The Pennsylvania State University
The Graduate School
Intercollege Graduate Program in Materials Science and Engineering

CORRELATED METALS AS TRANSPARENT CONDUCTORS

A Dissertation in
Materials Science and Engineering
by
Lei Zhang

© 2017 Lei Zhang

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2017
The dissertation of Lei Zhang was reviewed and approved* by the following:

Roman Engel-Herbert  
Professor of Materials Science and Engineering  
Dissertation Advisor  
Chair of Committee

Venkatraman Gopalan  
Professor of Materials Science and Engineering

Clive Randall  
Professor of Materials Science and Engineering

Joan Redwing  
Professor of Materials Science and Engineering

Srinivas Tadigadapa  
Professor of Electrical Engineering

Suzanne Mohney  
Chair, Intercollege Graduate Degree Program in Materials Science and Engineering  
Professor of Materials Science and Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The first section of this dissertation work discusses a new designing paradigm for transparent conductors which are widely used in energy and information technology. Most of previous efforts of developing high performance transparent conductors were given to the heavily-doped wide-bandgap semiconductors, which strike a delicate balance between electrical conductivity and optical transparency. However, the ideal conductors, metals, are much less considered and studied due to their nature of high reflection and high absorption in the visible spectrum (1.75~3.25 eV), making them unsuitable for the application as transparent conductors.

Here a sizeable electron-electron correlation effect and a favorable band structure of perovskite oxide-based correlated metal give arise to a much higher transparency and largely maintain the electrical conductivity. The test bed materials in this thesis are SrVO$_3$ and CaVO$_3$. Both materials are made of earth-abundant elements and have electron mean free paths that are less than ~5 nm, which enables the possibility of transferring to a scalable process with the polycrystalline form. High quality materials are successfully grown by hybrid molecular beam epitaxy (MBE) using an adsorption-controlled growth mode. By combining a DFT calculation of magnitude of interband transitions and a combined experimental approach of high-resolution x-ray diffraction (XRD), atomic force microscopy (AFM), spectroscopic ellipsometry and electrical transport measurements, the analysis of the materials is given in term of transparent conductor figure-of-merit. Both materials demonstrate a figure-of-merit that is on par with epitaxial ITO, the most widely used material in industry.

Beyond intrinsic correlated metals, a new strategy utilizes the aliovalent substitution of divalent element Sr with a trivalent element La in SrVO$_3$ is discussed. By carefully controlling the substitution level of La ($x$), a blue-shift of absorption peak at UV-range was observed and an increase of electrical conductivity was found. The optimal substitution level for the highest
figure-of-merit (~20% higher than that of SrVO₃) and the highest optical transparency are found, indicating that correlated metals are quite robust with extrinsic charged substitution.

The second section of this dissertation work discusses the monolithic integration of epitaxial complex oxide with Si using hybrid MBE. The monolithic integration of epitaxial complex oxide with Si could augment various functions that inherent to oxide, such as ferroelectricity, ferromagnetism, colossal magnetoresistance, superconductivity and multiferroic with industry work-horse Si. Hybrid MBE has advantages over thermal MBE in growing a thicker oxide template on Si, such as a higher growth rate and a better control of cation stoichiometry. The preparation of a high-quality SrTiO₃ buffer layer is the key that enables hybrid MBE growth of SrTiO₃ on Si substrate. A five-monolayer SrTiO₃ buffer layer was deposited on Si without oxygen at low temperature and subsequently annealed in vacuum at slightly high temperature. The temperature for the buffer layer growth must neither be too high to expedite the kinetic process of Si oxidization which would terminate the epitaxial growth or too low to prevent the decomposition of metal-organic precursor into TiO₂.

A two-step thermal anneal was then introduced. A high temperature anneal was employed to further reduce the rocking curve FWHM down to 0.2° while preserving a smooth film surface morphology. The sheet resistance of as-grown and post-annealed samples was increased by five orders of magnitude exceeding 10⁷ Ohm/sq using a lower temperature anneal. This two-step annealing method provides an easy and effective way to improve the crystalline quality of SrTiO₃ thin films on Si, providing a path towards the development of electrically insulating virtual perovskite substrates.
TABLE OF CONTENTS

List of Figures .................................................................................................................. vii
List of Tables .................................................................................................................... xv
Acknowledgements .......................................................................................................... xvi

Chapter 1 Introduction ....................................................................................................... 1
  1.1 Correlated metals as transparent conductors ......................................................... 1
  1.2 Monolithic integration of oxide on semiconductor ................................................ 5
  1.3 Statement of thesis ................................................................................................. 7

Chapter 2 Molecular beam epitaxy .................................................................................. 8
  2.1 Introduction to molecular beam epitaxy ................................................................. 8
  2.2 Kinetics process in molecular beam epitaxy ............................................................ 9
  2.3 Thermal oxide molecular beam epitaxy ................................................................. 14
     2.3.1 Introduction to thermal oxide molecular beam epitaxy .................................... 14
     2.3.2 Challenge in thermal oxide molecular beam epitaxy ....................................... 15
  2.4 Hybrid oxide molecular beam epitaxy ................................................................. 17
     2.4.1 Introduction to hybrid oxide molecular beam epitaxy ...................................... 17
     2.4.2 Metal-organic source inject system ............................................................... 22
  2.5 In-situ reflection high-energy electron diffraction .................................................. 24

Chapter 3 Experimental Details ...................................................................................... 30
  3.1 Structural Characterization .................................................................................... 30
     3.1.1 High-resolution x-ray diffraction .................................................................... 30
     3.1.2 Reciprocal space mapping .............................................................................. 34
     3.1.3 Atomic force microscopy .............................................................................. 36
  3.2 Spectroscopic ellipsometry ..................................................................................... 38
  3.3 Electrical Characterization .................................................................................... 40
     3.3.1 Resistivity measurement ............................................................................... 40
     3.3.2 Hall measurement ......................................................................................... 42
  3.4 Contact Photolithography ....................................................................................... 44

Chapter 4 Correlated metals as transparent conductors .................................................. 47
  4.1 Introduction ............................................................................................................. 47
  4.2 Growth of SrVO$_3$ and CaVO$_3$ ........................................................................ 51
  4.3 Electrical properties of SrVO$_3$ and CaVO$_3$ ....................................................... 55
  4.4 Optical properties of SrVO$_3$ and CaVO$_3$ ........................................................ 58
  4.5 Determination of the correlation strength ............................................................. 60
  4.6 DFT calculation ..................................................................................................... 63
  4.7 Figure-of-merit calculation for transparent conductors ........................................ 66
  4.8 Conclusion ............................................................................................................. 75
Chapter 5 Enhancing the performance of correlated metals as transparent conductors via A-site aliovalent substitution

5.1 Introduction ........................................................................................................... 77
5.2 Growth of La$_{x}$Sr$_{1-x}$VO$_3$ ............................................................................ 77
5.3 Optical properties of La$_{x}$Sr$_{1-x}$VO$_3$ .............................................................. 79
5.4 Electrical properties of La$_{x}$Sr$_{1-x}$VO$_3$ ........................................................... 83
5.5 Figure-of-merit calculation for transparent conductors ........................................ 86
5.6 Conclusion ........................................................................................................... 88

Chapter 6 Growth of SrTiO$_3$ on Si (001) by hybrid molecular beam epitaxy ................. 94

6.1 Introduction ........................................................................................................... 94
6.2 Experimental section ............................................................................................ 96
6.3 Buffer layer growth .............................................................................................. 98
6.4 Thin film growth and structural characterization .................................................. 101
6.5 Surface morphology of 600 ºC-grown film ......................................................... 107
6.6 The emergence of growth window ...................................................................... 109
6.7 Continuous strain modulation by thermal strains ................................................. 112
6.8 Conclusion ........................................................................................................... 115

Chapter 7 Improving the structural quality and electrical resistance of SrTiO$_3$ thin films on Si (001) via a two-step anneal .................................................................................. 117

7.1 Introduction ........................................................................................................... 117
7.2 Experimental section ............................................................................................ 119
7.3 Results and discussion ....................................................................................... 121
7.4 Conclusion ........................................................................................................... 123

Chapter 8 Future Work ............................................................................................. 134

8.1 Determination of work function for vanadates .................................................... 134
8.2 Understanding of low-temperature transport properties of vanadates .................. 139
8.3 Exfoliation of functional oxide from Si: a pathway to flexible application .......... 146

Reference .................................................................................................................. 149

Appendix Procedure of ultrafast reciprocal space mapping (RSM) with PIXcel$^{3D}$ ............. 173
LIST OF FIGURES

Figure 1-1. Application of transparent conductors, such as flat panel display, thin film solar cells, touchscreen devices and LED. ................................................................. 1

Figure 1-2. Average unit price of indium (US dollars per kilograms) as a function of year. (Data is acquired from ref11) ................................................................. 3

Figure 1-3. Mass fraction abundance of the elements in the Earth’s crust as function of atomic number. (Adapted from ref12) ......................................................... 4

Figure 1-4. (a) The challenge for integrating crystalline oxides with silicon, and both materials are chemically and structurally different. (b) The capacitance of the oxide as a function of applied voltage. (Adapted from ref24) ........................................ 6

Figure 2-1. (a) 1st MBE machine at Bell Labs in 1970. (Adapted from ref31) (b) History of improvements in the low-temperature mobility of electrons in GaAs, annotated with the technical innovation associated with the improvement of mobility. (Adapted from ref32) ......................................................... 8

Figure 2-2. (a) The schematic of the surface process occurring during film growth by MBE. (b) The schematic of potential as a function of distance in the physical and chemical adsorption. ........................................ 10

Figure 2-3. (a) Schematic of nucleation process on substrate during vapor deposition. (b) Thin film formation and three different growth modes: Frank-van der Merwe (FM) growth mode, Volmer-Weber (VW) growth mode and Stranski-Krastanov growth mode ........................................... 12

Figure 2-4. Some of institutions that host oxide MBE groups in United States .................. 14

Figure 2-5. Comparison of effusion cell temperatures needed to generate sufficient vapor pressure for acceptable growth rate (Adapted from Ref46). .............................. 16

Figure 2-6. The image of 2nd generation of hybrid MBE system at Penn State. The MBE reactor is on the left of figure. The buffer chamber connects the MBE and sputtering chamber to the loadlock. The turbo pump and cryopump are installed at the top and bottom of MBE chamber, respectively. ....................................... 17

Figure 2-7. (a) The chemical structure of TTIP. (b) Temperature dependence of vapor pressure for TTIP and its byproduct (Adapted from Ref46). .............................. 18

Figure 2-8. (a) High-resolution XRD of SrTiO3 thin films with different cation non-stoichiometry grown on SrTiO3 substrates (b) Out-of-plane lattice constant as a function of TTIP/Sr BEP ratio for SrTiO3 thin films grown on SrTiO3 substrate at different temperatures (Adapted from Ref52). ........................................... 19

Figure 2-9. (a) The image of a metal-organic precursor inlet system. (b) Schematic of a metal-organic precursor inlet system. .............................................................. 22
Figure 2-10. Schematic of a RHEED system.................................................................24

Figure 2-11. (a) Schematic of the Ewald's sphere where the constructive interference
conditions are met when the Ewald sphere intersects a reciprocal lattice point. (b)
RHEED patterns (shown on the left) that could be observed under different surface
morphology (shown on the right)...........................................................................................................27

Figure 2-12. (a) RHEED oscillation at [100] azimuth of 600 °C-grown SrTiO₃ thin film
on Si (001) substrate. (b) Schematic of RHHED intensity at one oscillation period as
a function of different fractions of surface coverage.................................................................28

Figure 3-1. Schematic of x-ray interference with the plane that obeys Bragg’s law.............30

Figure 3-2. (a) The PANalytical X’Pert Pro MRD used for the HRXRD measurements at
Penn State University (b) The available detectors: PIXcel area detector and triple-axis analyzer detector (c) Schematic view of all the rotatable axis of the sample
goniometer................................................................................................................................32

Figure 3-3. (a) A real thin film with mosaicity. (b) Rocking curve measurements of a
120-nm SrTiO₃ film on Si before and after thermal annealing..................................................33

Figure 3-4. (a) Schematic of relaxed, compressively strained and tensile-strained thin
films (b) Schematic of reciprocal lattice and the trace for 2θ scans, ω-θ scan, ω scans and RSM. Notes that the XRD measurements are not possible in two smaller
semicircles. The Edward’s sphere is constructed by the radius which equals to the
wave vector of the incident x-ray beam............................................................................................35

Figure 3-5. (a) Schematic of AFM set-up which mainly consists of a laser, a photodiode
and a cantilever with a sharp tip on its free end. (b) A typical AFM scan of a 45nm
SrVO₃ thin film on LSAT substrate..............................................................................................37

Figure 3-6. Schematic of (a) van der Pauw geometry and (b) Hall bar geometry. (c)
SrVO₃ thin films with van der Pauw geometry on a petri dish, and the indium dots
are used as probe contacts. (d) SrVO₃ thin film with 8 point Hall bar geometry in a
PPMS transport puck. .............................................................................................................................41

