially strained SrTiO<sub>3</sub> from first principles. *Phys. Rev. Mater.* **3**, 030601 (2019).
- 125. Weng, Y., Huang, X., Yao, Y. & Dong, S. Topological magnetic phase in LaMnO<sub>3</sub> (111) bilayer. *Phys. Rev. B Condens. Matter Mater. Phys.* **92**, 195114 (2015).
- 126. Xiao, D., Zhu, W., Ran, Y., Nagaosa, N. & Okamoto, S. Interface engineering of quantum Hall effects in digital transition metal oxide heterostructures. *Nat. Commun.* **2**, 1–8 (2011).
- 127. Yang, K.-Y. *et al.* Possible interaction-driven topological phases in (111) bilayers of LaNiO<sub>3</sub>. *Phys. Rev. B* **84**, 201104 (2011).
- 128. Rüegg, A., Mitra, C., Demkov, A. A. & Fiete, G. A. Lattice distortion effects on topological phases in (LaNiO<sub>3</sub>)<sub>2</sub>/(LaAlO<sub>3</sub>)<sub>N</sub> heterostructures grown along the [111] direction. *Phys. Rev. B* 88, 115146 (2013).
- 129. Wang, Y., Wang, Z., Fang, Z. & Dai, X. Interaction-induced quantum anomalous Hall phase in (111) bilayer of LaCoO<sub>3</sub>. *Phys. Rev. B Condens. Matter Mater. Phys.* 91, 125139 (2015).
- Chandra, H. K. & Guo, G. Y. Quantum anomalous Hall phase and half-metallic phase in ferromagnetic (111) bilayers of 4d and 5d transition metal perovskites. *Phys. Rev. B* 95, 134448 (2017).
- 131. Lu, H. S. & Guo, G. Y. Strain and onsite-correlation tunable quantum anomalous Hall phases in ferromagnetic (111) LaXO<sub>3</sub> bilayers (X=Pd,Pt). *Phys. Rev. B* **99**, 104405 (2019).
- 132. Kim, T. H. et al. Polar metals by geometric design. Nature 533, 68-72 (2016).
- 133. Grutter, A. *et al.* Enhanced magnetism in epitaxial SrRuO<sub>3</sub> thin films. *Appl. Phys. Lett.* **96**, (2010).
- 134. Rubi, D., Vlooswijk, A. H. G. & Noheda, B. Growth of flat SrRuO<sub>3</sub> (111) thin films suitable as bottom electrodes in heterostructures. *Thin Solid Films* **517**, 1904–1907 (2009).
- 135. Chang, J., Park, Y. S., Lee, J. W. & Kim, S. K. Layer-by-layer growth and growth-mode transition of SrRuO<sub>3</sub> thin films on atomically flat single-terminated SrTiO<sub>3</sub> (111) surfaces. *J. Cryst. Growth* **311**, 3771–3774 (2009).
- 136. Rastogi, A. *et al.* Metal-insulator transition in (111) SrRuO<sub>3</sub> ultrathin films. *APL Mater.* 7, 091106 (2019).
- Chang, J., Lee, J. W. & Kim, S. K. Layer-by-layer growth of SrFeO<sub>3-δ</sub> thin films on atomically flat single-terminated SrRuO<sub>3</sub>/SrTiO<sub>3</sub> (111) surfaces. *J. Cryst. Growth* **312**, 621–623 (2010).
- 138. Hallsteinsen, I. *et al.* Surface stability of epitaxial La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> thin films on (111)oriented SrTiO<sub>3</sub>. *J. Appl. Phys.* **113**, 183512 (2013).
- 139. Hamasaki, Y. *et al.* Epitaxial growth of metastable multiferroic AlFeO<sub>3</sub> film on SrTiO<sub>3</sub> (111) substrate. *Appl. Phys. Lett.* **104**, 082906 (2014).
- 140. Arab, A. *et al.* Electronic Structure of a Graphene-like Artificial Crystal of NdNiO<sub>3</sub>. *Nano Lett.* **19**, 8311–8317 (2019).
- 141. Anderson, T. J. *et al.* Metastable honeycomb SrTiO<sub>3</sub>/SrIrO<sub>3</sub> heterostructures. *Appl. Phys. Lett.* **108**, 151604 (2016).

- 142. Hallsteinsen, I. *et al.* Effect of Polar (111)-Oriented SrTiO<sub>3</sub> on Initial Perovskite Growth. *Cryst. Growth Des.* **16**, 2357–2362 (2016).
- Rout, P. K., Agireen, I., Maniv, E., Goldstein, M. & Dagan, Y. Six-fold crystalline anisotropic magnetoresistance in the (111) LaAlO<sub>3</sub>/SrTiO<sub>3</sub> oxide interface. *Phys. Rev. B* 95, 241107 (2017).
- Tang, Y. *et al.* A Coherently Strained Monoclinic [111]PbTiO<sub>3</sub> Film Exhibiting Zero Poisson's Ratio State. *Adv. Funct. Mater.* 29, 1901687 (2019).
- 145. Fan, J. *et al.* Optical transmission and carrier transport of epitaxial (001)- and (111)oriented Ba<sub>0.96</sub>La<sub>0.04</sub>SnO<sub>3</sub> thin films. *Ceram. Int.* **46**, 3523–3527 (2020).
- 146. Schmidt, S. *et al.* Atomic structure of (111) SrTiO<sub>3</sub>/Pt interfaces. *Appl. Phys. Lett.* **88**, 131914 (2006).
- 147. Catalano, S. *et al.* Tailoring the electronic transitions of NdNiO<sub>3</sub> films through (111)<sub>pc</sub> oriented interfaces. *APL Mater.* **3**, 062506 (2015).
- Albargi, H. *et al.* Magnetic and magneto-optical properties of films of multiferroic GdMnO<sub>3</sub> grown on LSAT [(LaAlO<sub>3</sub>)<sub>0.3</sub> (Sr<sub>2</sub>AlTaO<sub>6</sub>)<sub>0.7</sub>] (100) and (111). *Thin Solid Films* 645, 326–333 (2018).
- 149. Blok, J. L., Wan, X., Koster, G., Blank, D. H. A. & Rijnders, G. Epitaxial oxide growth on polar (111) surfaces. *Appl. Phys. Lett.* **99**, 151917 (2011).
- 150. Köksal, O. & Pentcheva, R. Chern and Z 2 topological insulating phases in perovskitederived 4d and 5d oxide buckled honeycomb lattices. *Sci. Rep.* **9**, 1–11 (2019).
- 151. Roshna, S. H., Prellier, W. & Padhan, P. Strain modulated magnetocaloric effect in (111) oriented La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>-SrRuO<sub>3</sub> superlattices. *Nanoscale* **12**, 5151–5158 (2020).
- 152. Gibert, M., Zubko, P., Scherwitzl, R., Íñiguez, J. & Triscone, J. M. Exchange bias in LaNiO<sub>3</sub>-LaMnO<sub>3</sub> superlattices. *Nat. Mater.* **11**, 195–198 (2012).
- 153. Ichikawa, N. *et al.* Multiferroism at room temperature in BiFeO<sub>3</sub>/BiCrO<sub>3</sub>(111) artificial superlattices. *Appl. Phys. Express* **1**, 1013021–1013023 (2008).
- 154. Middey, S. *et al.* Epitaxial growth of (111)-oriented LaAlO<sub>3</sub>/ LaNiO<sub>3</sub> ultra-thin superlattices. *Appl. Phys. Lett.* **101**, 261602 (2012).
- 155. Hu, M. *et al.* Reconstruction-stabilized epitaxy of LaCoO<sub>3</sub>/SrTiO<sub>3</sub>(111) heterostructures by pulsed laser deposition. *Appl. Phys. Lett.* **112**, 031603 (2018).
- 156. Flint, C. L. *et al.* Enhanced interfacial ferromagnetism and exchange bias in (111)oriented LaNiO<sub>3</sub>/CaMnO<sub>3</sub> superlattices. *Phys. Rev. Mater.* **3**, 064401 (2019).
- Belhadi, J., Yousfi, S., Bouyanfif, H. & El Marssi, M. Structural investigation of (111) oriented (BiFeO<sub>3</sub>)<sub>(1-x</sub>/(LaFeO<sub>3</sub>)<sub>x</sub> superlattices by X-ray diffraction and Raman spectroscopy. *J. Appl. Phys.* **123**, 154103 (2018).
- 158. Landau, L. D. The Theory of a Fermi Liquid. ZhETF (USSR) 30, 1058 (1956).
- 159. Baym, G. & Pethick, C. Landau Fermi-Liquid Theory. Landau Fermi-Liquid Theory: Concepts and Applications (Wiley, 1991). doi:10.1002/9783527617159.
- Sommerfeld, A. Zur Elektronentheorie der Metalle auf Grund der Fermischen Statistik I. Teil: Allgemeines, Strömungs- und Austrittsvorgänge. Zeitschrift für Phys. 47, 1–32 (1928).
- 161. Ashcroft, N. W. & Mermin, N. D. Solid state physics. (Holt, Rinehart and Winston, 1976).
- 162. Landau, L. D. Oscillations in a Fermi Liquid. Sov. Phys. JETP-USSR 5, 101–108 (1957).
- 163. Kaveh, M. & Wiser, N. Electron-electron scattering in conducting materials. *Adv. Phys.* 33, 257–372 (1984).

- 164. Baber, W. G. The contribution to the electrical resistance of metals from collisions between electrons. *Proc. R. Soc. London. Ser. A Math. Phys. Sci.* **158**, 383–396 (1937).
- 165. Lin, X., Fauqué, B. & Behnia, K. Scalable T<sup>2</sup> resistivity in a small single-component Fermi surface. *Science (80-. ).* **349**, (2015).
- 166. van der Marel, D., van Mechelen, J. L. M. & Mazin, I. I. Common Fermi-liquid origin of T-squared resistivity and superconductivity in n-type SrTiO<sub>3</sub>. *Phys. Rev. B - Condens. Matter Mater. Phys.* 84, (2011).
- 167. Kittel, C., Kroemer, H. & Scott, H. L. Thermal Physics, 2nd ed. Am. J. Phys. 66, 164–167 (1998).
- 168. Bass, J., Pratt, W. P. & Schroeder, P. A. The temperature-dependent electrical resistivities of the alkali metals. *Rev. Mod. Phys.* 62, 645–744 (1990).
- Mannari, I. Electrical Resistance of Ferromagnetic Metals. *Prog. Theor. Phys.* 22, 335–343 (1959).
- Kubo, K. & Ohatata, N. A Quantum Theory of Double Exchange. I. J. Phys. Soc. Japan 33, 21–32 (1972).
- 171. Abrahams, E. 50 Years Of Anderson Localization. (World Scientific Publishing Co., 2010).
- 172. Pfleiderer, C., Julian, S. R. & Lonzarich, G. G. Non-Fermi-liquid nature of the normal state of itinerant-electron ferromagnets. *Nature* **414**, 427–430 (2001).
- 173. Millis, A. J. Effect of a nonzero temperature on quantum critical points in itinerant fermion systems. *Phys. Rev. B* **48**, 7183–7196 (1993).
- 174. Wilson, A. H. & Fowler, R. H. The electrical conductivity of the transition metals. *Proc. R. Soc. A Math. Phys. Eng. Sci.* **167**, 580–593 (1938).
- 175. Zangwill, A. *Physics at Surfaces*. *Physics at Surfaces* (Cambridge University Press, 1988). doi:10.1017/cbo9780511622564.
- 176. Oura, K., Katayama, M., Zotov, A. V., Lifshits, V. G. & Saranin, A. A. Growth of Thin Films. in 357–387 (Springer, Berlin, Heidelberg, 2003). doi:10.1007/978-3-662-05179-5\_14.
- 177. Brahlek, M., Zhang, L., Eaton, C., Zhang, H.-T. & Engel-Herbert, R. Accessing a Growth Window for SrVO<sub>3</sub> Thin Films. **107**, 143108 (2015).
- Fork, D. K., Ponce, F. A., Tramontana, J. C. & Geballe, T. H. Epitaxial MgO on Si(001) for Y-Ba-Cu-O thin-film growth by pulsed laser deposition. *Appl. Phys. Lett.* 58, 2294– 2296 (1991).
- 179. Ohring, M. *The Materials Science of Thin Films*. *The Materials Science of Thin Films* (Elsevier Inc., 2013). doi:10.1016/C2009-0-22199-4.
- Queisser, H. J. & Haller, E. E. Defects in semiconductors: Some fatal, some vital. *Science* vol. 281 945–950 (1998).
- 181. Eaton, C. *et al.* Growth of SrVO<sub>3</sub> thin films by hybrid molecular beam epitaxy. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **33**, 061504 (2015).
- 182. Ruddlesden, S. N. & Popper, P. The compound Sr<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> and its structure. *Acta Crystallogr.* **11**, 54–55 (1958).
- Eckstein, W. Energy distributions of sputtered particles. *Nucl. Inst. Methods Phys. Res. B* 18, 344–348 (1986).
- 184. Simon, A. H. Sputter Processing. in *Handbook of Thin Film Deposition: Techniques, Processes, and Technologies: Third Edition* 55–88 (Elsevier Inc., 2012).

doi:10.1016/B978-1-4377-7873-1.00004-8.

- 185. Hou, S. Y., Kwo, J., Watts, R. K., Cheng, J. -Y. & Fork, D. K. Structure and properties of epitaxial Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub>/SrRuO<sub>3</sub>/ZrO<sub>2</sub> heterostructure on Si grown by off-axis sputtering. *Appl. Phys. Lett.* 67, 1387–1389 (1995).
- 186. Wang, L. M., Sung, H. H., Su, B. T., Yang, H. C. & Horng, H. E. Growth of ferromagnetic Nd<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub> films with an off-axis sputtering configuration. *J. Appl. Phys.* 88, 4236 (2000).
- 187. Bohra, M., Yeh, H. J., Wu, C. P. & Chou, H. Strain Relaxation in Atomic Flat SrRu<sub>1-xO3</sub>/SrTiO<sub>3</sub> Layers Grown by Off-Axis RF-Sputtering. *IEEE Trans. Magn.* 48, 4566–4569 (2012).
- 188. Anders, A. Discharge physics of high power impulse magnetron sputtering. *Surf. Coatings Technol.* **205**, S1–S9 (2011).
- 189. Sun, H. *et al.* Influence of power frequency on the performance of SiC thin films deposited by pulsed DC magnetron sputtering. *Journal of Adhesion Science and Technology* vol. 33 2181–2190 (2019).
- Gudmundsson, J. T., Brenning, N., Lundin, D. & Helmersson, U. High power impulse magnetron sputtering discharge. J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 30, 030801 (2012).
- 191. Lundin, D. & Sarakinos, K. An introduction to thin film processing using high-power impulse magnetron sputtering. *Journal of Materials Research* vol. 27 780–792 (2012).
- 192. Ghosh, S. *et al.* Deposition of thin films of different oxides of copper by RF reactive sputtering and their characterization. *Vacuum* **57**, 377–385 (2000).
- Meng, L.-J. & dos Santos, M. P. Investigations of titanium oxide films deposited by d.c. reactive magnetron sputtering in different sputtering pressures. *Thin Solid Films* 226, 22– 29 (1993).
- Karasawa, T. & Miyata, Y. Electrical and optical properties of indium tin oxide thin films deposited on unheated substrates by d.c. reactive sputtering. *Thin Solid Films* 223, 135– 139 (1993).
- 195. Sproul, W. D. Very high rate reactive sputtering of TiN, ZrN and HfN. *Thin Solid Films* **107**, 141–147 (1983).
- 196. Dubois, M.-A. & Muralt, P. Stress and piezoelectric properties of aluminum nitride thin films deposited onto metal electrodes by pulsed direct current reactive sputtering. *J. Appl. Phys.* **89**, 6389–6395 (2001).
- 197. Maruyama, T. & Morishita, T. Copper nitride thin films prepared by radio-frequency reactive sputtering. J. Appl. Phys. **78**, 4104–4107 (1995).
- 198. Fuchs, K., Rödhammer, P., Bertel, E., Netzer, F. P. & Gornik, E. Reactive and nonreactive high rate sputter deposition of Tungsten carbide. *Thin Solid Films* **151**, 383–395 (1987).
- 199. Zhang, K. *et al.* Reactive magnetron sputtering deposition and characterization of niobium carbide films. *Vacuum* **99**, 233–241 (2014).
- Shao, L.-X., Chang, K.-H. & Hwang, H.-L. Zinc sulfide thin films deposited by RF reactive sputtering for photovoltaic applications. *Appl. Surf. Sci.* 212–213, 305–310 (2003).
- Armantrout, G. A., Miller, D. E., Vindelov, K. E. & Brown, T. G. Formation of thin Cu<sub>2</sub>S (chalcocite) films using reactive sputtering techniques. *J. Vac. Sci. Technol.* 16, 212–215 (1979).

- 202. Iwahori, K., Furuta, M., Taki, Y., Yamamura, T. & Tanaka, A. Optical properties of fluoride thin films deposited by RF magnetron sputtering. *Appl. Opt.* **45**, 4598 (2006).
- 203. Lee, C.-C., Liao, B.-H. & Liu, M.-C. AlF<sub>3</sub> thin films deposited by reactive magnetron sputtering with Al target. *Opt. Express* **15**, 9152 (2007).
- 204. Choi, K. H. *et al.* Characteristics of flexible indium tin oxide electrode grown by continuous roll-to-roll sputtering process for flexible organic solar cells. *Sol. Energy Mater. Sol. Cells* **93**, 1248–1255 (2009).
- 205. Greer, J. A. In-Situ Growth of Y<sub>1</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> Thin Films on Three-Inch Wafers Using Laser-Ablation and an Atomic Oxygen Source. in *Superconductivity and Applications* 117–126 (Springer US, 1990). doi:10.1007/978-1-4684-7565-4\_10.
- 206. Eason, R. Pulsed Laser Deposition of Thin Films. Pulsed Laser Deposition of Thin Films (John Wiley & Sons, Inc., 2006). doi:10.1002/0470052120.
- 207. Greer, J. Large-Area Commercial Pulsed Laser Deposition. in Pulsed Laser Deposition of Thin Films: Applications-Led Growth of Functional Materials 191–213 (John Wiley & Sons, Inc., 2006). doi:10.1002/9780470052129.ch9.
- 208. Delmdahl, R. Thin Films for the Future. *PhotonicsViews* 17, 60–62 (2020).
- 209. Brahlek, M. *et al.* Frontiers in the Growth of Complex Oxide Thin Films: Past, Present, and Future of Hybrid MBE. *Adv. Funct. Mater.* 1702772 (2017) doi:10.1002/adfm.201702772.
- Eisenstein, J. P., Cooper, K. B., Pfeiffer, L. N. & West, K. W. Insulating and fractional quantum hall states in the first excited Landau level. *Phys. Rev. Lett.* 88, 768011–768014 (2002).
- 211. Pfeiffer, L. & West, K. W. The role of MBE in recent quantum Hall effect physics discoveries. in *Physica E: Low-Dimensional Systems and Nanostructures* vol. 20 57–64 (North-Holland, 2003).
- 212. Taylor, C. J. *et al.* Does Chemistry Really Matter in the Chemical Vapor Deposition of Titanium Dioxide? Precursor and Kinetic Effects on the Microstructure of Polycrystalline Films. *J. Am. Chem. Soc.* **121**, 5220–5229 (1999).
- 213. Zhang, H. T., Eaton, C., Ye, H. & Engel-Herbert, R. Phase stabilization of VO<sub>2</sub> thin films in high vacuum. *J. Appl. Phys.* **118**, 185306 (2015).
- 214. Roth, J., Arriaga, E., Brahlek, M., Lapano, J. & Engel-Herbert, R. Temperature-dependent growth window of CaTiO<sub>3</sub> films grown by hybrid molecular beam epitaxy. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **36**, 020601 (2018).
- 215. Jalan, B., Moetakef, P. & Stemmer, S. Molecular beam epitaxy of SrTiO<sub>3</sub> with a growth window. *Appl. Phys. Lett.* **95**, 032906 (2009).
- Matsubara, Y., Takahashi, K. S., Tokura, Y. & Kawasaki, M. Single-crystalline BaTiO<sub>3</sub> films grown by gas-source molecular beam epitaxy. *Appl. Phys. Express* 7, 125502 (2014).
- 217. Moetakef, P., Zhang, J. Y., Raghavan, S., Kajdos, A. P. & Stemmer, S. Growth window and effect of substrate symmetry in hybrid molecular beam epitaxy of a Mott insulating rare earth titanate. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **31**, 041503 (2013).
- 218. Eaton, C., Zhang, L., Brahlek, M., Lapano, J. M. & Engel-Herbert, R. Self-regulated growth of CaVO<sub>3</sub> by hybrid molecular beam epitaxy. *J. Vac. Sci. Technol. A* **351**, 061510 (2017).
- 219. Zhang, H.-T., Dedon, L. R., Martin, L. W. & Engel-Herbert, R. Self-regulated growth of LaVO<sub>3</sub> thin films by hybrid molecular beam epitaxy. *Cit. Appl. Phys. Lett* **106**, (2015).