Figure 3-7. Schematic of patterning process of Hall bar. (a) Deposit a thin film on a
substrate. (b) Spin the photoresist, (c) UV-exposure using a patterned mask, (e)
Develop the photoresist after baking. (e) Plasma etching the unwanted thin film (g)
Strip the unwanted photoresist. ........................................................................................................45

Figure 3-8. Etching thickness as a function of etching cycles of SrVO₃ by reactive
etching with BCl₃ gas...............................................................................................................................46

Figure 4-1. Design rules for transparent conductors. (a) Schematic of the ideal
transmittance, where the free carrier reflection edge is below 1.75 eV and the onset
of absorption due to strong interband optical transition is above 3.25 eV, opening a
transparent window over the entire visible spectrum. (b) Electrical conductivity
as a function of correlation strength \( Z_k = \frac{m^*_{band}}{m^*} \) 82,83, which is quantified by
In-plane conductivity was taken for materials with symbol.*. (c) Optimization of electrical conductivity under the constraint to keep free carrier reflection edge, represented by screened plasma frequency \( \omega_p \), below the visible spectrum. Correlated metals positioned between conventional metals and degenerately doped wide band gap semiconductors are suited to balance conductivity and free carrier reflection through strong electron correlation. Experimental data for Ag (red rhombus)\(^{84,85}\), Au (red up-pointing triangle)\(^{84,86}\), Al (red square)\(^{84,87}\), Cu (red left-pointing triangle)\(^{84,85}\), Ni (red down-pointing triangle)\(^{84,87}\), bulk c-ZnO (green circles, line is only guide to the eye)\(^{88}\), 500 nm epi-ITO (green rhombus, line is only guide to the eye)\(^{89}\), 300 nm epi-ZnO (half-filled green circle)\(^{90}\), 400 nm epi ITO (green square)\(^{91}\) and 20 nm SrVO\(_3\) (red four-point star) and 38 nm CaVO\(_3\) (blue four-point star) are shown for comparison. (Adapted from ref\(^{92}\)....48

Figure 4-2. High-resolution X-ray diffraction 2θ-ω scans of (a) SrVO\(_3\) films with varying thicknesses grown on LSAT substrates. (b) Experimental and calculated X-ray diffraction intensities of the 45-nm-thick SrVO\(_3\). (c) SrVO\(_3\) films with varying thicknesses grown on LSAT substrates. (d) Experimental and calculated X-ray diffraction intensities of the 38-nm-thick CaVO\(_3\). Film lattice parameter and thickness given in Table 4-1 and Table 4-2 were extracted from these fits. (Adapted from ref\(^{106}\))........................................................................................................53

Figure 4-3. Atomic force micrographs of SrVO\(_3\) and CaVO\(_3\) films. (Adapted from ref\(^{106}\)....54

Figure 4-4. Structure and electrical transport properties of vanadate films. (a) Crystal structure of SrVO\(_3\) and CaVO\(_3\). (b) Temperature dependent sheet resistance of SrVO\(_3\) and CaVO\(_3\) films. (c) Carrier concentration and (d) Carrier mobility of SrVO\(_3\) and CaVO\(_3\) films at room temperature. e, Thickness dependent conductivity of Ag (gray triangles)\(^{19}\) and Au (orange triangles)\(^{19}\), polycrystalline ITO (light green rhombus)\(^{93}\), PLD-grown ITO (light green squares)\(^{107}\) and epi-ITO (green rhombus) on LaAlO\(_3\) (200 nm ITO) and YSZ substrates\(^{91,109}\) (59 nm and 400 nm ITO), and SrVO\(_3\) (red circles) and CaVO\(_3\) (blue circles) films from this work. (Adapted from ref\(^{92}\))........................................................................................................55

Figure 4-5. (a) Schematic and (b) optical photograph of Hall bar devices, here for CaVO\(_3\). Temperature dependent resistivity of (c) 45-nm-thick SrVO\(_3\) and (d) 38-nm-thick CaVO\(_3\) films along the different directions. The scale bar indicates 500 μm. (Adapted from ref\(^{106}\))........................................................................................................57

Figure 4-6. (a) Optical properties of vanadates. (a) Transmission spectrum of SrVO\(_3\) films (top) and CaVO\(_3\) (bottom) with varying thicknesses on LSAT and SLAO substrates. The range of the visible spectrum is indicated. (b) Photographs of 4 nm and 12 nm SrVO\(_3\) and CaVO\(_3\) films on LSAT and SLAO substrates, respectively. (c) Complex dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) spectra of SrVO\(_3\) extracted from room temperature spectroscopic ellipsometry measurements and calculated from first principles calculations. Note the different scale for low energy \( \varepsilon \). (Adapted from ref\(^{92}\)).................58

Figure 4-7. (a) Optical conductivity as a function of frequency. (b) Sum-rule plasma frequency as a function of cut-off frequency. ........................................................................................................61
Figure 4-8. First principle calculation results of SrVO$_3$. (a) Band structure of SrVO$_3$ in the vicinity of the Fermi level EF (dotted line), comprised of nine bands originating from O 2p orbitals, three bands from V 3$d$ t$_{2g}$, and two bands from V 3$d$ e$_g$ orbitals. Interband transition (I) through (III) are indicated. (b) Brillouin zone of SrVO$_3$ containing the Fermi surfaces of the three t$_{2g}$ bands. Isosurface representation of the dipole matrix element M$^2$ for electronic states in the Brillouin zone for the interband transitions (c) (I): t$_{2g}^2$ to e$_g^1$, (d) (II): 2p$^1$ to t$_{2g}^1$, (e) (III): 2p$^1$ to t$_{2g}^3$ with 2p$^1$ the highest lying valence band, t$_{2g}^1$, t$_{2g}^2$, t$_{2g}^3$ the lowest middle and highest lying t$_{2g}$ bands, and e$_g^1$, e$_g^2$, e$_g^3$ the lowest, highest lying e$_g$ bands, respectively. The Fermi surface of the t$_{2g}$ band involved in the transition is indicated in c-e as well. (Adapted from ref$^{92}$). .................................................................63

Figure 4-9. Optical transmission of free standing films, accounting for reflection and interference, at a wavelength $\lambda = 550$ nm [Eqns. (H), (I), (K), (L)], and averaged over the range of the visible spectra [Eqn. (N)]. Data of the complex refractive index of Ag, ITO, SrVO$_3$ and CaVO$_3$ were taken from Refs$^{126,127}$ and this work. (Adapted from ref$^{106}$) ........................................................................................................68

Figure 4-10. Thickness dependence of the sheet resistance $R_s$ for (a) SrVO$_3$ (b) CaVO$_3$ (c) ITO, and (d), Ag taking the thickness dependent resistivity into account. The increase in resistivity $\Delta \rho$ normalized to the bulk resistivity $\rho_0$ is shown below. Data for Ag, ITO, SrVO$_3$ and CaVO$_3$ were taken from Refs$^{19,133}$ and this work, respectively. (Adapted from ref$^{106}$) ........................................................................................................70

Figure 4-11. Consideration for the figure of merit (FOM) for transparent conductors. Solid black line: FOM defined after Haacke$^{124}$, calculated for light at wavelength $\lambda = 550$ nm. Dashed gray line: FOM using transmission value taken as average across the visible spectrum. Dotted blue line: Averaged transmission incorporating multiple reflection and interference effects from top and bottom interface of a free standing film by calculating the transmission averaging over the visible range, see Fig. 4-9. Thick solid green line. Figure of merit includes thickness dependent increase of electrical conductivity due to enhanced surface scattering for films with thicknesses below the electron mean free path, see Fig. 4-10. (a) Example of Ag representing ultrathin metal films. (b) Example of ITO representing degenerately doped wide band gap semiconductors. (Adapted from ref$^{106}$) ........................................................................................................72

Figure 4-12. Figure of merit $\Phi_{TC}$ for transparent conducting materials. Experimental data compiled for Au (orange circles), Ag (grey circles)$^{19,134}$, polycrystalline ITO (green circles)$^{93,126}$, epi-ITO (solid triangle$^{109}$, empty triangle$^{126}$, cross triangle$^{135}$) and SrVO$_3$ (red circles) and CaVO$_3$ (blue rhombus) from this work. Lines are from $\Phi_{TC}$ calculations (see supplement). Deviations between experiment and calculation for Au and missing experimental data of Ag for thicknesses less than 10 nm are due to inferior percolation behavior of ultrathin metal films. (Adapted from ref$^{125}$) ..........74

Figure 5-1. (a) 26-ω scans around the 002 LSAT substrate peak for La$_x$Sr$_{1-x}$VO$_3$ films with various La compositions. (b) Out-of-plane lattice parameters versus La compositions (The black solid line is a guide to the eye). Reciprocal space mapping of La$_x$Sr$_{1-x}$VO$_3$ films with (c) $x=0.11$ and (d) $x=0.03$. ........................................................................................................80
Figure 5-2. 2θ-ω scans (red dots) around the 002 LSAT substrate peak for La$_x$Sr$_{1-x}$VO$_3$ films and their fitting results (solid black line) with La compositions (a) $x=0.18$; (b) $x=0.11$; (a) $x=0.03$; (a) $x=0.02$; (a) $x=0.01$; (e) $x=0.00$; .................................................. 82

Figure 5-3. (a) The schematic of optical absorption between O 2p and V $t_{2g}$ band for SrVO$_3$ and La$_x$Sr$_{1-x}$VO$_3$. (b) Real (top panel) and imagery (bottom panel) part of the dielectric function of La$_x$Sr$_{1-x}$VO$_3$ films extracted from spectroscopic ellipsometry measurements. (c) The calculated transmission as a function of photon energy for 10-nm-thick La$_x$Sr$_{1-x}$VO$_3$ films with $x=0.03$, 0.11 and 0.18. The 80% transmission is drawn by a dash line. The inset shows the photon energy at which the dash line crossed the transmission curves as a function of La compositions. ........................................ 83

Figure 5-4. (a) Temperature-dependent resistivity of La$_x$Sr$_{1-x}$VO$_3$ films. (b) RRR ($\rho_{300K}/\rho_{2K}$) of La$_x$Sr$_{1-x}$VO$_3$ films as a function of La compositions. (c) Room temperature carrier concentration (top panel), mobility (middle panel) and resistivity (bottom panel) as a function of La compositions, respectively. ................................. 86

Figure 5-5. The optical transmission integrated from 400 to 800 nm (solid line) and optical transmission at a fixed wavelength of 550 nm (dash line) for La$_x$Sr$_{1-x}$VO$_3$ films with $x=0.18$, $x=0.03$ and $x=0.00$.......................................................... 89

Figure 5-6. (a) Figure of merit $\Phi_{TC}$ of La$_x$Sr$_{1-x}$VO$_3$ films as a function of film thickness. (b) The highest figure of merit $\Phi_{TC}$ of La$_x$Sr$_{1-x}$VO$_3$ films as a function of La compositions $x$. The film thickness at which the highest figure of merit is acquired is displaced next to the symbol. Figure of merit of epitaxial ITO$^{92}$ (red dashed line) and polycrystalline ITO$^{92}$ (blue dashed line) is included as references. ........................................ 91

Figure 6-1. (a) The residual gas spectrum of the hybrid MBE reactor chamber before and after Sr getter deposition. RHEED pattern of Si (001) surface along the 110 azimuth after (b) a heat flash at 900 °C containing diffraction spot from the 3C-SiC overlayers encircled by a dotted line, (c) Sr getter step and Sr-promoted SiO$_2$ desorption revealing a (2$\times$1) reconstruction and no 3C-SiC features, indicating a clean and oxygen-free surface. (d) 5ML SrTiO$_3$ buffer layer deposition and subsequent anneal (e) SrTiO$_3$ film after growth.............................................. 99

Figure 6-2. (a) 2θ-ω X-ray diffraction scans of SrTiO$_3$ films grown at various TTIP gas inlet pressures $P_{TTIP}$ showing only 00L peaks of SrTiO$_3$. (b) XRD $\varphi$ scans of SrTiO$_3$ 101 and Si 202 reflection. (c) Out-of-plane lattice constant $a_\perp$ of SrTiO$_3$ on Si (001) as a function of TTIP gas inlet pressure $P_{TTIP}$, extracted from 2θ-ω scans. The lattice constant of bulk SrTiO$_3$ (3.905 Å) and the calculated $a_\perp$ value for tensile strained SrTiO$_3$ grown on Si at 600 °C (3.895 Å) are indicated as well. Reciprocal spaces maps (RSMs) around the (d) 103 and (e) 103 reflections of the SrTiO$_3$ film grown on Si (001) at $P_{TTIP}=54$ mTorr. The maps are given in reciprocal lattice units [r.l.u.] of bulk SrTiO$_3$ with a lattice parameter of 3.905 Å. .............................................. 102

Figure 6-3. High resolution transmission electron microscope images of the SrTiO$_3$ film grown at $P_{TTIP}=54$ mTorr taken in cross-section along the Si [110] zone axis. (a) Lower magnification image shows only few defects extended throughout the film.
Figure 7-4. Atomic force microscopy (AFM) scans of 600°C-grown SrTiO$_3$ films grown on Si grown at different TTIP gas inlet pressures of (a) 52 mTorr, (b) 54 mTorr and (c) 62 mTorr. The sides of square islands in (a) were either parallel or perpendicular to Si [110]. RMS roughness values of the films were taken from the boxes in (b) and (c), as discussed in the text. 

Figure 6-4. (a) RHEED intensity oscillation of the 01 reflection spot taken along the (100) azimuth of an 11-ML-thick SrTiO$_3$/Si buffer layer grown at 600 °C. RHEED pattern of SrTiO$_3$/Si after growth, taken along the (b) (100), (c) (110) and (d) (210) azimuth. (e) Wide range XRD 20-ω scan of a 120 nm SrTiO$_3$ film on Si (001) 

Figure 7-3. Rocking curve FWHM of the 002 SrTiO$_3$ peak of (a) 46-nm-thick SrTiO$_3$ and (b) 120-nm-thick SrTiO$_3$ on Si (001) before and after 1050 °C thermal anneal. (c) Rocking curve FWHM of the 002 SrTiO$_3$ peak as a function of annealing temperature for 5 hours. (d) Rocking curve FWHM of the 002 SrTiO$_3$ peak as a function of annealing duration at 950 °C. 

Figure 7-4. Comparison of FWHM values of the 002 SrTiO$_3$ rocking curve scan as a function of film thickness (Reference: Gu et al. $^{171}$, Panomsuwan et al. $^{223}$, Méchin et al. $^{29}$, Méchin et al. (1999) $^{224}$, Lettieri et al. $^{225}$, Niu et al. $^{182}$, Gsell et al. $^{226}$, Yu et al. $^{169}$, Yong et al. $^{227}$, McDaniel et al. $^{175}$, Spreitzer et al. $^{235}$, Bauer et al. $^{236}$, and Guo et al. $^{237}$). Arrows and dashed lines are guide to the eyes.
Figure 7.5. AFM scans of (a) as-grown (b) 800 °C annealed (c) 950 °C annealed and (d) 1050 °C annealed 120-nm-thick SrTiO$_3$ on Si. The scale bar corresponds to 0.5 µm. (e) RMS surface roughness versus different annealing temperatures before and after anneal. (f) Rocking curve FWHM of the 002 SrTiO$_3$ peak versus RMS roughness values for samples annealed at different temperatures. The lines are guide to the eyes. ................................................................. 128

Figure 7-6. (a) Sheet resistance, resistivity and (b) estimated oxygen vacancy concentration of 120-nm-thick SrTiO$_3$/Si versus second step annealing temperature. Data for the comparison sample (120 nm SrTiO$_3$/LSAT) is shown as well. .................. 130

Figure 8-1. (a) Band structure of a Si heterojunction solar cell with intrinsic amorphous Si layer. The work function of transparent conductor at both side play an important role in the contact resistance. (b) Schottky model of a metal-semiconductor interface. The upper and lower parts of the figure show the interface before and after contact, respectively. The left, middle and right parts of the figure show three conditions: accumulation, neutral and depletion. Schottky barrier forms in the condition of depletion. ........................................................................................................ 135

Figure 8-2. Schematic of current-voltage-temperature and capacitance-voltage measurement that can be use to extract barrier height. ................................................................. 136

Figure 8-3. RHEDD images at different azimuths and height of sample stage after growth at 200°C for 10nm SrVO$_3$ thin films on Nb-SrTiO$_3$ substrates with (a) Nb doping of 0.5%, (b) Nb doping of 0.7%, (c) Nb doping of 0.1% and (d) Nb doping of 0.05%. (e) Schematic of influence of different surface termination of Nb-SrTiO$_3$ substrates on the interface of SrVO$_3$/Nb-SrTiO$_3$. Note that the final interface of SrVO$_3$/Nb-SrTiO$_3$ is independent of starting termination................................................................. 138

Figure 8-4. Derivative of hall resistance as a function of magnetic field at different temperatures (Photo courtesy of Matthew Brahlek). ................................................................. 140

Figure 8-5. Simulated Hall resistance as a function of magnetic field if both carriers are holes. .................................................................................................................................. 142

Figure 8-6. Simulated Hall resistance as a function of magnetic field if both carriers are electrons. .................................................................................................................................. 143

Figure 8-7. Simulated Hall resistance as a function of magnetic field if both one type of carriers is electron and the other is hole........................................................................ 145

Figure 8-8. Schematic of processing steps for heterostructure growth, oxide membrane release and transfer. (Adapted from ref 255) ................................................................. 147

Figure 8-9. Schematic for epitaxial lift-off of single-crystal Au foil. (A) Miscut n-type Si(111) wafer without the native oxide layer. (B) Epitaxial electrodeposition of Au on Si(111) from a 0.1 mM HAuCl$_4$ solution at −1.9 V versus Ag/AgCl with prepolarized electrode. (C) Photoelectrochemical oxidation of Si under irradiation of light in 0.5 M H$_2$SO$_4$ solution at 0.75 V versus Ag/AgCl. (D) A polymer adhesive
(tape/hot glue) is applied to the surface of Au to aid the foil separation. (E) A sacrificial SiO\textsubscript{x} interlayer is etched using dilute (5\%) hydrofluoric acid to separate the foil from the Si substrate. (F) Single-crystal Au foil completely detached from the Si surface. (Adapted from ref\textsuperscript{259})

Figure 8-10. Thickness of SiO\textsubscript{x} layer at the interface of SrTiO\textsubscript{3} thin film on Si wafer as a function of annealing temperature for 5 hours. The color of SrTiO\textsubscript{3}/Si shown in the figure is a good indication of various thickness of SiO\textsubscript{x} as an antireflection coating layer on Si wafer. (Photo courtesy of Yuanxia Zheng.)

Figure A-1. The structure information of substrate and thin film can be added in “User Setting”→ “Unit Cell”.

Figure A-2. The information of lattice and choice of primary and secondary axis can be added to build “Reciprocal Space Map”.

Figure A-3. The goniometer can be moved to desired substrate peak by clicking the diffraction peak in “Reciprocal space map” in “Catch HKL mode”.

Figure A-4. Change the detector to “frame based” mode and couples scans can be performed.
LIST OF TABLES

Table 4-1. Thickness series of SrVO$_3$ grown on LSAT samples. Lattice parameter and film thickness has been extracted from XRD spectra shown in Fig. 4-2. ..........................53

Table 4-2. Thickness series of CaVO$_3$ grown on SLAO samples. Lattice parameter and film thickness has been extracted from XRD spectra shown in Fig. 4-2. .................53

Table 4-3. Calculation of the electron mean free path (EMPF) for selected materials at room temperature. Data for Cu, Ag and Al were taken from Ref. $^{19}$, ITO from Ref. $^{131}$ and SrVO$_3$ from this work..................................................69

Table 5-1. Thickness series of La$_{x}$Sr$_{1-x}$VO$_3$ grown on LSAT samples. Lattice parameter and film thickness has been extracted from XRD spectra shown in Fig. 5-1. .............81

Table 6-1. Normalized intensity and full width at half maximum (FWHM) of the 002 SrTiO$_3$ peak from the 20-0 scans shown in Fig. 6-2 (a) for films grown at different TTIP gas inlet pressures P$_{TTIP}$. The peak intensity was normalized to the average background between 55° to 60° of the 20-0 scan.................................................................102

Table 8-1. Carrier density and mobility used in Fig. 8-5..................................................142

Table 8-2. Carrier density and mobility used in Fig. 8-6..................................................143

Table 8-3. Carrier density and mobility used in Fig. 8-7..................................................145
ACKNOWLEDGEMENTS

First, I would like to express my sincere gratitude to my advisor, Prof. Engel-Herbert, for his guidance on my research topics and providing me one of the most expensive “toys” in material synthesis. He has a very broad knowledge in physics, materials science and solid state devices, and we had many insightful and delightful discussions throughout my entire graduate study. While being helpful for my scientific research, his good personality leaves me a pleasant memory for my PhD study. What I appreciated the most is his kindness, consideration and politeness toward students and post-docs which I wish to learn more.

I would also like to thank Prof. Gopalan, Prof. Randall, Prof. Redwing and Prof. Tadigadapa for serving on my dissertation committee and providing suggestion. I am very fortunate to be surrounded by many talented post-docs and graduate students. Particularly, I would like to thank Dr. Matthew Brahlek for countless scientific discussion, his enthusiasm in MBE and physics and his coffee; thank Dr. Craig Eaton (now at Intel) for getting me started on hybrid MBE; thank Yuanxia Zheng for ellipsometry measurements and the nights we signed each other as buddies in the cleanroom; thank Hai-Tian Zhang and we always discussed the most recent papers and works in the fields; thank Dr. Ryan Haaslmaier (now at University of Minnesota), Dr. Arnab Sen Gupta, Dr. Jarret Moyer, Jason Lapano, Joseph Roth, Yaqiang Wang for support and help as group members.

I would also like to thank Dr. Weiwei Zhao (now at Harbin Institute of Technology), Jue Jiang, James Kelly and Prof. Moses M. H. Chan for allowing me use PPMS and the help with the measurements; thank Yuanjun Zhou (now at Columbia University) and Prof. Karin Rabe from Rutgers University for the collaboration on DFT; thank Lu Guo (now at University of Wisconsin) and Prof. Gopalan for FTIR and some of the UV-Vis-IR measurements; thank Yakun Yuan and Shiming Lei in Prof. Gopalan’s group for second harmonic generation measurements and sample
polishing; thank Prof. Podraza for the ellipsometry measurements; thank Smitha Shetty and Prof. Trolier-McKinstry for teaching me to use PE-loop measurement set-up; thank Prof. Redwing for letting me use hall measurement set-up; thank Dr. Ke Wang and Dr. Bernd Kabius for taking TEM images for me.

I would also like to thank MCL staffs (Nichole, Tim, Josh and Mandy) and NanoFab staffs (Bangzhi, Bill, Mike, Kathleen, Guy and Shane) for training me on various tools. Penn State has a world-class facility which significantly facilitates my research. I would also thank Peg, Mandy and Jason from department of materials science and engineering for helping me process countless forms and make my life much easier. I would like to thank all my friends. A five-year stay at State College is a very delightful in my life.

Last but not least, I want to thank my wife and my parents. Their unconditional support makes me could go through all the struggles in my graduate study. Marrying my wife, Chaoran, is the happiest moment in my life in the past five years.
Chapter 1

Introduction

1.1 Correlated metals as transparent conductors

Transparent conductors play essential roles in display (flat-panel display and touchscreen devices), solid state lighting, as well as active energy generation (photovoltaics, such as thin film solar cell, HIT solar cell) and passive energy preservation (architectural low-emissivity glass, smart windows), as shown Fig. 1-1.

![Figure 1-1. Application of transparent conductors](image)

Oxidized or partially oxidized CdO is widely considered as the first transparent conductor\(^5\). One of the first applications for transparent conductor is the transparent heating layer for plane cockpit window. Starting at 1950s, tin-doped indium oxide (ITO), a heavily-doped wide-bandgap semiconductor, is currently used in most, if not all the applications\(^6\). ITO could be deposited on
glasses or flexible substrates such as PET by physical vapor deposition, such as magnetron sputtering\textsuperscript{7}, which is a mature process and compatible with the semiconductor industry. ITO strikes the best balance between electrical conductivity and optical transparency, and it could also be easily patterned with wet-etching. Around 90\% (Year 2015)\textsuperscript{8} of transparent conductors were ITO, while the rest were more economical replacements with slightly lower performance, such as Al-doped ZnO or F-doped SnO\textsubscript{2}.

P-type transparent conductors are also of great interest in recent years, since they could form PN-junction with n-type transparent conductors and open the gate to invisible functional devices. Previously p-type transparent conductors typically have the Cu based delafossite structure with a chemical formula of CuXO\textsubscript{2} (X=Al, Ga, In, Sc, Y, La, etc.)\textsuperscript{9}, since a large hybridization of the oxygen orbitals with 3d\textsuperscript{10} electrons in the Cu\textsuperscript{1+} closed shell could dramatically lower the oxygen character and lead to a dispersive valance band and thus lower effective masses and higher carrier mobilities\textsuperscript{10}.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{chart.png}
\caption{Price of transparent conductors over time.}
\end{figure}
Figure 1-2. Average unit price of indium (US dollars per kilograms) as a function of year. (Data is acquired from ref\textsuperscript{11})

For n-type transparent conductor, In is not a cheap and abundant element. Figure 1-2 shows the unit price of In from Year 2000 and Year 2015 (the money of individual year is also converted to the money of 2015 to avoid the effect of inflation on the unit value, as shown in red circle) from United States Geological Survey\textsuperscript{11}. The average unit price of In is ~$600 per kilogram over the past 10 years, which is about the same as Ag. Large fluctuations of price are also seen in Fig. 1-2, as most of In is only produced in limited countries, indicating the global price is quite volatile.