- 220. Brahlek, M. *et al.* Mapping growth windows in quaternary perovskite oxide systems by hybrid molecular beam epitaxy. *Appl. Phys. Lett.* **109**, 101903 (2016).
- 221. Prakash, A. *et al.* Hybrid molecular beam epitaxy for the growth of stoichiometric BaSnO<sub>3</sub>. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **33**, 060608 (2015).
- 222. Lapano, J. *et al.* Scaling growth rates for perovskite oxide virtual substrates on silicon. *Nat. Commun.* **10**, 1–7 (2019).
- 223. Ahadi, K. & Stemmer, S. Novel Metal-Insulator Transition at the SmTiO<sub>3</sub>/SrTiO<sub>3</sub> Interface. *Phys. Rev. Lett.* **118**, 236803 (2017).
- 224. Xu, P., Phelan, D., Seok Jeong, J., Andre Mkhoyan, K. & Jalan, B. Stoichiometry-driven metal-to-insulator transition in NdTiO<sub>3</sub>/SrTiO<sub>3</sub> heterostructures. *Appl. Phys. Lett.* **104**, 082109 (2014).
- 225. Wang, T. *et al.* Defect-driven localization crossovers in MBE-grown La-doped SrSnO<sub>3</sub> films. *Phys. Rev. Mater.* **1**, 061601 (2017).
- 226. Chamberland, B. L. & Danielson, P. S. Alkaline-earth vanadium (IV) oxides having the AVO<sub>3</sub> composition. *J. Solid State Chem.* **3**, 243–247 (1971).
- 227. Nishikawa, S. & Kikuchi, S. Diffraction of cathode rays by calcite. *Nature* vol. 122 726 (1928).
- 228. Ichimiya, A. & Cohen, P. I. *Reflection high energy electron diffraction*. (Cambridge University Press, 2004).
- 229. Csiszár, S. X-ray diffraction and X-ray absorption of strained CoO and MnO thin films. (Rijksuniversiteit Groningen, 2005).
- 230. Nahar, S. Phase-Separation Characteristics of Bitumen and their Relation to Damage-Healing. (2013).
- 231. Zhong, Q., Inniss, D., Kjoller, K. & Elings, V. B. Fractured polymer/silica fiber surface studied by tapping mode atomic force microscopy. *Surf. Sci.* **290**, L688–L692 (1993).
- 232. Lyubchenko, Y. L. & Shlyakhtenko, L. S. AFM for analysis of structure and dynamics of DNA and protein-DNA complexes. *Methods* **47**, 206–213 (2009).
- 233. Bauer, G., Li, J. H. & Holy, V. High resolution X-ray reciprocal space mapping. *Acta Phys. Pol. A* **89**, 115–127 (1996).
- 234. Gates-Rector, S. & Blanton, T. The Powder Diffraction File: a quality materials characterization database. *Powder Diffr.* **34**, 352–360 (2019).
- 235. Pecharsky, V. & Zavalij, P. Fundamentals of Powder Diffraction and Structural Characterization of Materials, Second Edition. Fundamentals of Powder Diffraction and Structural Characterization of Materials (Springer US, 2009). doi:10.1007/978-0-387-09579-0\_1.
- 236. Björck, M. & Andersson, G. GenX: an Extensible X-ray Reflectivity Refinement Program Utilizing Differential Evolution. J. Appl. Cryst **40**, 1174–1178 (2007).
- 237. Van der Pauw, L. J. A method of measuring the resistivity and Hall coefficient on lamellae of arbitrary shape. *Philips Tech. Rev.* **20**, 220–224 (1958).
- 238. Van der Pauw, L. J. A method of measuring specific resistivity and Hall effect of discs of arbitrary shape. *Philips Res. Rep* **13**, 1–9 (1958).
- 239. Onsager, L. Reciprocal relations in irreversible processes. I. *Phys. Rev.* **37**, 405–426 (1931).
- 240. Onsager, L. Reciprocal relations in irreversible processes. II. *Phys. Rev.* **38**, 2265–2279 (1931).

- 241. The Hall Effect | NIST. *NIST* https://www.nist.gov/pml/nanoscale-devicecharacterization-division/popular-links/hall-effect/hall-effect (2019).
- 242. Brahlek, M. et al. Hidden transport phenomena in an ultraclean correlated metal. (2021).
- 243. Ziman, J. M. *Electrons and Phonons : The Theory of Transport Phenomena in Solids*. (Oxford University Press, 2001). doi:10.1093/acprof.
- 244. Hurd, C. M. *The Hall effect in metals and alloys*. (Plenum Press, 1972).
- 245. Ong, N. P. Geometric interpretation of the weak-field Hall conductivity in twodimensional metals with arbitrary Fermi surface. *Phys. Rev. B* **43**, 193–201 (1991).
- 246. Fujiwara, H., Koh, J., Rovira, P. & Collins, R. Assessment of effective-medium theories in the analysis of nucleation and microscopic surface roughness evolution for semiconductor thin films. *Phys. Rev. B* **61**, 10832–10844 (2000).
- 247. Fujiwara, H. Spectroscopic ellipsometry : principles and applications. (John Wiley & Sons, 2007).
- 248. Jellison, G. E. & Modine, F. A. *Handbook of Ellipsometry*. *Handbook of Ellipsometry* (Elsevier, 2005). doi:10.1016/B978-081551499-2.50008-3.
- 249. Fujiwara, H. & Collins, R. Spectroscopic Ellipsometry for Photovoltaics. Springer Series in Optical Sciences vol. 214 (Springer Verlag, 2018).
- 250. Born, M. et al. Principles of Optics. Principles of Optics (Cambridge University Press, 1999). doi:10.1017/cbo9781139644181.
- 251. Li, K. & Xue, D. Estimation of electronegativity values of elements in different valence states. *J. Phys. Chem. A* **110**, 11332–11337 (2006).
- 252. Ridgley, D. & Ward, R. The Preparation of a Strontium-Niobium Bronze with the Perovskite Structure. *J. Am. Chem. Soc.* 77, 6132–6136 (1955).
- 253. Isawa, K., Sugiyama, J., Matsuura, K., Nozaki, A. & Yamauchi, H. Synthesis and Transport Properties of Sr<sub>x</sub>NbO<sub>3</sub> (0.75≤ x ≤0.90). *Phys. Rev. B* **47**, 2849–2853 (1993).
- Hessen, B., Sunshine, S. A., Siegrist, T. & Jimenez, R. Crystallization of Reduced Strontium and Barium Niobate Perovskites From Borate Fluxes. *Mater. Res. Bull.* 26, 85– 90 (1991).
- 255. Xu, X., Randorn, C., Efstathiou, P. & Irvine, J. T. S. A Red Metallic Oxide Photocatalyst. *Nat. Mater.* **11**, 595–598 (2012).
- 256. Kaneko, M., Mishima, K. & Yamashita, K. First-principles study on visible light absorption of defected SrNbO<sub>3</sub>. J. Photochem. Photobiol. A Chem. **375**, 175–180 (2019).
- 257. Balasubramaniam, K. R. *et al.* Phase and Structural Characterization of Sr<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub> and SrNbO<sub>3</sub> Thin Films Grown via Pulsed Laser Ablation in O<sub>2</sub> or N<sub>2</sub> Atmospheres. *J. Solid State Chem.* **181**, 705–714 (2008).
- Tomio, T., Miki, H., Tabata, H., Kawai, T. & Kawai, S. Control of Electrical Conductivity in Laser Deposited SrTiO<sub>3</sub> Thin Films with Nb Doping. J. Appl. Phys. 76, 5886–5890 (1994).
- Oka, D., Hirose, Y., Nakao, S., Fukumura, T. & Hasegawa, T. Intrinsic High Electrical Conductivity of Stoichiometric SrNbO<sub>3</sub> Epitaxial Thin Films. *Phys. Rev. B* 92, 205102 (2015).
- 260. Blaha, P., Schwarz, K., Madsen, G., Kvasnicka, D. & Luitz, J. WIEN2k: An Augmented Plane Waves Plus Local Orbitals Program for Calculating Crystal Properties. *wien2k.at* (2001).
- 261. Monkhorst, H. J. & Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B*