The high price of In is attributed to the scarcity of In in the earth crust and also the difficulty in In purification. Figure 1-3 shows the element-abundance in the earth crust, which also serves as a good reference to design and select materials for transparent conductors\textsuperscript{12}. The green zone which contains rock-forming elements represents the most abundant elements, names “rock-forming elements”, which includes Si, Al, Ca, Mg, O, K, etc. The yellow zone which contains the rarest metals represents the scarcest elements, which includes Ag, Au, Ru, Pr, Ir, etc. The abundance of In (highlighted in red) is just right above the yellow zone, as shown in Fig. 1-3. Secondly, indium is only a minor by-product of zinc mining with a lesser extent to Pb and Sn. There is no driving force of profit for zinc-mining industry to increase the production of zinc for the purpose of extracting additional quantities of indium, since the value of In mined in 2012 only represents ~1.4% of the value of zinc market\textsuperscript{13}. In addition to the cost issue, the material performance of degenerately doped wide band gap semiconductors in general and ITO in particular have been largely pushed to their intrinsic limits by the continuing efforts of engineers and scientists, and further improvements in the electrical conductivity are hampered by the solid solution limit of dopants and sizeable contributions from charged impurity scattering at high dopant concentrations.
There are currently some candidates that can potentially replacing ITO, which includes multilayer graphene, metal mesh, Ag nanowires and PEDOT: PSS. Graphene only contains a “rock-forming” element, carbon, and a single-layer graphene only has a transmission of 97.4%. However, the transmission will rapidly drop as the numbers of layers increase. The conductance of multilayer graphene can hardly meet the requirement for application as large scale flat panel display. The fabrication process of graphene still remains complicated and hard to reproducible, which includes high-temperature (~1000 °C) chemical vapor deposition process on Cu foil, dissolution of Cu foil, lamination of graphene on glass and doping activation. Among all the alternative solutions, Ag nanowires and metal mesh which utilize the large aspect ratio of metals...
are the most promising ones. However, for metal mesh, in order to avoid Moiré pattern originated from the finite width of metal lines, more expensive patterning process is needed. Extreme thin metal lines are also to vulnerable to external forces and perturbation. In addition to solve the problem of haze from the random distribute nanowires, for the cost of raw material, Ag nanowire also doesn’t show any advantage over In in ITO.

While conventional metals are ideal conductors and were considered as transparent conductors if deposited as ultrathin film form\textsuperscript{18,19}, they are not ideal material choices compared to ITO due to the much lower optical transparency. Metals have high plasma frequencies ($\omega_p$) and are thus highly reflective in the visible range (1.75-3.25 eV); some metals have strong interband transitions in the visible range leading to strong absorptions\textsuperscript{20-22}. In this dissertation work, I focus on proposing a new designing paradigm for transparent conductors that utilize a sizable electron-electron correlation to increase the optical transparency of correlated metals, while largely maintain the electrical conductivity by keeping a high electron density, and experimentally demonstrate it with vanadate materials with perovskite structures, SrVO$_3$, CaVO$_3$ and La$_x$Sr$_{1-x}$VO$_3$.

1.2 Monolithic integration of oxide on semiconductor

Si-based metal-oxide-semiconductor field-effect transistor or MOSFET used SiO$_2$ as the gate dielectric until the scaling down of SiO$_2$ reached about 1.2 nm or less. A substantial gate tunneling current is seen with SiO$_2$, and thus alternative high-k dielectric materials such as SrTiO$_3$, are needed for maintaining high gate capacitance. The first attempt of integrating SrTiO$_3$ on Si was accomplished by depositing a thick SrO buffer layer, which resulted in a polycrystalline form\textsuperscript{23}. However, the monolithic integration of SrTiO$_3$ on Si (001) is highly desirable, since only an amorphous or crystalline oxide can be used the gate dielectric. It’s until 1998, McKee \textit{et al.} firstly
grew crystalline SrTiO$_3$ epitaxial layer on Si (001) using a $\frac{1}{2}$ SrO buffer layer by oxide molecular beam epitaxy$^{24}$. 

Since then, a new age of integrating of crystalline functional perovskite oxides on Si (001) started. Integrating crystalline oxide devices on semiconductors is considered a pathway to augment conventional semiconductor devices with unique functionalities inherent to oxides, such as resistive-switching behavior$^{25}$, ferroelectric$^{26}$, piezoelectric$^{27}$, (anti)ferromagnetic$^{28,29}$ and multiferroic properties$^{30}$. The insulating nature of SrTiO$_3$ (band gap of 3.2 eV) electrically decouples the oxide layers from the Si substrate, providing a wafer-size platform for all-oxide electronic device technologies. Scaling up the substrate size to reduce manufacturing costs would therefore make novel functionalities emerging at oxide heterointerfaces and oxide thin film properties economically more attractive, providing a path to utilize these phenomena and develop a marketable technology.
1.3 Statement of thesis

This thesis focuses on two parts: exploring the possibility of perovskite oxide-based correlated metals as high-performance transparent conductors and monolithically integrating high-quality SrTiO$_3$ on Si (001) as virtual oxide substrate. Both are pursued with an experimental means named hybrid molecular beam epitaxy (hybrid MBE), which is introduced in Chapter 2. Chapter 3 discusses the experimental details including high-resolution x-ray diffraction (XRD) and electrical transport measurement. Chapter 4 discusses the new designing paradigm of correlated metals as transparent conductors, the experimental realization with perovskite-based correlated metals, SrVO$_3$ and CaVO$_3$, and the comparison with state-of-art, epitaxial ITO. In Chapter 5, the aliovalent substitution is introduced as an effective means to further improve the performance of SrVO$_3$ as transparent conductors. Chapter 6 discusses the integration of high-quality SrTiO$_3$ thin film on Si (001) substrate by hybrid MBE, with an emphasis on the formation of buffer layer and the control of cation stoichiometry. In Chapter 7, an ex-situ annealing process is utilized to improve the electrical and structural properties of as-grown SrTiO$_3$ thin films on Si (001) substrate. In Chapter 8, the future work is proposed with some preliminary results.
Chapter 2
Molecular beam epitaxy

2.1 Introduction to molecular beam epitaxy

The term “epitaxy” comes from two ancient Greek words, “epi (ἐπί)”, meaning "placed or resting upon", and “taxis (τάξις)”, meaning "arrangement or an ordered manner", which refers to extended single-crystal film formation on top of a crystalline substrate. Molecular beam epitaxy (MBE) is an epitaxy method for thin-film deposition in ultra-high vacuum. It supplies well-controlled thermal beams of atoms or molecules with an unparalleled control of accuracy down to one a single-atomic-layer.

Figure 2-1. (a) 1st MBE machine at Bell Labs in 1970. (Adapted from ref31) (b) History of improvements in the low-temperature mobility of electrons in GaAs, annotated with the technical innovation associated with the improvement of mobility. (Adapted from ref32)

The first MBE was invented by two scientists at Bell telephone laboratories, J. R. Arthur and Alfred Y. Cho in the late 1960s to grow GaAs33, as shown in Fig. 2-1 (a). With the rapid
development of MBE techniques and growth strategy, the low-temperature mobility in GaAs-based two-dimensional gas progressively increased to 31 million cm$^2$ V$^{-1}$ s$^{-1}$ (≈35 cm$^2$ V$^{-1}$ s$^{-1}$ by 2007$^{34}$, comparing with 1500 cm$^2$ V$^{-1}$ s$^{-1}$ of Si and 3900 cm$^2$ V$^{-1}$ s$^{-1}$ of Ge in semiconductors), as shown in Fig. 2-1 (b), indicating an incredible level of purity in this semiconductor. With the cleanest materials, new physics phenomena, the integer quantum Hall effect and the fractional quantum Hall effect, were observed, which later lead to Nobel Prized in physics in 1985 and 1998, respectively. Not only did MBE facilitate the development of modern condensed materials physics and materials science, some of the III-V semiconductor products by MBE are also widely used in the manufacturing of today’s power and optoelectronic devices.

In the MBE chamber, the evaporated atoms do not interact with each other or other gases until they reach the substrate, which requires the mean free path of the particle larger than the geometrical size the chamber. Mean free path is defined as$^{35}$:

$$I = \frac{k_B T}{\sqrt{2\pi p d^2}}$$

Where $k_B$ is the Boltzmann constant, $T$ is the temperature, $d$ is the diameter of molecule and $p$ is the pressure. For a MBE chamber pressure of $10^{10}$ Torr (The base pressure of MBE is typically around $10^9$–$10^{11}$ Torr), the mean free path of nitrogen gas is around 70,000 m, far exceeding the geometric dimension of MBE chamber. This is the key that the evaporated atoms could reach the substrate without any collisions and bring minimum energy and damage to the substrate.

2.2 Kinetics process in molecular beam epitaxy

The growth and kinetic process have a direct influence on the ultimate structure of MBE-grown films and their properties. Figure 2-2 (a) shows the growth process of thin film when the
impinging atomic beam reaches the surface of the substrate. Depending on the kinetic energy of the incoming atoms and the temperature of the substrate, processes such as surface diffusion, surface migration, nucleation, desorption or interdiffusion can take place.

Figure 2-2. (a) The schematic of the surface process occurring during film growth by MBE. (b) The schematic of potential as a function of distance in the physical and chemical adsorption.
The incident molecular beams go through adsorption, surface diffusion and condensation, before the nucleation and the growth of thin film. There are two kinds of adsorptions, namely physical adsorption (physisorption) and chemical adsorption (chemisorption). They can be distinguished from the strength of atomic interaction. Physical adsorption is typically due to the weak force, such as Van der waals force, the interaction of electrical dipole or electrical quadrupole. Chemical adsorption involves the formation of new chemical bonding. The physisorption and chemisorption processes can be explained by the curves shown in Fig. 2-2 (b), which shows the potential energy of interaction as a function of distance of particle to the substrate surface. When the distance is sufficient long, the particle could be treated as free. It could be seen that the physisorption occurs further from the surface. Typical absorption energy or heat of physisorption and chemisorption, or \( H_p \) and \( H_c \), are typically around 0.25 eV and 1~10 eV, respectively. However, if the substrate temperature is too high, then the atom will exchange the energy with surface and be ejected into vacuum. As depicted in Fig. 2-2 (b), if the atom could overcome the barrier, \( E_a \), the adsorption process will transit from physisorption to chemisorption, where there is a transfer or sharing of electrons, or breaking of the adsorbate into different atoms or radicals. At the meantime, lots of heat (or energy) will be released through chemical reactions. The chemical bonding can be covalent boning, metallic bonding or ionic bonding with substrate atoms.

Once the atom is adsorbed by the surface, it loses the kinetic energy perpendicular to the substrate surface and retains the kinetic energy normal to the surface, which could be used for surface diffusion process. The activation energy for surface diffusion is usually much less than \( H_c \), which is about 1/6~1/2 of \( H_c \). The average diffusion length depends on the activation energy, as well as the temperature. The smaller the activation energy is, the longer the average diffusion length is. The long diffusion length is essential for condensation and the epitaxial growth.
Figure 2-3. (a) Schematic of nucleation process on substrate during vapor deposition. (b) Thin film formation and three different growth modes: Frank-van der Merwe (FM) growth mode, Volmer-Weber (VW) growth mode and Stranski-Krastanov growth mode.

As shown in Fig. 2-3 (a), assume atoms or molecules in the vapor phase impinge on the substrate and create a nuclei, the free-energy change with the formation of such an aggregate is given by\(^{36}\):

\[
\Delta G = a_1 r^3 \Delta G_v + a_1 r^2 \gamma_{fv} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv}
\]

\[
a_1 = 2\pi (1 - \cos \theta),
\]
\[
a_2 = \pi \sin^2 \theta,
\]
\[
a_3 = \pi (2 - 3 \cos \theta + \cos^3 \theta) / 3
\]
Where $\Delta G_v$ is the chemical free-energy change per unit volume in the homogenous nucleation, which is the driving force for the condensation reaction, $\gamma_{fv}$, $\gamma_{fs}$ and $\gamma_{sv}$ are the interfacial energy between gas, substrate and thin film and $\theta$ is the contact or wetting angle.

The mechanic equilibrium of the interfacial tensions at the horizontal direction yields Young’s equation:

$$\gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos \theta$$

There are three idealized growth modes in thin film growth, which strongly depends on the substrate temperature, the deposition rate and available surface energy, as shown in Fig. 2-3 (b). They could be better understood by using Young’s equation:

1. When $\theta > 0$, or $\gamma_{sv} < \gamma_{fs} + \gamma_{fv}$, it is island growth or Volmer-Weber mode (V-W).

   V-W growth mode involves the formation of 3D islands on the surface. The surface tension of the films exceeds that of the substrate. Deposited metals, such as Au, tend to cluster or ball up on SiO$_2$ substrate.

2. When $\gamma_{sv} \geq \gamma_{fs} + \gamma_{fv}$, the growth mode will transit to layer by layer, or Frank-van der Merwe mode (F-M). F-M growth mode is the ideal mode for MBE growth, since the next monolayer forms only after the first has finished.