**13**, 5188–5192 (1976).

- Georges, A., Kotliar, G., Krauth, W. & Rozenberg, M. J. Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions. *Reviews of Modern Physics* vol. 68 13–125 (1996).
- 263. Fuchs, K. The conductivity of thin metallic films according to the electron theory of metals. *Math. Proc. Cambridge Philos. Soc.* **34**, 100–108 (1938).
- 264. Sondheimer, E. H. The mean free path of electrons in metals. Adv. Phys. 1, 1–42 (1952).
- O'Connor, B., Haughn, C., An, K. H., Pipe, K. P. & Shtein, M. Transparent and conductive electrodes based on unpatterned, thin metal films. *Appl. Phys. Lett.* 93, 223304 (2008).
- Orita, M., Ohta, H., Hirano, M. & Hosono, H. Deep-ultraviolet transparent conductive β-Ga<sub>2</sub>O<sub>3</sub> thin films. *Appl. Phys. Lett.* 77, 4166 (2000).
- 267. Minami, T. Transparent conducting oxide semiconductors for transparent electrodes. *Semicond. Sci. Technol.* **20**, S35 (2005).
- 268. Farzana, E., Ahmadi, E., Speck, J. S., Arehart, A. R. & Ringel, S. A. Deep level defects in Ge-doped (010) β-Ga<sub>2</sub>O<sub>3</sub> layers grown by plasma-assisted molecular beam epitaxy. J. Appl. Phys. **123**, 161410 (2018).
- 269. Leedy, K. D. *et al.* Highly conductive homoepitaxial Si-doped Ga<sub>2</sub>O<sub>3</sub> films on (010) β-Ga<sub>2</sub>O<sub>3</sub> by pulsed laser deposition. *Appl. Phys. Lett.* **111**, 012103 (2017).
- 270. Galazka, Z. *et al.* Ultra-wide bandgap, conductive, high mobility, and high quality meltgrown bulk ZnGa<sub>2</sub>O<sub>4</sub> single crystals. *APL Mater.* 7, 22512 (2019).
- 271. Du, X. *et al.* Preparation and Characterization of Sn-Doped β-Ga<sub>2</sub>O<sub>3</sub> Homoepitaxial Films by MOCVD. *J. Mater. Sci.* **50**, 3252–3257 (2015).
- Benfatto, L. & Sharapov, S. G. Optical-conductivity sum rule in cuprates and unconventional charge density waves: A short review. *Low Temp. Phys.* 32, 533–545 (2006).
- Benfatto, L., Cappelluti, E., Ortenzi, L. & Boeri, L. Extended Drude model and role of interband transitions in the midinfrared spectra of pnictides. *Phys. Rev. B - Condens. Matter Mater. Phys.* 83, 224514 (2011).
- 274. Allen, J. W. & Mikkelsen, J. C. Optical properties of CrSb, MnSb, NiSb, and NiAs. *Phys. Rev. B* 15, 2952–2960 (1977).
- 275. Qazilbash, M. M. *et al.* Electronic correlations in the iron pnictides. *Nat. Phys.* **5**, 647–650 (2009).
- 276. Kamo, T. *et al.* RF Magnetron Sputtering Growth of Epitaxial SrRuO<sub>3</sub> Films with High Conductivity. *Jpn. J. Appl. Phys.* **46**, 6987–6990 (2007).
- 277. Jung, D. H., So, H. S. & Lee, H. Structural and Electrical Properties of Transparent Conductor SrVO<sub>3</sub> Thin Films Grown Using Radio Frequency Sputtering Deposition. J. Vac. Sci. Technol. A 37, 021507 (2019).
- 278. Leshchenko, P. P., Shevchenko, A. V, Lykova, L. N., Kovba, L. M. & Ippolitova, E. A. The System SrO-Nb<sub>2</sub>O<sub>5</sub>. *Izv Akad Nauk SSSR, Neorg Mater* **18**, 1202–1205 (1982).
- Glazer, A. M. Simple Ways of Determining Perovskite Structures. Acta Crystallogr. Sect. A 31, 756–762 (1975).
- 280. SrNbO<sub>3</sub> Crystal Structure. *SpringerMaterials* https://materials.springer.com/isp/crystallographic/docs/sd\_1523210 (2016).
- 281. Roth, J. et al. Sputtered Sr<sub>x</sub>NbO<sub>3</sub> as a UV transparent conducting film. ACS Appl. Mater.

Interfaces 12, 30520–30529 (2020).

- 282. Wang, T., Ganguly, K., Marshall, P., Xu, P. & Jalan, B. Critical Thickness and Strain Relaxation in Molecular Beam Epitaxy-Grown SrTiO<sub>3</sub> Films. *Appl. Phys. Lett.* 103, 212904 (2013).
- 283. Freund, L. B. The Stability of a Dislocation Threading a Strained Layer on a Substrate. *J. Appl. Mech.* **54**, 553 (1987).
- 284. Perovich, S. M., Calasan, M. P. & Toskovic, R. On the Exact Analytical Solution of Some Families of Equilibrium Critical Thickness Transcendental Equations. *AIP Adv.* **4**, 117124 (2014).
- Speck, J. S. & Pompe, W. Domain Configurations Due to Multiple Misfit Relaxation Mechanisms in Epitaxial Ferroelectric Thin Films. I. Theory. J. Appl. Phys. 76, 466–476 (1994).
- 286. Xu, Y. Q., Wu, S. Y., Guo, J. X., Wu, L. N. & Peng, L. First-Principles Investigation on the Structural, Elastic and Electronic Properties and Mechanism on the Photocatalytic Properties for SrNbO<sub>3</sub> and Sr<sub>0.97</sub>NbO<sub>3</sub>. J. Phys. Chem. Solids **111**, 403–409 (2017).
- 287. Turzhevsky, S. A., Novikov, D. L., Gubanov, V. A. & Freeman, A. J. Electronic Structure and Crystal Chemistry of Niobium Oxide Phases. *Phys. Rev. B* **50**, 3200–3208 (1994).
- 288. Hoffman, D. W. Intrinsic Resputtering—Theory and Experiment. J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 8, 3707–3712 (1990).
- Ophus, C., Ciston, J. & Nelson, C. T. Correcting Nonlinear Drift Distortion of Scanning Probe and Scanning Transmission Electron Microscopies From Image Pairs with Orthogonal Scan Directions. *Ultramicroscopy* 162, 1–9 (2016).
- 290. Li, C. *et al.* Atomic Scale Characterization of Point and Extended Defects in Niobate Thin Films. *Ultramicroscopy* **203**, 82–87 (2019).
- 291. Dhamdhere, A. R., Hadamek, T., Posadas, A. B., Demkov, A. A. & Smith, D. J. Structural Characterization of Niobium Oxide Thin Films Grown on SrTiO<sub>3</sub> (111) and (La,Sr)(Al,Ta)O<sub>3</sub> (111) Substrates. *J. Appl. Phys.* **120**, 245302 (2016).
- 292. Kim, H. *et al.* Effect of Film Thickness on the Properties of Indium Tin Oxide Thin Films. *J. Appl. Phys.* **88**, 6021–6025 (2000).
- 293. Kim, D.-H., Park, M.-R., Lee, H.-J. & Lee, G.-H. Thickness Dependence of Electrical Properties of ITO Film Deposited on a Plastic Substrate by RF Magnetron Sputtering. *Appl. Surf. Sci.* **253**, 409–411 (2006).
- 294. Wei, M. *et al.* High Electrical Conducting Deep-Ultraviolet-Transparent Oxide Semiconductor La-doped SrSnO<sub>3</sub> Exceeding ~3000 S cm<sup>-1</sup>. *Appl. Phys. Lett.* **116**, 022103 (2020).
- 295. Akaiwa, K., Kaneko, K., Ichino, K. & Fujita, S. Conductivity Control of Sn-Doped α-Ga<sub>2</sub>O<sub>3</sub> Thin Films Grown on Sapphire Substrates. *Jpn. J. Appl. Phys.* 55, 1202BA (2016).
- 296. Guo, E.-J. *et al.* Structure and characteristics of ultrathin indium tin oxide films. *Appl. Phys. Lett.* **98**, 011905 (2011).
- 297. Gordon, R. G. Criteria for Choosing Transparent Conductors. MRS Bull. 25, (2000).
- 298. Fleischer, K., Norton, E., Mullarkey, D., Caffrey, D. & Shvets, I. V. Quantifying the Performance of p-Type Transparent Conducting Oxides by Experimental Methods. *Mater. (Basel, Switzerland)* **10**, (2017).
- 299. *Handbook of Transparent Conductors*. (Springer US, 2011). doi:10.1007/978-1-4419-1638-9.