3. When $\gamma_{sv} > \gamma_{fs} + \gamma_{fv}$, the growth mode could also be Stranski-Krastanov (S-K) mode.

   S-K growth mode is an intermediate mode consisting of 3D islands with a wetting layer. S-K is less well understood, and this is where the overlayer grows into the surface due to large scale chemical intermixing and high reactivity. For example, because of film-substrate lattice mismatch, strain energy could accumulate in the growing films. If released, the high energy at the deposit interface may trigger island formation.
In general, thin films with low surface energy tend to wet substrates with high surface energy. The growth variable within MBE for given sources could be flux rate, which is the number of atoms arriving at the substrate surface and substrate temperature. In principle, higher temperatures result in more mobile surface atoms and thus more highly oriented material with better crystalline quality. However, too high temperature could result in less-abrupt interface due to the increased interdiffusion.

2.3 Thermal oxide molecular beam epitaxy

2.3.1 Introduction to thermal oxide molecular beam epitaxy

Figure 2-4. Some of institutions that host oxide MBE groups in United States.
The first complex oxide thin film grown by MBE was LiNbO$_3$ in 1985. LiNbO$_3$ has broken inversion symmetry and exhibits strong nonlinear effects and ferroelectricity, which is widely used in optical modulators and surface acoustic wave devices. Motivated by the discovery of high-$T_c$ superconducting oxides in late 1980s, MBE has been used to grow many other oxides, such as DyBa$_2$Cu$_3$O$_{7-\delta}$ and (La, Sr)$_2$CuO$_4$. Other functional oxides grown by MBE include ferroelectrics, such as BaTiO$_3$ and PbTiO$_3$, multiferroics such as BiFeO$_3$, oxides with colossal magnetoresistance, such as (La, Ca)MnO$_3$, oxides that host two dimensional gas at the interface. Figure 2-4 displays some of oxide MBE groups in United States.

Some elements such as Cu and Bi have relatively low oxidation potential, and thus the oxidation of those elements require high oxygen pressure. However, chamber pressure has to be kept at a relatively low level ($<10^{-5}$ Torr) to maintain a long gas mean free path (The mean free oath of nitrogen gas is 0.7 m at a chamber pressure of $1\times10^{-5}$ Torr, which is about the length-scale of dimension of MBE chamber). Therefore, reactive oxygen sources, such as distilled ozone and activated oxygen from radio-frequency plasma source are developed and then employed in oxide MBE.

2.3.2 Challenge in thermal oxide molecular beam epitaxy

Oxide MBE has a precise control of beam flux on individual effusion cells, which leads to a precise control of doping in the material. Comparing with pulsed laser deposition (PLD), oxide MBE utilizes species with low kinetic energies, which has a less chance creating point defect from energetic species. However, there are still a few challenges in thermal oxide MBE, such as the control of cation stoichiometry and the slow growth rate.

First, compare with GaAs and other binary semiconductors, growing complex oxides were far more challenging due to the lack of an adsorption-controlled growth window, which
makes an accurate control of cation stoichiometry extremely difficult. The second challenge in the growth of complex oxides materials by MBE is the limited growth rate, which is around 10 Å per min. The maximum operation temperature for effusion cell is ~2000°C. For complex oxides that contain low-vapor-pressure elements, such as tantalates, molybdates, zirconate, hafnates, niobates, tungstates, germinates, ruthenates and osmates, the situation is even worse since using effusion cell is almost impossible. Figure 2-5 shows the temperature of effusion cell that can provide a reasonable flux rate.

The third challenge is the stability of the flux and the duration of source material. For example, Ti is known to form solid solution with common crucible materials such as Ta. Instead, a Ti sublimation pump (or Ti-ball, Ti-Ball is a registered trademark of Varian Vacuum Products) was modified into a sublimation source to supply Ti flux. However, the lifetime is only ~ 50 hours and it needs to be frequently replaced⁴⁷.

To tackle these difficulties, Jalan et al. at University of California, Santa Barbara firstly introduced metal-organic source in oxide MBE to supply low vapor-pressure elements and
achieved high-quality SrTiO$_3$ thin film with a record-high mobility at low-temperature, which will be introduced in the next section$^{18,49}$.

2.4 Hybrid oxide molecular beam epitaxy

2.4.1 Introduction to hybrid oxide molecular beam epitaxy

![Image of hybrid oxide MBE system](image)

Figure 2-6. The image of 2nd generation of hybrid MBE system at Penn State. The MBE reactor is on the left of figure. The buffer chamber connects the MBE and sputtering chamber to the loadlock. The turbo pump and cryopump are installed at the top and bottom of MBE chamber, respectively.

DCA M600 oxide MBE in this work is the 2nd generation of hybrid MBE. The MBE chamber was held under ultra-high vacuum using a combination of turbo pump (Pfeiffer-vacuum,
pumping speed by N₂: 1900 l/s) and CTI cryogenic pump (CTI Cryo-Torr 8, pumping speed by air: 1500 l/s). When cryogenic panel is filled with liquid nitrogen, the chamber base pressure could reach ~3×10⁻¹⁰ Torr measured by an ion gauges that was positioned next to the gate valve of the turbo pump. Wafers with sizes up to 3 inch can be loaded in MBE and heated up to 1000 °C measured by a S-type thermocouple that was positioned just above the sample. A residual gas analyzer (RGA, Stanford Research System 200) equipped with an electron impact ionization source and a quadrupole mass spectrometer was connected to the reactor for identifying residual gas species. A quartz crystal microbalance (QCM) was used to monitor and calibrate growth rate at the sample growth position. The typical growth rate for Sr and Ca is about 2.5×10¹³ atoms cm⁻² s⁻¹, which corresponds to a growth rate of ~50 nm per hour.

Figure 2-7. (a) The chemical structure of TTIP. (b) Temperature dependence of vapor pressure for TTIP and its byproduct (Adapted from Ref46).

Hybrid MBE combines the advantages of conventional MBE and metal organic vapor deposition techniques. Metal-organic sources have weak bonding and can be easily broken up. Some metal-organic precursors contain oxygen atoms, which can also provide additional oxygen to oxidize the metal element. Titanium (IV)-tetraisopropoxide (TTIP) is used to supply Ti. TTIP
is four-fold coordinated to oxygen atoms, as illustrated in Fig. 2-7, and it can decompose into 
TiO$_2$ and other volatile by-products with following reaction:

$$\text{Ti(OC}_3\text{H}_7)\text{$_4$} \rightarrow \text{TiO}_2 + 4\text{C}_3\text{H}_6 + 2\text{H}_2\text{O}$$

The high volatility of metal-organic precursor was supplied without using carrier gas, 
which minimizes the additional gas load in the system, and thus increases the mean free path of 
the molecules. SrTiO$_3$ thin films can be grown by TTIP both with and without oxygen plasma$^{50}$. 
The growth rate is also significantly increased using metal-organic precursor, compared to that 
using low-vapor-pressure metal source. For example, the growth rate of SrTiO$_3$ thin film using 
hybrid MBE technique can be as fast as $\sim$200 nm per hour$^{51}$.

![Graph](image)

Figure 2-8. (a) High-resolution XRD of SrTiO$_3$ thin films with different cation non-stoichiometry 
grown on SrTiO$_3$ substrates (b) Out-of-plane lattice constant as a function of TTIP/Sr BEP ratio 
for SrTiO$_3$ thin films grown on SrTiO$_3$ substrate at different temperatures (Adapted from Ref$^{52}$).

XRD of SrTiO$_3$ thin films grown on SrTiO$_3$ substrates was used to investigate the crystal 
quality at different TTIP/Sr ratios. The lattice expansion is a typical characteristic for both Ti-rich
and Sr-rich thin films. In Fig. 2-8, the out-of-plane lattice of SrTiO$_3$ thin film overlaps with the lattice parameter of bulk SrTiO$_3$ within a wide range of TTIP/Sr beam-equivalent-pressure (BEP) ratio, indicating the existence of a large “growth window” for stoichiometric SrTiO$_3$.

Such a finding indicates that metal-organic source could be utilized to thermodynamically provide an adsorption-controlled regime where excess volatile species can desorb to yield a self-regulated growth, and additional constituents such as TTIP can be desorbed and the stoichiometry of growing thin films could be self-maintained.

The existence of growth window at 700°C and the shift of growth window toward higher TTIP/Sr BEP ratio at 725°C and 800°C in Fig. 2-8 (b) can be qualitatively understood in the following way. There are competing processes during the growth of SrTiO$_3$ by hybrid MBE. The 1st one is that TTIP desorbs from the surface due to its volatility at the growth temperature, which is typically used to explain the mass transport-limited regime of conventional chemical vapor deposition:

$$\text{Ti(OC}_3\text{H}_7)\_4 \text{ (TTIP) } \rightarrow \text{TTIP (g)}$$

The competing reaction is that TTIP decomposes into TiO$_2$, and this deposition process could be significantly enhanced by the existence of SrO on the surface.

$$\text{TTIP } \rightarrow \text{TiO}_2 + 4\text{C}_3\text{H}_6 + 2\text{H}_2\text{O}$$

$$\text{TiO}_2 + \text{SrO} \rightarrow \text{SrTiO}_3$$

The existence of SrO will consume TiO$_2$ and form the final complex oxide product of SrTiO$_3$, which is the starting point of the growth window, as seen in bottom panel of Fig. 2-8 (b). As TTIP/Sr BEP ratio increases, the lack of SrO will significantly slow down of reaction of TTIP$\rightarrow$TiO$_2$ + TiO$_2$ + 4C$_3$H$_6$ + 2H$_2$O, and almost all slightly excess TTIP will desorb from the growing surface. However, once the excess TTIP reaches a critical point, it will mostly stay as point defect or even second phase of TiO$_2$ in thin films, which is the ending point of growth window.
When the temperature increases, both the starting point and ending point will increase, e.g., from TTIP/Sr BEP ratio of $P_s$ and $P_e$ to $P_s+\Delta P_1$ and $P_e+\Delta P_2$, where $\Delta P_1<\Delta P_2$, which can be understood in the way that the desorption rate of TTIP increases at higher temperature. Since $\Delta P_1<\Delta P_2$, the growth window in the top (800°C) and middle panel (725°C) of Fig. 2-8 (b) is thus larger than that in bottom panel (700°C).
2.4.2 Metal-organic source inject system

Figure 2-9. (a) The image of a metal-organic precursor inlet system. (b) Schematic of a metal-organic precursor inlet system.
The basic difference of system set-up between a hybrid oxide MBE and a thermal oxide MBE is the metal-organic precursor inlet system, as shown by picture (Fig. 2-9 (a)) and schematic (Fig. 2-9 (b)). Hybrid MBE utilizes a heated bubbler as the vessel to store the metal-organic precursor, a gas injector to introduce the metal-organic into the MBE chamber and a gas inlet system to connect both systems. All components are heated up to the temperature that is above the condensation temperature of a given metal-organic precursor, but below the decomposition temperature of a given metal-organic precursor.

In Fig. 2-9 (a), the gas inlet system is heated by heating tapes and covered by Al foils, and the temperatures are measured by thermocouples. The inlet pressure of the metal-organic precursor can be measured by a capacitance manometer (MKS Baratron, with a resolution of 0.1 mTorr and a upper pressure limit of 1 Torr, self-heated to 150°C for TTIP) and throttling by a linear variable leak valve which is highlighted in pink in Fig. 2-9 (b). The gas injector is mounted on an effusion cell port, and has pneumatic valves which could be switched to either to the main MBE reactor chamber or through a bypass line into pump station, as highlighted in green in Fig. 2-9 (b). The pump station mainly consists of a cryopump which accepts purged materials to ensure the stabilized metal-organic precursor is available immediately upon starting growth, as shown in Fig. 2-9.

TTIP (VTIP) bubbler is held at a constant temperature of ~110 °C (~70 °C) using heating tapes and Al foil, as the melting and boiling point of TTIP are 17 °C, and 232 °C, respectively. No carrier gas is required since the vapor pressure is sufficient considering the gas conductance between the bubbler and the MBE chamber. The TTIP leak valve pressure can be cross-calibrated using a beam flux monitor in the MBE chamber (a modified ion gauge) where the fluxes do not drift by more than 1% throughout a typical growth period.
2.5 *In-situ* reflection high-energy electron diffraction

One of greatest advantage of MBE is the ultra-high vacuum environment that makes *in-situ* diagnostic technique available, such as reflection high-energy electron diffraction (RHEED). RHEED provides a precise measure of growth rate for a layer-by-layer growth mode and also provides information such as surface morphology and crystallinity. Since RHEED doesn’t physically interfere with deposition source in the system, it is usually the preferred real-time film characterization accessory. Figure 2-10 shows a schematic for a typical RHEED set-up. The phosphor-coated screen is placed inside of a glass viewport and the diffraction patterns could be displayed and recorded by the CCD camera at the atmospheric side of the window. During the operation of RHEED, the electron beam is accelerated to 10-14 kV and incidents on the sample surface at a grazing angle of up to a few degrees (0.5~2.0°). Since a grazing incidence is used, despite the high energy of the electrons, the component of the electron momentum that is perpendicular to the surface is small. Therefore, the penetration of electrons remains to a few monolayer and makes RHEED a surface sensitive technique.

![Figure 2-10. Schematic of a RHEED system.](image)
The diffraction can be considered as interference of the electron beam with the 2D lattice, and the interpretation of the diffraction pattern could be better illustrated with Ewald’s construction in the reciprocal space of a crystalline lattice. The interpretation arises assuming that there is no multiple scattering or resonances and the electrons incident in the form of a flat wave with a wavelength of $\lambda$. The wavelength could be calculated using the following equations, taking the relativistic correction for the mass of the electron into account:\(^53:\)

$$
\lambda = \frac{\hbar c}{\sqrt{eV(eV + 2m_0c^2)}} = \frac{2\pi}{|k_i|}
$$

Where $\hbar$ is the Plank’s constant, $e$ is the elementary charge, $c$ is the speed of light, $m_0$ is the resting mass of the electron, $k_i$ is the wavevector of the incident beam and $V$ is the acceleration voltage for the electrons. If an acceleration voltage of 12 kV is used, $\lambda$ is ~0.10 Å and $|k_i|$ is ~50 Å$^{-1}$.

The Ewald’s sphere is then constructed with radius of $2\pi\lambda$, representing a conservation of energy and momentum during elastic scattering, as shown in Fig. 2-11 (a). The difference between the incident and scattered beam must equal to a vector in the reciprocal network, which is reflected by that the reciprocal lattice rods meet the diffraction conditions when they intersect the Ewald’s sphere, as described by:\(^53:\)

$$
G_{hkl} = \Delta k = k - k_i
$$

Where $k$ is the wavevector of the scattered beam, $\Delta k$ is the phase difference between incident and scattered beam, $G_{hkl}$ is the wave vector in the reciprocal lattice of the sample.

The radium of the Ewald’s sphere is much larger than the spacing between reciprocal lattices rods, since very short wavelengths of high-energy electrons are used (~0.10 Å as mentioned in the previous paragraph). The curvature of the Ewald sphere could intercept several
different lines of the reciprocal network. This intersection defines a Laue zone of the diffraction. The diffraction pattern can be seen on the RHEED fluorescent screen. The specular reflection of the incident beam corresponds to the diffraction at the origin, labelled by (0, 0). Each successive intersection of a rod and the sphere refers a higher order reflection, as exampled by (0, 1), (0, 2), etc. The diffraction model described is idealized. An elongation of the points occurs towards the lines of the reciprocal lattice, forming stripes. This is due to the small dispersion of energy of the incident electron beam, giving the sphere of Ewald a finite "thickness".
Figure 2-11. (a) Schematic of the Ewald's sphere where the constructive interference conditions are met when the Ewald sphere intersects a reciprocal lattice point. (b) RHEED patterns (shown on the left) that could be observed under different surface morphology (shown on the right).

In reality, the disturbances in the periodic potential of the crystal lattice and the deviation from the smooth surface could make RHEED pattern even more complicated. For example, a real surface containing defects, disorder and roughness could produce a superposition of a diffraction pattern by a transmission pattern. Transmission diffraction originated from the surface of the Ewald sphere intersecting with a three-dimensional reciprocal network leads to an image of dots on the screen rather than stripes. For polycrystalline sample, “polycrystalline rings” centered on the specular spot can be seen. Some works of analytic calculation can be found elsewhere. Amorphous thin films can also be identified by the disappearance of RHEED patterns, due to lack of long range order to construct a reciprocal lattice.

On the other hand, it makes RHEED provide a qualitative analysis of the growth topography of the thin film. Figure 2-11 (b) shows some of the possible surface morphologies of a thin film sample and the corresponding pattern then can be seen on the fluorescent screen.
Figure 2-12. (a) RHEED oscillation at [100] azimuth of 600 °C-grown SrTiO$_3$ thin film on Si (001) substrate. (b) Schematic of RHHED intensity at one oscillation period as a function of different fractions of surface coverage.

The second application of RHEED is to monitor the growth rate. For films that can be grown in a layer-by-layer growth mode, RHEED oscillation can be observed and provides a very fast and accurate method to determine the growth rate. Figure 2-12 (a) shows the RHEED oscillation for 600 °C-grown SrTiO$_3$ thin film on Si (001) substrate. The intensity integrated around the RHEED spot can be related to the surface coverage of the sample. A smooth and fully-covered surface provides an intense and coherent RHEED spot, while a partially-covered surface provides a weak and incoherent spot. Therefore, RHHED intensity corresponds to the fraction of a ML growth. A low intensity for a 0.5 ML-deposited film could be seen, and a maximum intensity could be achieved at 1 full ML, which is shown schematically in Fig. 2-12 (b).
oscillations will dampen out which depends on the change of surface morphology or whether the growth will transit into step-flow mode.

Surface reconstruction can also be monitored by RHEED due to its surface sensitivity. The atoms at the outer layer of thin films have dangling bonds. In order to minimize the overall surface energy, the surface atoms can rearrange themselves and deviate from the positions of the bulk, leading to a change in the surface structure that is different from the bulk. Wood’s notation is the simplest and most common method for describing a surface structure. Wood’s notation first involves specifying the lengths of the two overlayer vectors, \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \), in terms of \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) respectively: \( (|\mathbf{b}_1|/|\mathbf{a}_1| \times |\mathbf{b}_2|/|\mathbf{a}_2|) \). It is the length of primitive translation vectors and rotation with respect to the substrate unit cell, respectively.
3.1 Structural Characterization

3.1.1 High-resolution x-ray diffraction

X-ray diffraction is a technique used to characterize the structural properties of materials. Bragg’s law which is valid for constructive interference arising from an integral phase offset from incident x-ray and reflected x-ray beams is used to relate diffraction peaks to the lattice spacing in the material, as defined by, as shown in Fig. 3-1:

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

Where \( d \) is the distance between atomic layers in a crystal, \( \lambda \) is the wavelength of the incident x-ray beam and \( n \) is an integer.

Figure 3-1. Schematic of x-ray interference with the plane that obeys Bragg’s law.
X-ray diffractometers consist of three basic elements: the x-ray generator (Cu-source), the sample stage and the x-ray detector. Philips X’pert Pro MRD is used in this dissertation work, as shown in Fig. 3-2 (a). A cathode ray tube is used to generate x-ray by heating the filament to produce electrons and accelerating the electrons toward a target with a voltage bias, and bombarding the target material with electrons. X-ray characteristic spectra consist of several components, such as Kα and Kβ. Kα consists of Kα1 and Kα2, and Kα1 has a slightly shorter wavelength and twice the intensity as Kα2. In this dissertation, Cu is the target material and Kα1 with a wavelength of 1.5406 Å were used. This wavelength is sufficient to revolve the lattice spacing of most materials. The x-ray tube is set at 45 kV, with a current of 40 mA. A monochromator is used to generate monochromatic X-rays, and a 4 × Ge 220 hybrid monochromator is used. A 1/4° slit with a 10 cm mask is used confine the x-ray beam to the sample. The X-ray detector is used to record and X-ray signal. In most of the work of this thesis, a PIXcel3D area detector is used, as shown in Fig. 3-2 (b). Triple-axis analyzer could also be used instead of area detector to achieve the measurement results with a much higher resolution.
The sample with small size ($<1\times1$ cm$^2$) is mounted on a glass before being placed onto a stainless steel sample stage to prevent diffraction from the metal background. For the thin film sample, the most important step is to ensure that the crystal axes of the substrate is aligned with the goniometer axes. Four different axes could be adjusted for the goniometer, which is the reason that it is called four-circle XRD, as shown schematically in Fig. 3-2 (c). The first two axes...
are $2\theta$ and $\omega$. $2\theta$ is the angle between the incident and reflected beam, while $\omega$ is defined between the X-ray source and the sample. $2\theta$ equals twice of $\omega$ for symmetric scans. The axis of $\phi$ is in the out-of-plane direction of thin film sample. Once the crystal is aligned to the goniometer axis, the different scans such as $2\theta$-$\omega$ cans could be performed. The location of film peak and Laue oscillation between film and substrate peak could give information such as lattice parameters and film thickness. By comparing it with the lattice parameter of the substrate, strain state could also be estimated.

![Diagram](image)

Figure 3-3. (a) A real thin film with mosaicity. (b) Rocking curve measurements of a 120-nm SrTiO$_3$ film on Si before and after thermal annealing.

The rocking curve scans, or $\omega$ scans are used to investigate the mosaicity in the thin film. The position of x-ray source and detector is fixed while the sample is rocked around the Bragg peak slightly. Planes deviated from the ideal position will cause the peak spread, as shown in Fig. 3-3 (a). A typical rocking curve measurement of a 120-nm SrTiO$_3$ film on Si before and after the thermal annealing is shown in Fig. 3-3 (b). The width of the rocking curve peak is used as an important indicator of the material quality. For an ideal epitaxy, the full width at half-maximum of rocking curves of the films is very close to that of the substrate.
3.1.2 Reciprocal space mapping

Reciprocal space mapping (RSM) is a technique that is widely used in thin film epitaxy. Information about chemical composition, mismatch and relaxation, defects and crystal size and lattice parameters for thin films on a single-crystalline substrate could be understood through the measurements of RSM.

RSM measurement could be understood as $\omega$-$2\theta$ scans at different $2\theta$ angles. The scans could be better understood in the plot of a reciprocal space. For thin film epitaxy, the strained film on substrate could be either tensile-strained or compressive-strained, as shown in Fig. 3-4 (a). The difference of lattice parameter between thin films and substrates are usually very small and no more than $\sim$3% (this limit can be very different for different material systems). For thin films with a lattice mismatch larger than $\sim$3% or a thickness beyond the critical thickness, they will relaxed through dislocation and restore to their bulk lattice parameters.
Figure 3-4. (a) Schematic of relaxed, compressively strained and tensile-strained thin films (b) Schematic of reciprocal lattice and the trace for 2θ scans, 2θ-ω scan, ω scans and RSM. Notes that the XRD measurements are not possible in two smaller semicircles. The Edward’s sphere is constructed by the radius which equals to the wave vector of the incident x-ray beam.

Next, the reciprocal lattice is constructed. $d_{hk,l}$ is the vector draw from the origin of the unit cell to intersect the crystallographic plane (hkl) at a 90° angles, while the reciprocal vector $d_{hk,l}^*$ is defined as $1/d_{hk,l}$. Figure 3-4 (b) shows a two-dimensional projection from 3D reciprocal lattice. The vertical axis is defined as the out-of-plane direction of the sample. In the reciprocal lattice, each point can represent a set of Bragg planes. Assuming the lattice parameter of the substrate is shorter than that of thin film, the reciprocal vector will be larger than that of thin film as shown in Fig. 3-4 (b). Ewald’s sphere is defined by the wavelength of x-ray beam, indicating the range of reciprocal space the system could measure. The two small semicircles indicate the
regions where the diffracted beam is below the sample surface and the incident beam below the sample surface. The peaks that should be measured also depend on the structure factors, which can be easily found in the literatures. The peak should contain a sufficient intensity which depends on the film thickness and quality. 103 diffraction peaks are used in this dissertation work for perovskite oxides.

In Fig. 3-4 (b), the rocking curve ($\omega$ scan) is an arc centered at the Bragg peak, the detector scan ($2\theta$ scan) is a tilted arc and the couple scan ($\omega$-$2\theta$ scan) is a straight line toward the origin. RSM is the region highlighted in the figure. For PIXcel$^{3D}$ area detector, a limit of $2.5^\circ$ for $2\theta$ angle is due to the finite opening of the detector. However, the measurement time could be significantly reduced from tens of hours to a couple of minutes. The $2\theta$ and $\omega$ angle could be converted to reciprocal vector by the following equations:

$$q_x = R[\cos(\omega) - \cos(2\theta - \omega)]$$
$$q_y = R[\sin(\omega) - \cos(2\theta - \omega)]$$

$$R = 1 / \lambda$$

Where $\omega$ is the angle between x-ray source and sample surface, $2\theta$ is the angle between x-ray source and detector and $\lambda$ is the wavelength. If the straight line defined by the origin (000) and the Bragg lattice point (hkl) of the film overlaps with the straight line defined by the origin (000) and the Bragg lattice point (hkl) of the substrate, the thin film is fully relaxed. If the straight line defined by Bragg lattice point (hkl) of the film and the Bragg lattice point (hkl) of the substrate is parallel to the out-of-plane direction, the thin film is fully strained.

3.1.3 Atomic force microscopy

Atomic force microscopy (AFM) is a scanning probe microscopy that is primarily used to image surface morphology and electric or magnetic domains. Unlike scanning tunneling
microscopy, STM can be used to study insulator, as well as conductors. In this dissertation work, AFM is used to provide the information of surface morphology and perform quantitative measurements. The probe used in an AFM set-up is a sharp tip, typically less than 10 nm in diameter at the apex. The tip is located on the free end of a ~500 µm-long cantilever. The working principle of AFM is to use optical techniques to detect the movement of the cantilever, as the cantilever is brought in close proximity with the sample until it interact with the sample surface mechanically. In most cases (Figure 3-5), a light beam from a laser was incident on the back of the cantilever and reflected back into a photodetector, as the cantilever bends by the force from the sample surface, the position of the laser beam on the photodetector also changes. The path length between the cantilever and the photodetector is much larger than the movement of the cantilever itself. By analyzing the signal received from the photodetector, the system has the capability of resolving sub-Angstrom vertical movements.