- 300. Würtele, M. A. *et al.* Application of GaN-Based Ultraviolet-C Light Emitting Diodes UV LEDs For Water Disinfection. *Water Res.* **45**, 1481–1489 (2011).
- Seah, M. P. Summary of ISO/TC 201 Standard: VII ISO 15472 : 2001- Surface Chemical Analysis - X-ray Photoelectron Spectrometers - Calibration of Energy Scales. *Surf. Interface Anal.* 31, 721–723 (2001).
- 302. Isawa, Itti, Sugiyama, Koshizuka & Yamauchi. Photoelectron Spectroscopic Study of Sr<sub>x</sub>NbO<sub>3</sub>. *Phys. Rev. B. Condens. Matter* **49**, 3534–3538 (1994).
- 303. Demirer, F. E. Investigation of a Charge Transfer at Complex Oxide Interfaces. (University of Twente, 2017).
- 304. Bigi, C. *et al.* Direct insight into the band structure of SrNbO<sub>3</sub>. *Phys. Rev. Mater.* **4**, 025006 (2020).
- Ambrosch-Draxl, C. & Sofo, J. O. Linear Optical Properties of Solids Within the Full-Potential Linearized Augmented Planewave Method. *Comput. Phys. Commun.* 175, 1–14 (2006).
- 306. Perdew, J. P. Density Functional Theory and the Band Gap Problem. *Int. J. Quantum Chem.* **28**, 497–523 (2009).
- 307. Wang, Z. J., Chu, J. R., Maeda, R. & Kokawa, H. Effect of bottom electrodes on microstructures and electrical properties of sol-gel derived Pb(Zr<sub>0.53</sub>Ti<sub>0.47</sub>)O<sub>3</sub> thin films. *Thin Solid Films* **416**, 66–71 (2002).
- 308. Simões, A. Z. *et al.* Enhanced ferroelectric properties of La-substituted BiFeO<sub>3</sub> thin films on LaSrCoO<sub>3</sub>/Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si (1 0 0) substrates prepared by the soft chemical method. *Ceram. Int.* **38**, 3841–3849 (2012).
- Potrepka, D. M. *et al.* Characterization of IrO<sub>x</sub> sputtering for IrO<sub>2</sub> and IrO<sub>2</sub>/Pt bottomelectrode piezoelectric micro-electro-mechanical systems applications. *Thin Solid Films* 638, 127–137 (2017).
- Zhang, L. *et al.* Continuously Tuning Epitaxial Strains by Thermal Mismatch. *ACS Nano* 12, 1306–1312 (2018).
- 311. Giannakopoulou, V., Odier, P., Bassat, J. M. & Loup, J. P. SrVO<sub>3</sub> and Sr<sub>2</sub>VO<sub>4</sub>, electrical properties below and above room T. *Solid State Commun.* **93**, 579–583 (1995).
- 312. Lan, Y. C., Chen, X. L. & He, M. Structure, magnetic susceptibility and resistivity properties of SrVO<sub>3</sub>. *J. Alloys Compd.* **354**, 95–98 (2003).
- 313. Sheets, W. C., Mercey, B. & Prellier, W. Effect of charge modulation in (LaVO3)m(SrVO 3)n superlattices on the insulator-metal transition. *Appl. Phys. Lett.* **91**, 192102 (2007).
- 314. Ritums, D. L., Wu, N. J., Chen, X., Liu, D. & Ignatiev, A. Conducting and Interfacial Properties of Epitaxial SVO Films. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **420**, 46104 (1998).
- Mirjolet, M., Sánchez, F. & Fontcuberta, J. High Carrier Mobility, Electrical Conductivity, and Optical Transmittance in Epitaxial SrVO<sub>3</sub> Thin Films. *Adv. Funct. Mater.* 29, 1808432 (2019).
- 316. Nagata, H., Tsukaharat, T., Yoshimoto, M. & Koinuma, H. Laser molecular beam epitaxy of single-crystal SrVO<sub>3-x</sub> films. *Thin Solid Films* **208**, 268 (1992).
- 317. Kim, D. H. *et al.* Electrical properties of SrVO<sub>3</sub>/SrTiO<sub>3</sub> superlattices grown by laser molecular beam epitaxy. *Solid State Commun.* **114**, 473–476 (2000).
- 318. Shoham, L., Baskin, M., Han, M., Zhu, Y. & Kornblum, L. Scalable Synthesis of the Transparent Conductive Oxide SrVO<sub>3</sub>. *Adv. Electron. Mater.* **6**, 1900584 (2020).

- 319. Fischler, M. A. & Bolles, R. C. Random sample consensus: A Paradigm for Model Fitting with Applications to Image Analysis and Automated Cartography. *Commun. ACM* 24, 381–395 (1981).
- 320. Bérini, B. *et al.* Control of High Quality SrVO<sub>3</sub> Electrode in Oxidizing Atmosphere. *Adv. Mater. Interfaces* **3**, 1600274 (2016).
- 321. Gu, M., Wolf, S. A. & Lu, J. Two-Dimensional Mott Insulators in SrVO<sub>3</sub> Ultrathin Films. *Adv. Mater. Interfaces* **1**, 1300126 (2014).
- 322. Anderson, P. W. Absence of Diffusion in Certain Random Lattices. *Phys. Rev.* 109, (1958).
- 323. Nakamae, S. *et al.* Electronic ground state of heavily overdoped nonsuperconducting La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>. *Phys. Rev. B Condens. Matter Mater. Phys.* **68**, 100502 (2003).
- 324. Maekawa, T., Kurosaki, K. & Yamanaka, S. Physical properties of polycrystalline SrVO<sub>3-δ</sub>. *J. Alloys Compd.* **426**, 46–50 (2006).
- 325. Parveen, A. & Gaur, N. K. Elastic and thermodynamic properties of AVO<sub>3</sub> (A=Sr, Pb) perovskites. *Phys. B Condens. Matter* **407**, 500–504 (2012).
- 326. Nagai, I. *et al.* Highest conductivity oxide SrMoO<sub>3</sub> grown by a floating-zone method under ultralow oxygen partial pressure. *Appl. Phys. Lett.* **87**, 024105 (2005).
- 327. Inoue, I. H., Goto, O., Makino, H., Hussey, N. E. & Ishikawa, M. Bandwidth control in a perovskite-type-correlated metal I. Evolution of the electronic properties and effective mass. *Phys. Rev. B Condens. Matter Mater. Phys.* **58**, 4372–4383 (1998).
- 328. Taguchi, Y., Tokura, Y., Arima, T. & Inaba, F. Change of electronic structures with carrier doping in the highly correlated electron system Y<sub>1-x</sub>Ca<sub>x</sub>TiO<sub>3</sub>. *Phys. Rev. B* **48**, 511–518 (1993).
- 329. Okuda, T., Nakanishi, K., Miyasaka, S. & Tokura, Y. Large thermoelectric response of metallic perovskites: Sr<sub>1-x</sub>La<sub>x</sub>TiO<sub>3</sub> (0 ≤ x ≤ 0.1). *Phys. Rev. B Condens. Matter Mater. Phys.* 63, 113104 (2001).
- 330. Inoue, I. H., Goto, O., Makino, H., Hussey, N. E. & Ishikawa, M. Bandwidth control in a perovskite-type 3d1 correlated metal Ca<sub>1-x</sub>Sr<sub>x</sub>VO<sub>3</sub>. I. Evolution of the electronic properties and effective mass. *Phys. Rev. B* **58**, 4372–4383 (1998).
- 331. Kozuka, Y., Hikita, Y., Bell, C. & Hwang, H. Y. Dramatic mobility enhancements in doped SrTiO<sub>3</sub> thin films by defect management. *Appl. Phys. Lett.* **97**, 012107 (2010).
- 332. Mikheev, E. *et al.* Limitations to the room temperature mobility of two- and threedimensional electron liquids in SrTiO<sub>3</sub>. *Appl. Phys. Lett.* **106**, (2015).
- Gu, M., Wolf, S. A. & Lu, J. Metal-insulator transition induced in SrTi<sub>1-x</sub>V<sub>x</sub>O<sub>3</sub> thin films. *Cit. Appl. Phys. Lett* 103, 7056 (2013).
- 334. Liang, Y. *et al.* Homoepitaxial SrTiO<sub>3</sub> (111) Film with High Dielectric Performance and Atomically Well-Defined Surface. *Sci. Rep.* **5**, 1–7 (2015).
- Paisley, E. A. *et al.* Surfactant assisted growth of MgO films on GaN. *Appl. Phys. Lett.* 101, 092904 (2012).
- 336. Paisley, E. A. *et al.* Surfactant-enabled epitaxy through control of growth mode with chemical boundary conditions. *Nat. Commun.* **2**, 1–7 (2011).
- 337. Jalan, B., Engel-Herbert, R., Wright, N. J. & Stemmer, S. Growth of high-quality SrTiO<sub>3</sub> films using a hybrid molecular beam epitaxy approach. *J. Vac. Sci. Technol. A* 27, 461 (2009).
- 338. Kim, S. K. et al. Formation of high ultraviolet transparent SrVO<sub>x</sub>/Ag-based conducting

electrode. Ceram. Int. 46, 19484-19490 (2020).

- 339. Boileau, A. *et al.* Tuning of the Optical Properties of the Transparent Conducting Oxide SrVO<sub>3</sub> by Electronic Correlations. *Adv. Opt. Mater.* **7**, 1801516 (2019).
- 340. Xu, R. *et al.* Perovskite Transparent Conducting Oxide for the Design of a Transparent, Flexible, and Self-Powered Perovskite Photodetector. *ACS Appl. Mater. Interfaces* **12**, 16462–16468 (2020).
- 341. Xu, R. *et al.* Optical and electrical properties of (111)-oriented epitaxial SrVO<sub>3</sub> thin films. *Ceram. Int.* **45**, 11304–11308 (2019).
- 342. Roth, J. *et al.* Self-regulated growth of [111]-oriented perovskite oxide films using hybrid molecular beam epitaxy. *APL Mater.* **9**, 021114 (2021).
- 343. Andersen, T. K., Wang, S., Castell, M. R., Fong, D. D. & Marks, L. D. Single-layer TiO<sub>x</sub> reconstructions on SrTiO<sub>3</sub> (111):  $(\sqrt{7} \times \sqrt{7})$ R19.1°  $(\sqrt{13} \times \sqrt{13})$ R13.9° and related structures. *Surf. Sci.* 675, 36–41 (2018).
- 344. Russell, B. C. & Castell, M. R. Surface of sputtered and annealed polar  $SrTiO_3$  (111): TiO<sub>x</sub>-Rich (n × n) reconstructions. *J. Phys. Chem. C* **112**, 6538–6545 (2008).
- 345. Yang, F. *et al.* Controlled growth of complex polar oxide films with atomically precise molecular beam epitaxy. *Frontiers of Physics* vol. 13 136802 (2018).
- 346. Nozaki, A., Yoshikawa, H., Wada, T., Yamauchi, H. & Tanaka, S. Layered perovskite compounds Sr<sub>n+1</sub>V<sub>n</sub>O<sub>3n+1</sub> (n=1, 2, 3, and). *Phys. Rev. B* **43**, 181–185 (1991).
- 347. Takeno, S., Nakamura, S. ichi, Fukushima, N. & Ando, K. A structural irregularity of the stacking sequence in the Sr<sub>3</sub>V<sub>2</sub>O<sub>7</sub> compound. *J. Alloys Compd.* **187**, 31–37 (1992).
- 348. Zhang, J. *et al.* High Quantum Yield Blue Emission from Lead-Free Inorganic Antimony Halide Perovskite Colloidal Quantum Dots. *ACS Nano* **11**, 9294–9302 (2017).
- 349. Guo, W. H. *et al.* Two-Dimensional 111-Type in -Based Halide Perovskite Cs<sub>3</sub>In<sub>2</sub>X<sub>9</sub> (X=Cl, Br, I) with Optimal Band Gap for Photovoltaics and Defect-Insensitive Blue Emission. *Phys. Rev. Appl.* **13**, 024031 (2020).
- 350. Shi, M. *et al.* Understanding the Effect of Crystalline Structural Transformation for Lead-Free Inorganic Halide Perovskites. *Adv. Mater.* **32**, 2002137 (2020).
- 351. Kallel, A. & Bats, J. W. Tris(trimethylammonium) nonachlorodiantimonate(III), [NH(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>[Sb<sub>2</sub>Cl<sub>9</sub>]. Acta Crystallogr. Sect. C Cryst. Struct. Commun. 41, 1022–1024 (1985).
- 352. Ortiz-Cervantes, C., Carmona-Monroy, P. & Solis-Ibarra, D. Two-Dimensional Halide Perovskites in Solar Cells: 2D or not 2D? *ChemSusChem* **12**, 1560–1575 (2019).
- Abrahams, E., Anderson, P. W., Licciardello, D. C. & Ramakrishnan, T. V. Scaling theory of localization: Absence of quantum diffusion in two dimensions. *Phys. Rev. Lett.* 42, 673–676 (1979).
- 354. Karplus, R. & Luttinger, J. M. Hall effect in ferromagnetics. *Phys. Rev.* **95**, 1154–1160 (1954).
- 355. Nagaosa, N., Sinova, J., Onoda, S., MacDonald, A. H. & Ong, N. P. Anomalous Hall effect. *Rev. Mod. Phys.* 82, 1539–1592 (2010).
- Pu, Y., Chiba, D., Matsukura, F., Ohno, H. & Shi, J. Mott relation for anomalous hall and nernst effects in Ga<sub>1-x</sub>Mn<sub>x</sub>As ferromagnetic semiconductors. *Phys. Rev. Lett.* 101, 117208 (2008).
- 357. Tian, Y., Ye, L. & Jin, X. Proper scaling of the anomalous hall effect. *Phys. Rev. Lett.* **103**, 087206 (2009).

- 358. Yang, S. Y. *et al.* Giant, unconventional anomalous Hall effect in the metallic frustrated magnet candidate, KV<sub>3</sub>Sb<sub>5</sub>. *Sci. Adv.* **6**, 6003–6034 (2020).
- 359. van der Laan, G. & Figueroa, A. I. X-ray magnetic circular dichroism A versatile tool to study magnetism. *Coordination Chemistry Reviews* vol. 277 95–129 (2014).
- 360. Van Der Laan, G. & Thole, B. T. Strong magnetic x-ray dichroism in 2p absorption spectra of 3d transition-metal ions. *Phys. Rev. B* **43**, 13401–13411 (1991).
- 361. Gloter, A. *et al.* Vanadium valency and hybridization in V-doped hafnia investigated by electron energy loss spectroscopy. *Eur. Phys. J. B* **22**, 179–186 (2001).
- 362. Van Der Laan, G. & Kirkman, I. W. The 2p absorption spectra of 3d transition metal compounds in tetrahedral and octahedral symmetry. *J. Phys. Condens. Matter* **4**, 4189–4204 (1992).
- 363. Wu, M., Zheng, J. C. & Wang, H. Q. Investigation of the vanadium L<sub>23</sub> -edge x-ray absorption spectrum of SrVO<sub>3</sub> using configuration interaction calculations: Multiplet, valence, and crystal-field effects. *Phys. Rev. B* **97**, 245138 (2018).
- 364. Sharma, A. *et al.* Mechanistic insights on the electronic properties and electronic/atomic structure aspects in orthorhombic SrVO<sub>3</sub> thin films: XANES-EXAFS study. *Phys. Chem. Chem. Phys.* **19**, 6397–6405 (2017).
- 365. Adachi, S. Properties of Semiconductor Alloys. (Wiley, 2009).
- 366. Son, J. *et al.* Epitaxial SrTiO<sub>3</sub> films with electron mobilities exceeding 30,000 cm2 V-1s-1. *Nat. Mater.* **9**, 482–484 (2010).
- Zhang, L., Wang, Y. & Engel-Herbert, R. Improving the structural quality and electrical resistance of SrTiO<sub>3</sub> thin films on Si (001) via a two-step anneal. *J. Appl. Phys.* 119, 045301 (2016).
- 368. Schlaf, R., Murata, H. & Kafafi, Z. . Work function measurements on indium tin oxide films. *J. Electron Spectros. Relat. Phenomena* **120**, 149–154 (2001).
- 369. Lagerstedt, O. & Monemar, B. Variation of lattice parameters in GaN with stoichiometry and doping. *Phys. Rev. B* **19**, 3064–3070 (1979).
- 370. Zhang, T. Thermal Stability and Degradation Analysis of GaN/AlGaN Heterostructure. (University of California, 2018).
- 371. Zhang, L. & Engel-Herbert, R. Growth of SrTiO<sub>3</sub> on Si(001) by hybrid molecular beam epitaxy. *Phys. status solidi Rapid Res. Lett.* **8**, 917–923 (2014).
- Oku, T. Crystal Structures of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and Related Perovskite Compounds Used for Solar Cells. in *Solar Cells - New Approaches and Reviews* (InTech, 2015). doi:10.5772/59284.
- Cui, Y., Briscoe, J. & Dunn, S. Effect of ferroelectricity on solar-light-driven photocatalytic activity of BaTiO<sub>3</sub> - Influence on the carrier separation and stern layer formation. *Chem. Mater.* 25, 4215–4223 (2013).
- 374. Spanier, J. E. *et al.* Power conversion efficiency exceeding the Shockley-Queisser limit in a ferroelectric insulator. *Nat. Photonics* **10**, (2016).
- 375. Wemple, S. H. Polarization fluctuations and the optical-absorption edge in BaTiO<sub>3</sub>. *Phys. Rev. B* **2**, 2679–2689 (1970).
- Dharmadhikari, V. S. & Grannemann, W. W. Photovoltaic properties of ferroelectric BaTiO<sub>3</sub> thin films rf sputter deposited on silicon. *J. Appl. Phys.* 53, 8988–8992 (1982).
- 377. Björck, M. GenX Home. https://genx.sourceforge.io/ (2020).

# **Appendix A: Fitting XRD Data with GenX**

High resolution  $2\theta \cdot \omega$  X-ray diffraction scans can be analyzed using several methods to obtain structural information including orientation, thickness, and lattice parameter of films and heterostructures. Most of these methods utilize the Scherrer equation to determine crystallite sizes in powder diffraction, which can also be applied in the case of thin films to determine their thickness. The Scherrer equation is shown in Eq. A1 where  $\tau$  is the size of the crystal or film,  $\lambda$  is the X-ray wavelength,  $\theta$  is the Bragg angle,  $\Delta(2\theta)$  is the peak width of the X-ray reflection at half of the diffracted intensity, and *K* is a dimensionless shape factor that is close to unity.

$$\tau = \frac{K\lambda}{\Delta(2\theta)\cos\theta}$$
 Eq. A1

In addition,  $2\theta$ - $\omega$  scans of films with atomically smooth interfaces exhibit thin film interference fringes in addition to the film peaks, which provide further information of the film thickness. These features in addition to structure factor modeling of the substrate and films are widely incorporated into XRD fitting software. In this thesis, all high resolution  $2\theta$ - $\omega$  X-ray diffraction scans were analyzed using GenX, a python-based software that was released in 2007 by Dr. M. Björck and Dr. G. Andersson and is continually being developed at the time of writing.<sup>236,377</sup>

GenX has the capability to fit surface X-ray diffraction, X-ray reflectivity, and neutron reflectivity data; however, only surface X-ray diffraction is discussed here. In the simplest cases, measurements of a single film on a substrate are fit but complex fits of multilayer materials or compositionally varying materials are also possible. Below, the typical workflow for fitting single films is discussed followed by an example fitting script and example material structure information. Additional information can be found on the GenX website.<sup>377</sup>

# Workflow for fitting high resolution XRD data with GenX

1. Raw theta and intensity data must first be converted into 1-space following Eq. A2 where d is the out of plane lattice parameter of the substrate and  $\lambda$  is the incident wavelength.

$$l = \frac{2 * d * \sin\theta}{\lambda}$$
 Eq. A2

2. GenX requires input data to be in the following tab delimited arrangement:

Н	K	L	Intensity	Intensity Error
0	0	#####	#####	##### or 0

3. Open GenX

5.