Figure 3-5. (a) Schematic of AFM set-up which mainly consists of a laser, a photodiode and a cantilever with a sharp tip on its free end. (b) A typical AFM scan of a 45nm SrVO₃ thin film on LSAT substrate.

There are two main working modes for AFM, contact AFM and tapping mode. In contact mode, the tip is in direct contact with the surface of the sample. The tip is attached to the free end
of a cantilever with a relatively low spring constant. The effective force by the sample surface will bend the tip to accommodate the changes with the surface. Tapping mode is to tap the surface with an oscillating tip. The oscillation amplitude will change to accommodate the change of surface topography. Tapping mode could eliminate the possibility of damaging sample with the tip, and it could also be used to measure liquid or some other gas interface. In this dissertation work, tapping mode is used to avoid any damage to the sample.

3.2 Spectroscopic ellipsometry

Room temperature ellipsometric spectra (in $\Delta, \Psi$) were collected at $\Theta_i = 70^\circ$ angle of incidence using single rotating-compensator spectroscopic ellipsometers\textsuperscript{55,56} over the IR to UV (0.74 to 5.89 eV; M-2000 J. A. Woollam Co.) and IR (0.049 to 0.75 eV, FTIR-VASE J. A. Woollam Co.) spectral ranges. The complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) and microstructural parameters (film layer thickness $d_f$, surface roughness thickness $d_s$) were first extracted using a least squares regression analysis and an unweighted error function\textsuperscript{57} to fit the experimental ellipsometric spectra collected over the near IR to UV range to an optical model consisting of a semi-infinite substrate / film / surface roughness layer / air ambient. Free parameters corresponded to the thicknesses of thin film and the surface roughness layer and a parameterization of $\varepsilon$ for thin film. The parameterization of $\varepsilon$ utilized combinations of Sellmeier, Lorentz, and Tauc-Lorentz oscillators, as well as a constant additive term to $\varepsilon_1$ represented by $\varepsilon_\infty$. Each Sellmeier oscillator is represented as\textsuperscript{58}:

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

Where $A$ and $E_0$ are the amplitude and resonance energy, respectively, and $E_0$ must be outside the spectral range. Each Lorentz oscillator is represented by\textsuperscript{58}:
\[ \varepsilon = \frac{A \Gamma E_0}{E_0^2 - E^2 - i\Gamma E} \]

Where \( A \) is the amplitude, \( \Gamma \) is the broadening, and \( E_0 \) is the resonance energy. Each Tauc-Lorentz oscillator is represented by\(^{59,60}\):

\[
\varepsilon_2 = \begin{cases} 
A E_0 \Gamma & \text{if } E > E_g \\
\frac{(E - E_g)^2}{(E_0^2 - E^2)^2 + \Gamma^2 E^2} & \text{if } E \leq E_g \\
0 & \text{otherwise}
\end{cases}
\]

\[
\varepsilon_1 = \frac{2}{\pi} \int_{E_g}^{\infty} \frac{E_g}{E_g^2 - E^2} dE
\]

Where \( A, \Gamma, \) and \( E_0 \) correspond to amplitude, broadening, and resonance energy, while \( E_g \) represents an absorption onset determined by assuming a parabolic band, constant momentum matrix element. A Drude oscillator represented by\(^{58}\):

\[
\varepsilon = \frac{-\hbar^2}{\varepsilon_0 \rho (\tau E^2 - i\hbar E)}
\]

Where \( \rho \) is the electrical resistivity, \( \tau \) is the mean free relaxation time, \( \varepsilon_0 \) the vacuum permittivity and \( \hbar \) the reduced Planck constant, is used to interpret the intraband response due to free carrier absorption at low energies.

The optical properties of the surface roughness layer are represented using the Bruggeman effective medium approximation\(^{61}\) consisting of a half of void volume fractions. This surface roughness layer was initially included in the model, however it was not detectable during the data analysis, which is consistent with the film surface being atomically smooth as verified by AFM. Parameters describing \( \varepsilon \) as well as the optically-determined thicknesses for the nominally were then determined. After thicknesses were obtained using the parametric model, numerical inversion\(^{62}\) was used to extract \( \varepsilon \) directly from the experimental ellipsometric spectra.
3.3 Electrical Characterization

3.3.1 Resistivity measurement

The electrical resistivity is one of the most important properties for electronic materials. There are generally two types of measurement techniques: two-point probe and four-point probe. Two-point probe method can be performed much easier than four-point probe. Total resistance can be written by \(^63\): 

\[ R_T = \frac{V}{I} = 2R_w + 2R_{contact} + R_{DUT} \]

However, the interpretation of the measurement data is more difficult. Since the wire or probe \((R_w)\) and the contact resistance \((R_{DUT})\) are also included in the total resistance. The other type of measurement is four-point probe measurements. The current path is identical to that of two-point measurement, but the voltage is now measured with two additional contacts. The current flowing through the voltage path is very low due to the high impedance of the voltmeter. Therefore, the voltage drops across wire and contacts are can be neglected, and the measured voltage is essentially the voltage drop across the sample.

Two sample geometries could be used for four-point probe measurements, Hall bar geometry and van der Pauw geometry\(^64\). Van der Pauw geometry could be used to accurately measure the resistivity of a sample of any arbitrary shape, so long as the following requirements are meet: (1) the sample is two-dimensional, and the diameter of the contact electrodes \((D)\) and the sample thickness \((d)\) is much smaller than the distance between different contact electrodes \((L)\); (2) the sample is homogeneous, and the sample interior should contain no contacts or holes; and (3) the contact electrodes are placed on its perimeter\(^64\).
Figure 3-6. Schematic of (a) van der Pauw geometry and (b) Hall bar geometry. (c) SrVO$_3$ thin films with van der Pauw geometry on a petri dish, and the indium dots are used as probe contacts. (d) SrVO$_3$ thin film with 8 point Hall bar geometry in a PPMS transport puck.

Basic van der Pauw contact arrangement is defined in the way that four contacts made to the sample are numbered counterclockwise in ascending order, when the magnetic field perpendicular to the sample, as illustrated in Fig. 3-6 (a) and (c). Figure 3-6 (c) shows 10 nm (top right), 5 nm (center right) SrVO$_3$ thin films on double side polishing LSAT substrate (bare substrate is shown on bottom right) with van der Pauw geometry. The diameter of contact, $D$, and the thickness of sample, $d$, must be much smaller than the distance between the contacts, $L$. $I_{12}$ is defined as dc current I inject from contact 1 and come out from contact 2. $V_{43}$ is defined as dc voltage measured between contacts 4 and 3 ($V_4 - V_3$) in the zero field. For homogeneous sample with ideal spacing between the contacts,
\[ R_A = \frac{V_{43}}{I_{12}} \]
\[ R_B = \frac{V_{14}}{I_{23}} \]
\[ \exp(-\pi R_A / R_S) + \exp(-\pi R_B / R_S) = 1 \]
\[ \rho = \frac{R_S}{d} \]

Where \( R_S \) is the sheet resistance, and it could be solved numerically, \( \rho \) is the resistivity. \( F \) is a transcendental function of the ratio \( R_r \), and \( R_r \) is defined as:

\[ R_r = \frac{V_{43} I_{23}}{V_{12} V_{14}} = \frac{R_A}{R_B} \quad \text{or} \quad R_r = \frac{V_{12} V_{14}}{V_{43} I_{23}} = \frac{R_B}{R_A} \]

Whichever is great, and \( F \) could be found by solving the following equation:

\[ \frac{R_r - 1}{R_r + 1} = \frac{F}{\ln(2)} \cosh\left\{ \exp\left[\frac{\ln(2) / F}{2}\right] \right\} \]

\( F = 1 \) will occur with symmetrical samples like circles or squares when the contacts are equally spaced, and the best measurement accuracy could be obtained. In this dissertation, van der Pauw geometry will be used. For SrTiO₃, the Al/Ni/Au stacking contacts (40 nm / 20 nm / 120 nm) are used as Ohmic contacts⁴⁹, and the indium dot is used to connect the contacts to the external probe of the meter. For SrVO₃, indium dot is also used as contact material, since SrVO₃ is a metal. The temperature-dependent resistivity and Hall measurements are performed with PPMS (Quantum Design).

### 3.3.2 Hall measurement

Both van der Pauw and Hall bar geometries could both be used for Hall measurement. Van der Pauw geometry is more popular, primarily because the sample with arbitrary shape could be measurement. However, the van der Pauw geometry is more susceptible to errors due to the
finite sized of the contacts than the Hall bar. Furthermore, Hall bar geometry could be easily used to confine current-flowing directions for samples with large in-plane anisotropy. It is also recommended that magnetoresistance measurement should be done with Hall bar geometry. In this work, typical Hall measurement is done with the van der Pauw geometry, and angular-dependent Hall and magnetoresistance measurements are done with Hall bar geometry.\(^{65}\)

Following the definition in Section 3.3.1, the Hall voltage between leads 2 and 4 with positive magnetic field is defined as \(V_{24P}\), likewise \(V_{24N}\), \(V_{31P}\) and \(V_{31N}\). The sheet carrier density can be calculated from\(^{65}\):

\[
p_x = 4 \times 10^{-8} IB / [q(V_{42P} - V_{42N} + V_{13P} - V_{13N})]
\]

Where \(B\) is the magnetic field (in units of gauss, or G) and \(I\) is the dc current. The carrier density could be obtained from:

\[
p = p_S / d
\]

The Hall mobility can be calculated from the sheet carrier density and the sheet resistance, and can be obtained even without knowing \(d\):

\[
\mu = \frac{1}{p_S e R_S}
\]

Where \(e\) is the elementary charge. In Fig. 3-6 (b) and (d), the Hall bar geometry is shown schematically and on a real sample, respectively. In this geometry, the resistivity can be obtained by:

\[
\rho = \frac{V_{23}}{2I_{56}} \frac{wt}{b}
\]

Where \(w\) is the width of Hall bar, \(t\) is the thickness of the sample, \(b\) is the distance between contact 2 and contact 3. The sheet carrier density can be calculated from:

\[
p_x = 2 \times 10^{-8} IB / [q(V_{23P} - V_{23N})]
\]
Where B is the magnetic field (in units of gauss, or G) and I is the dc current. The carrier density could be obtained from:

\[ p = \frac{p_s}{d} \]

The Hall mobility can be calculated from the sheet carrier density and the sheet resistance by:

\[ \mu = \frac{1}{\frac{p_s e R_s}{s}} \]

### 3.4 Contact Photolithography

The fabrication of Hall bar of SrVO₃ could be done by standard contact photolithography techniques. Figure 3-7 (a)–(f) shows a step-by-step process for contact photolithography and plasma etching. The sample after growth is firstly cleaned by rinsing in acetone, then isopropanol (IPA), and then DI water. Dehydrate the sample by blowing pressurized nitrogen gas and placing it on a hot-plate with a temperature of 100 °C for one minute. Cool the sample for one minute before putting the sample on the chunk. Dispense and spread HMDS on the sample surface, which could help the wetting of the photoresist in the next step. Bake the sample at 100 °C for one minute and cool the sample for another minute. Now dispense and spread photoresist SPR3012 with scaled pipette. Depends on the rotation speed (typically at a speed 4000~5000 rpm for 45 seconds), the photoresist could be one to a few microns, as shown in Fig. 3-7 (b). Bake the photoresist by putting the sample on a hot plate at ~100 °C for one minute.
Figure 3-7. Schematic of patterning process of Hall bar. (a) Deposit a thin film on a substrate. (b) Spin the photoresist, (c) UV-exposure using a patterned mask, (e) Develop the photoresist after baking. (d) Plasma etching the unwanted thin film (g) Strip the unwanted photoresist.

Next the Hall bar pattern is transferred to the sample from a patterned Cr mask, as shown in Fig. 3-7 (c). The unpatterned area allows the UV light to go through the mask, while the Cr layer reflect and absorb the UV light (The exposure time is, 8 second; the gap between the sample surface and Cr mask is 70µm; “hard contact” mode is chosen). Bake the sample at 115°C for one minute after exposure. After exposure, the exposed photoresist areas are removed by developing
the sample in a bath of CD-26 developer solution for one minute and rinsing the sample in DI water for another minute, as shown in Fig. 3-7 (d).

Figure 3-8. Etching thickness as a function of etching cycles of SrVO₃ by reactive etching with BCl₃ gas.