- 4. Under Settings, go to Data Loader and set it to: sls\_sxrd
  - Then insert an empty data set and upload your data.
    - a. Make sure to delete the original data file.
- 6. Write the script for your particular sample.
- 7. Press simulate (F9)
- 8. Click Grid and set up the parameters to fit
- 9. Press Start Fit (Ctrl-F)



Figure A-0-1: GenX workspace with a fit for a [001]-oriented SrVO<sub>3</sub> thin film grown on LSAT.

The workspace for GenX is shown in Figure A-1. The fitting parameters can additionally be set to initial values with upper and lower boundaries. Note that the fitting values for the film lattice parameters are given with respect to the substrate and the thicknesses are given as the number of unit cells.

# Setting up a GenX script

- 1. First set up the basic unit cell of the substrate, for this you need the lattice parameters and the angles that define the lattice:
  - Ex)  $Al_2O_3$ : unitcell = model.UnitCell(4.754, 4.754, 12.993, 90, 90, 120)

LSAT: unitcell = model.UnitCell(3.868, 3.868, 3.868, 90, 90, 90)

- 2. Define the instrument details including the X-ray wavelength: inst = model.Instrument(wavel = 1.5406, alpha = 18.5)
- 3. Define the atomic positions of each unique atom in the unit cell of the substrate. To do this:
  - a. Open the .cif file of the material to view the crystal structure.
  - b. Reduce the unit cell such that only non-repeating atoms are shown
  - c. Insect each element's relative positions and put them into the script
  - d. (See end of this document for examples)
- 4. Define the film with a lattice parameter with respect to that of the substrate STO = model.Slab(c=1.02)
- 5. Repeat the process of defining the atomic positions of the film
- 6. Define the symmetry between the film and the substrate

p1 = [model.SymTrans([[1, 0], [0, 1]])]

sample.set\_surface\_sym(p1)

7. Define the structure of the overall sample, if multiple films are present, add them with their respective thickness (in unit cells) here

sample = model.Sample(inst, bulk, 130\*[STO], unitcell)

# Examples of atomic positions for materials

### LSAT (001):

bulk.add\_atom('La', 'la', 0.0, 0.0, 0.0, 0.08, 0.3) bulk.add\_atom('Sr', 'sr', 0.0, 0.0, 0.0, 0.08, 0.7) bulk.add\_atom('Al', 'al', 0.5, 0.5, 0.5, 0.08, 0.65) bulk.add\_atom('Ta', 'ta', 0.0, 0.5, 0.5, 0.08, 0.35) bulk.add\_atom('O1', 'o', 0.5, 0.5, 0.0, 0.08, 1.0) bulk.add\_atom('O2', 'o', 0.0, 0.5, 0.5, 0.08, 1.0) bulk.add\_atom('O3', 'o', 0.5, 0.0, 0.5, 0.08, 1.0)

## LSAT (111):

bulk.add\_atom('La1', 'la', 0.0, 0.0, 0.0, 0.08, 0.3) bulk.add\_atom('Sr1', 'sr', 0.0, 0.0, 0.0, 0.08, 0.7) bulk.add\_atom('O1', 'o', 0.5, 0.0, 0.0, 0.08, 1.0) bulk.add\_atom('O2', 'o', 0.25, 0.43301, 0.0, 0.08, 1.0) bulk.add\_atom('O3', 'o', -0.25, 0.43301, 0.0, 0.08, 1.0) bulk.add\_atom('A11', 'al', 0.5, 0.288675, 0.5, 0.08, 0.65) bulk.add\_atom('Ta1', 'ta', 0.5, 0.288675, 0.5, 0.08, 0.35)

bulk.add\_atom('La2', 'la', 0.0, 0.57735, 1.0, 0.08, 0.3) bulk.add\_atom('Sr2', 'sr', 0.0, 0.57735, 1.0, 0.08, 0.7) bulk.add\_atom('O4', 'o', 0.25, 0.1443376, 1.0, 0.08, 1.0) bulk.add\_atom('O5', 'o', 0.75, 0.1443376, 1.0, 0.08, 1.0) bulk.add\_atom('O6', 'o', 0.5, 0.57735, 1.0, 0.08, 1.0) bulk.add\_atom('Al2', 'a', 0.0, 0.0, 1.5, 0.08, 0.65) bulk.add\_atom('Ta2', 'ta', 0.0, 0.0, 1.5, 0.08, 0.35)

bulk.add\_atom('La3', 'la', 0.5, 0.288675, 2.0, 0.08, 0.3) bulk.add\_atom('Sr3', 'sr', 0.5, 0.288675, 2.0, 0.08, 0.7) bulk.add\_atom('O7', 'o', 0.25, 0.1443376, 2.0, 0.08, 1.0) bulk.add\_atom('O8', 'o', -0.25, 0.1443376, 2.0, 0.08, 1.0) bulk.add\_atom('O9', 'o', 0.0, 0.288675, 2.0, 0.08, 1.0) bulk.add\_atom('A13', 'al', 0.0, 0.57735, 2.5, 0.08, 0.65) bulk.add\_atom('Ta3', 'ta', 0.0, 0.57735, 2.5, 0.08, 0.35)

### c-plane Al<sub>2</sub>O<sub>3</sub>:

bulk.add\_atom('Al', 'al', 0.3333, 0.6667, 0.0189, 0.08, 1.0) bulk.add\_atom('Al2', 'al', 0.0, 0.0, 0.1477, 0.08, 1.0) bulk.add\_atom('Al3', 'al', 0.6667, 0.3333, 0.1856, 0.08, 1.0) bulk.add\_atom('Al4', 'al', 0.3333, 0.6667, 0.3144, 0.08, 1.0) bulk.add\_atom('Al5', 'al', 0.0, 0.0, 0.3523, 0.08, 1.0) bulk.add\_atom('Al6', 'al', 0.6667, 0.3333, 0.4811, 0.08, 1.0) bulk.add\_atom('Al7', 'al', 0.3333, 0.6667, 0.5189, 0.08, 1.0) bulk.add\_atom('Al8', 'al', 0.0, 0.0, 0.6477, 0.08, 1.0) bulk.add\_atom('Al9', 'al', 0.6667, 0.3333, 0.6856, 0.08, 1.0) bulk.add\_atom('A110', 'al', 0.3333, 0.6667, 0.8144, 0.08, 1.0) bulk.add\_atom('A111', 'al', 0.0, 0.0, 0.8523, 0.08, 1.0) bulk.add\_atom('A111', 'al', 0.0, 0.0, 0.8523, 0.08, 1.0) bulk.add\_atom('A111', 'al', 0.0, 0.0, 0.8523, 0.08, 1.0)

bulk.add atom('O', 'o', 0.3603, 0.3333, 0.0833, 0.08, 1.0) bulk.add atom('O2', 'o', 0.9731, 0.6397, 0.0833, 0.08, 1.0) bulk.add atom('O3', 'o', 0.6667, 0.0269, 0.0833, 0.08, 1.0) bulk.add atom('O4', 'o', 0.0, 0.3064, 0.25, 0.08, 1.0) bulk.add atom('O5', 'o', 0.6936, 0.6936, 0.25, 0.08, 1.0) bulk.add atom('O6', 'o', 0.3064, 0.0, 0.25, 0.08, 1.0) bulk.add atom('O7', 'o', 0.0269, 0.6667, 0.4167, 0.08, 1.0) bulk.add atom('08', 'o', 0.6397, 0.9731, 0.4167, 0.08, 1.0) bulk.add atom('09', 'o', 0.3333, 0.3603, 0.4167, 0.08, 1.0) bulk.add atom('O10', 'o', 0.6667, 0.6397, 0.5833, 0.08, 1.0) bulk.add atom('O11', 'o', 0.3603, 0.0269, 0.5833, 0.08, 1.0) bulk.add atom('O12', 'o', 0.9731, 0.3333, 0.5833, 0.08, 1.0) bulk.add atom('O13', 'o', 0.0, 0.6936, 0.75, 0.08, 1.0) bulk.add atom('014', 'o', 0.3064, 0.3064, 0.75, 0.08, 1.0) bulk.add atom('015', 'o', 0.6936, 0.0, 0.75, 0.08, 1.0) bulk.add atom('O16', 'o', 0.3333, 0.9731, 0.9167, 0.08, 1.0) bulk.add atom('O17', 'o', 0.0269, 0.3603, 0.9167, 0.08, 1.0) bulk.add atom('018', 'o', 0.6397, 0.6667, 0.9167, 0.08, 1.0)

### Bi<sub>2</sub>Se<sub>3</sub>:

BSe.add\_atom('Bi', 'bi', 0.3333, 0.6667, 0.0675, 0.08, 1.0) BSe.add\_atom('Bi2', 'bi', 0.3333, 0.6667, 0.2659, 0.08, 1.0) BSe.add\_atom('Bi3', 'bi', 0.0, 0.0, 0.4008, 0.08, 1.0) BSe.add\_atom('Bi4', 'bi', 0.0, 0.0, 0.5992, 0.08, 1.0) BSe.add\_atom('Bi5', 'bi', 0.6667, 0.3333, 0.7341, 0.08, 1.0) BSe.add\_atom('Bi6', 'bi', 0.6667, 0.3333, 0.9325, 0.08, 1.0)

BSe.add\_atom('Se', 'se', 0.0, 0.0, 0.0, 0.08, 1.0) BSe.add\_atom('Se2', 'se', 0.6667, 0.3333, 0.1216, 0.08, 1.0) BSe.add\_atom('Se3', 'se', 0.0, 0.0, 0.2117, 0.08, 1.0) BSe.add\_atom('Se4', 'se', 0.6667, 0.3333, 0.3333, 0.08, 1.0) BSe.add\_atom('Se5', 'se', 0.3333, 0.6667, 0.4550, 0.08, 1.0) BSe.add\_atom('Se6', 'se', 0.6667, 0.3333, 0.5450, 0.08, 1.0) BSe.add\_atom('Se7', 'se', 0.3333, 0.6667, 0.6667, 0.08, 1.0) BSe.add\_atom('Se8', 'se', 0.0, 0.0, 0.7883, 0.08, 1.0) BSe.add\_atom('Se9', 'se', 0.3333, 0.6667, 0.8784, 0.08, 1.0)

#### SrTiO<sub>3</sub> (001):

STO.add\_atom('Sr', 'sr', 0.0, 0.0, 0.0, 0.08, 1.0) STO.add\_atom('Ti', 'ti', 0.5, 0.5, 0.5, 0.08, 1.0) STO.add\_atom('O1', 'o', 0.5, 0.0, 0.5, 0.08, 1.0) STO.add\_atom('O2', 'o', 0.0, 0.5, 0.5, 0.08, 1.0) STO.add\_atom('O3', 'o', 0.5, 0.5, 0.0, 0.08, 1.0)

## SrVO<sub>3</sub> (111):

SVO.add\_atom('Sr1', 'sr', 0.0, 0.0, 0.0, 0.08, 1.0) SVO.add\_atom('O1', 'o', 0.5, 0.0, 0.0, 0.08, 1.0) SVO.add\_atom('O2', 'o', 0.25, 0.43301, 0.0, 0.08, 1.0) SVO.add\_atom('O3', 'o', -0.25, 0.43301, 0.0, 0.08, 1.0) SVO.add atom('V1', 'v', 0.5, 0.288675, 0.5, 0.08, 1.0)

SVO.add\_atom('Sr2', 'sr', 0.0, 0.57735, 1.0, 0.08, 1.0) SVO.add\_atom('O4', 'o', 0.25, 0.1443376, 1.0, 0.08, 1.0) SVO.add\_atom('O5', 'o', 0.75, 0.1443376, 1.0, 0.08, 1.0) SVO.add\_atom('O6', 'o', 0.5, 0.57735, 1.0, 0.08, 1.0) SVO.add\_atom('V2', 'v', 0.0, 0.0, 1.5, 0.08, 1.0)

SVO.add\_atom('Sr3', 'sr', 0.5, 0.288675, 2.0, 0.08, 1.0) SVO.add\_atom('O7', 'o', 0.25, 0.1443376, 2.0, 0.08, 1.0) SVO.add\_atom('O8', 'o', -0.25, 0.1443376, 2.0, 0.08, 1.0) SVO.add\_atom('O9', 'o', 0.0, 0.288675, 2.0, 0.08, 1.0) SVO.add\_atom('V3', 'v', 0.0, 0.57735, 2.5, 0.08, 1.0)
## Appendix B: Multicarrier fitting for [001]-oriented SrVO<sub>3</sub>

This appendix details the multicarrier fitting of SrVO<sub>3</sub> with varying levels of disorder in Chapter 6. The temperature dependent transverse Hall resistance,  $R_{xy}$ , is shown in Figure B-1 for eight respective SrVO<sub>3</sub> samples with disorder ranging from the disordered limit with RRR=4 to the ultraclean limit with RRR=187. At temperatures below 200 K, distinct nonlinearities emerged as shown in contour plots of  $dR_{xy}/dB$  as a function of disorder and temperature in Figure B-2.

The transverse Hall resistance was then fit following the procedure outlined in Section 3.2.3 where Eq. 3.27 was used to model the experimentally determined transverse resistivity with an arbitrary number of carrier channels. For this study, the sign of the Hall coefficient was accounted for by choosing a negative carrier concentration for the electron channels. Following previous multicarrier fitting of SrVO<sub>3</sub>, two electron channels and a single hole channel were used.<sup>242</sup> A choice of three carrier channels results in a fitting of six variables; therefore, to simplify the fitting,  $R_{xx}$  and  $dR_{xy}/dB$  at zero field were used as additional fitting constraints. Fitting was done in Mathematica using a nonlinear model fit with 1000 iterations. For each sample, single carrier fits were first performed at room temperature. Fits at progressively lower temperatures were then completed using the previous fit as the starting condition. As nonlinearities in  $R_{xy}$  emerged, the addition of a hole channel was required to achieve reasonable fits. At temperatures below 40 K, the two-carrier model could no longer capture the nonlinearities and a three-carrier model was used. Experimentally measured data for each sample with corresponding fits are shown as  $dR_{xy}/dB$  versus B plots in Figure B-1.



Figure B-1: Temperature dependent transverse Hall resistance for samples of varying RRR ranging from (a) ultraclean SrVO<sub>3</sub> with RRR=187 to (h) highly disordered SrVO<sub>3</sub> with RRR=4 for 2 K < T < 300 K.



Figure B-2: Contour plots of the first derivative of the transverse hall resistance as a function of temperature for samples of varying RRR ranging from (a) ultraclean SrVO<sub>3</sub> with RRR=187 to (h) highly disordered SrVO<sub>3</sub> with RRR=4 for 2 K < T < 300 K.



Figure B-3:  $dR_{xy}/dB$  as a function of magnetic field strength with corresponding multicarrier fits for SrVO<sub>3</sub> with RRR=187.



Figure B-4:  $dR_{xy}/dB$  as a function of magnetic field strength with corresponding multicarrier fits for SrVO<sub>3</sub> with RRR=158.





Figure B-5:  $dR_{xy}/dB$  as a function of magnetic field strength with corresponding multicarrier fits for SrVO<sub>3</sub> with RRR=98.



Figure B-6:  $dR_{xy}/dB$  as a function of magnetic field strength with corresponding multicarrier fits for SrVO<sub>3</sub> with RRR=88.

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Figure B-7:  $dR_{xy}/dB$  as a function of magnetic field strength with corresponding multicarrier fits for SrVO<sub>3</sub> with RRR=56.



Figure B-8:  $dR_{xy}/dB$  as a function of magnetic field strength with corresponding multicarrier fits for SrVO<sub>3</sub> with RRR=28.



Figure B-9:  $dR_{xy}/dB$  as a function of magnetic field strength with corresponding multicarrier fits for SrVO<sub>3</sub> with RRR=10.



Figure B-10:  $dR_{xy}/dB$  as a function of magnetic field strength with corresponding multicarrier fits for SrVO<sub>3</sub> with RRR=4.

# VITA

#### Joseph Roth

## Education

April 2021
May 2016

#### **Selected Publications**

- 1. Brahlek, M., <u>Roth, J.</u>, Zhang, L., Briggeman, M., Irvin, P., Lapano, J., Levy, J., Birol, T., Engel-Herbert, R., Hidden transport phenomena in an ultraclean correlated metal (In review *Nature Communications*).
- <u>Roth, J.</u>, Kuznetsova, T., Miao, L., Pogrebnyakov, A., Alem, N., Engel-Herbert, R. Selfregulated Growth of [111]-Perovskite Oxide Films using Hybrid Molecular Beam Epitaxy, *APL Materials* 9, 021114 (2021)
- 3. <u>Roth, J.</u>, Paul, A., Goldner, N., Pogrebnyakov, A., Agueda, K., Birol, T., Alem, N., Engel-Herbert, R., Sputtered Sr<sub>x</sub>NbO<sub>3</sub> as a UV transparent conducting film, *ACS Applied Materials and Interfaces* 12, 27 (2020)
- Kotsonis, G., Meisenheimer, P., Miao, L., <u>Roth, J.</u>, Wang, B., Shafer, P., Engel-Herbert, R., Alem, N., Heron, J., Rost, C., Maria, J-P. Property and cation valence engineering in entropystabilized oxide thin films. *Physical Review Materials* 4, 10 (2020)
- Park, Y., <u>Roth, J.</u>, Oka, D., Hirose, Y., Hasegawa, T., Paul, A., Pogrebnyakov, A., Gopalan, V., Birol, T., Engel-Herbert, R., SrNbO<sub>3</sub> as a transparent conductor in the visible and ultraviolet spectra, *Communications Physics* 3, 102 (2020)
- Lapano, J., Brahlek, M., Zhang, L., <u>Roth, J.</u>, Pogrebnyakov, A., Engel-Herbert, R., Scaling growth rates for perovskite oxide virtual substrates on silicon, *Nature Communications* 10, 2464 (2019)
- <u>Roth, J.</u>, Arriaga, E., Brahlek, M., Lapano, J., and Engel-Herbert, R., Temperature-dependent growth window of CaTiO<sub>3</sub> films grown by hybrid molecular beam epitaxy, *Journal of Vacuum Science & Technology A*, 36, 20601 (2018)
- 8. Brahlek, M., Sen Gupta, A., Lapano, J., <u>Roth, J.</u>, Zhang, H.-T., Zhang, L., Haislmaier, R., Engel-Herbert, R. Frontiers in the growth of complex oxide thin films: past present and future, *Advanced Functional Materials*, 1702772 (2017)