Then the SrVO₃ thin film with photoresist is etched by Plasma-Therm Versalock 700 with BCl₃ at a flow rate of 60 sccm, as shown in Fig. 3-7 (e). Each etching cycle consist of a 30 second-etching and another 30 second-stabilization for heat dissipation to avoid the over-heat of the sample. The total etching thickness as a function of etching cycles is shown in Fig. 3-8. The average etching speed is ~2.65 nm/cycle. Once the dry etching processing is complete, the rest of photoresist layers can be removed by using J.T.Baker PRS™-3000 photoresist stripper by immersing the sample into a heated bath (65-85°C) for ~20 minutes. Finally, rinse the sample with DI water and carefully dry by a pressurized nitrogen air gun from one side of the sample to the other.
Chapter 4
Correlated metals as transparent conductors


4.1 Introduction

The growing demand of high performance and cost effective material solutions for transparent conductors has been fueled by the rapid-growing markets of display technologies, photovoltaics, smart windows and solid-state lighting industries. However, the development of thin films exhibiting high electrical conductivity and high optical transparency in the visible spectrum has proven challenging. It requires minimization of photon absorption and reflection while preserving a high carrier concentration and low carrier scattering. Ideally, the free carrier reflection edge is below 1.75 eV, while absorption due to strong interband optical transition is above 3.25 eV, opening a transparency window over the entire visible spectrum [Fig. 4-1 (a)].

The reflection edge, represented by the screened plasma energy:

\[ \hbar \omega_p = \hbar \left( \frac{e}{\sqrt{\varepsilon_0 \varepsilon_r}} \right) \sqrt{n / m^*} \]

Where \( \varepsilon_0, \varepsilon_r \) are the vacuum and relative permittivity and \( e \) is the elemental charge, can be minimized by choosing an appropriate ratio of free carrier concentration \( n \) and effective carrier mass \( m^* \). The electrical conductivity with carrier mobility and scattering time also has to be maximized, making the ratio \( n / m^* \) the key factor in optimizing the performance of transparent conducting materials. It should be increased to enhance electrical conductivity, yet limited to keep the free carrier reflection edge below the visible spectrum.
The current design strategy for state-of-the-art transparent conductors is to degenerately dope wide band gap semiconductors to balance the trade-offs between $\tau$, $m^*$, and $\sigma$. A wide-band-gap semiconductor is chosen as a host material to ensure interband transitions to occur above the visible range (> 3.25 eV), while dopant concentration is maximized to increase the electrical conductivity. However, the highest carrier concentrations achieved do not exceed $3 \times 10^{21}$ cm$^{-3}$ due to solubility limit of the dopants and pronounced self-compensation. Reduction of the total scattering time dominated by phonon scattering $\tau_{ph}$ at room temperature, by due to an enhanced ionized and neutral impurity scattering from the high dopant concentration marks a second limitation to this design strategy.

Figure 4-1. Design rules for transparent conductors. (a) Schematic of the ideal transmittance, where the free carrier reflection edge is below 1.75 eV and the onset of absorption due to strong interband optical transition is above 3.25 eV, opening a transparent window over the entire visible spectrum. (b) Electrical conductivity as a function of correlation strength $Z_s = m_{band}^* / m^*$, which is quantified by $(\omega_p^{\text{Exp}} / \omega_p^{\text{DFT}})^2$. In-plane conductivity was
taken for materials with symbol*. (c) Optimization of electrical conductivity under the constraint to keep free carrier reflection edge, represented by screened plasma frequency $\omega_p$, below the visible spectrum. Correlated metals positioned between conventional metals and degenerately doped wide band gap semiconductors are suited to balance conductivity and free carrier reflection through strong electron correlation. Experimental data for Ag (red rhombus)\textsuperscript{84,85}, Au (red up-pointing triangle)\textsuperscript{84,86}, Al (red square)\textsuperscript{84,87}, Cu (red left-pointing triangle)\textsuperscript{84,85}, Ni (red down-pointing triangle)\textsuperscript{84,87}, bulk c-ZnO (green circles, line is only guide to the eye)\textsuperscript{88}, 500nm epi-ITO (green rhombus, line is only guide to the eye)\textsuperscript{89}, 300nm epi-ZnO (half-filled green circle)\textsuperscript{90}, 400nm epi ITO (green square)\textsuperscript{91} and 20nm SrVO\textsubscript{3} (red four-point star) and 38nm CaVO\textsubscript{3} (blue four-point star) are shown for comparison. (Adapted from ref\textsuperscript{92})

As the screened plasma energy is much below the visible range for these carrier concentrations, semiconductors with a low electron effective mass $m^*$ are chosen to further increase $n/m^*$. Most of them are oxides and referred to as transparent conducting oxides (TCOs)\textsuperscript{67,93}. They are typically comprised of the post-transition metal cations Zn\textsuperscript{2+}, Cd\textsuperscript{2+}, In\textsuperscript{3+} and Sn\textsuperscript{4+} - the “TCO cations” - because their strongly delocalized vacant s-orbital forms the conduction band, ensuring large band widths and thus small effective masses\textsuperscript{94}. Efforts to enhance the performance of TCOs were focused on increasing carrier concentration without compromising electronic transport\textsuperscript{95,96}. Among all TCOs tin-doped indium oxide (ITO) strikes the best balance of high optical transparency and high electrical conductivity, and is therefore most widely used. However, the increasing price of indium significantly increased the cost of ITO recently\textsuperscript{93}. The highest conductivities achieved for epitaxial grown ITO of just above $1 \times 10^4$ S/cm, result in a reduced plasma energy of 0.77 eV for carrier concentration of $3 \times 10^{21}$ cm$^{-3}$, leaving optimization potential unused if $n/m^*$ is not further increased\textsuperscript{93}. Choosing conventional metals with much higher carrier concentration and slightly higher effective mass would dramatically improve the conductivities, but the free carrier reflection edge would shift to energies above the visible spectrum. The free carrier reflection can be mitigated by reducing the film thickness, however the scaling towards ultrathin films (< 10 nm) is accompanied by a reduction of $\tau$ due to enhanced surface scattering for thicknesses below the electron mean free path (EMFP), negatively affecting conductivity.
Here, we propose a different route towards transparent conductors, making thin metal films more transparent by shifting the reduced plasma energy to below the visible range (< 1.75 eV). Rather than changing the carrier concentration \( n \), the electron effective mass \( m* \) is utilized to simultaneously optimize \( \omega_p \) and \( \sigma \). The systems of interest are correlated metals with high carrier concentration, but small conduction band width \( W \), and with minimal strength for interband transitions in the optical range. Many-body effects emerging from a strong electron-electron interaction \( U \) result in an enhancement of the effective electron mass \( m^* \). The deviation from the behavior expected for a free non-interacting electron with an effective mass \( m^* \), which only captures the effect of the underlying periodic potential of the crystal, is accounted for by incorporating the many-body interaction through carrier mass renormalization , where \( Z_k \) is the renormalization factor\(^97,99\). In case of non-interacting electrons, \( Z_k = 1 \). Increasing electron correlation, either by reducing the conduction band width or increasing \( U \), reduces the renormalization factor and increases the effective mass, which ultimately diverges in the Mott insulating state (\( Z_k = 0 \)\(^98\). This marks the metal-to-insulator transition where all itinerant carriers are localized at the lattice sites due to the strong on-site Coulomb repulsion\(^98\). \( Z_k \) is therefore intimately tied to the correlation strength. Figure 4-1 (b) shows selected correlated metals along with their room-temperature conductivities and respective correlation strengths \( Z_k \). Increasing \( Z_k \) reduces the conductivity, however even in the vicinity of the Mott transition conductivities are comparable to record values reported for epi-ZnO and epi-ITO. The candidate materials shown here only represent a small fraction of potential materials that could be considered as transparent conductors: superconductors, such as cuprates\(^{68,69}\), \( \text{MgB}_2 \)\(^{70,71}\), iron pnictides\(^{72,73}\); Mott conductors with perovskite structure, \textit{e.g.} vanadates (\( \text{SrVO}_3 \) and \( \text{CaVO}_3 \)) and molybdates (\( \text{LaNiO}_3 \)\(^{74}\), \( \text{SrMoO}_3 \)\(^{75,76}\) and \( \text{CaMoO}_3 \)\(^{76}\)), delafossite (\( \text{Na}_x\text{CoO}_2 \)\(^{100}\) and \( \text{PdCoO}_2 \)\(^{77}\)) or
tungsten bronze structure \((\text{NaxWO}_3)\), as well as MIT materials with high conductivities of their metallic phase \((\text{VO}_2\) and \(\text{TaS}_2\)). The anisotropy ratio of resistivity is provided in supplement.

Figure 4-1 (c) compiles the room-temperature conductivity and reduced plasma energies reported for degenerately-doped wide-band-gap semiconductors \(\text{ZnO}\) and \(\text{ITO}\), conventional metals, and the two correlated metals \(\text{SrVO}_3\) and \(\text{CaVO}_3\). Both, \(\text{SrVO}_3\) and \(\text{CaVO}_3\) exceed the conductivity and have a larger reduced plasma energy than epi-ITO, yet smaller than 1.75 eV. Therefore their parameter combination of \(n\), \(m^*\) and \(\tau\) represents a better trade-off not attainable by conventional conductors in the absence of strong electron correlation, bringing both, \(\text{SrVO}_3\) and \(\text{CaVO}_3\), closer to ideal transparent conductors.

This alternative design strategy is very promising for several reasons. (1) The cation choice is not limited to only a few elements; a much wider selection of abundant transition metal elements is possible (2) Dopant or alloying scheme is obviated, allowing the positioning of the intraband absorption edge closer to the ideal value of 1.75 eV. (3) In comparison with conventional metals, electrons in correlated materials have a weaker Drude response that scales inversely with \(Z^2\). (4) A smaller electron mean free path (EMFP) in correlated systems with high carrier concentration but identical \(n/m^*\) ratio compared to a conventional conductor enables thinner, thus more transparent films without suffering from enhanced surface scattering.

### 4.2 Growth of \(\text{SrVO}_3\) and \(\text{CaVO}_3\)

The two correlated metals \(\text{SrVO}_3\) and \(\text{CaVO}_3\) were selected to verify this alternative approach. The crystal structures of \(\text{SrVO}_3\) and \(\text{CaVO}_3\) are shown in Fig. 4-4 (a). \(\text{SrVO}_3\) is a cubic perovskite with \(c = 3.842 \text{ Å}\) while \(\text{CaVO}_3\) is orthorhombically distorted with \(c = 3.770 \text{ Å}\) with similar electronic structure around the Fermi level. While the valence band is derived from the oxygen \(2p\) orbitals, the five \(3d\) orbitals of vanadium split into a higher lying duplet state \(eg\) and a
lower lying triplet state $t_{2g}$ due to the crystal field imposed by oxygen, the latter forming the conduction band. Previous work suggests interband transitions in the optical range are weak\textsuperscript{104}. Both materials have a $3d^1$ configuration with nominally one electron per unit cell and are considered simple Fermi liquid systems, showing pronounced spectral weight transfer due to the strong electron correlation present\textsuperscript{105}.
Figure 4-2. High-resolution X-ray diffraction 2θ-ω scans of (a) SrVO$_3$ films with varying thicknesses grown on LSAT substrates. (b) Experimental and calculated X-ray diffraction intensities of the 45-nm-thick SrVO$_3$. (c) SrVO$_3$ films with varying thicknesses grown on LSAT substrates. (d) Experimental and calculated X-ray diffraction intensities of the 38-nm-thick CaVO$_3$. Film lattice parameter and thickness given in Table 4-1 and Table 4-2 were extracted from these fits. (Adapted from ref$^{106}$)

On-axis 2θ-ω scans were performed for all films. X-ray intensity of SrVO$_3$ (CaVO$_3$) recorded in the 2θ interval from 45-49° (42-51°) is shown in Fig. 4-2 (a) (Fig. 4-2 (c)). Pronounced thickness fringes evidenced the high quality of the thin films. The XRD data were fitted using a simple model by taking into account film thickness as well as film and substrate lattice parameters$^1$. The results are summarized in Table 4-1 (Table 4-2), the comparisons of experimental data and fit is shown for the 45 nm SrVO$_3$ film (38nm CaVO$_3$ film) in Fig. 4-2 (b) (Fig. 4-2 (c)).

Table 4-1. Thickness series of SrVO$_3$ grown on LSAT samples. Lattice parameter and film thickness has been extracted from XRD spectra shown in Fig. 4-2.

<table>
<thead>
<tr>
<th>Nominal film thickness</th>
<th>Lattice parameter (Å)</th>
<th>film thickness (nm)</th>
<th>$\rho$ (300 K) (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 nm</td>
<td>3.822 ± 0.001</td>
<td>45.9 ± 0.2</td>
<td>2.90x10$^{-5}$</td>
</tr>
<tr>
<td>20 nm</td>
<td>3.824 ± 0.001</td>
<td>20.1 ± 0.1</td>
<td>2.84x10$^{-5}$</td>
</tr>
<tr>
<td>15 nm</td>
<td>3.825 ± 0.001</td>
<td>14.9 ± 0.3</td>
<td>3.28x10$^{-5}$</td>
</tr>
<tr>
<td>12 nm</td>
<td>3.828 ± 0.002</td>
<td>12.0 ± 0.3</td>
<td>4.15x10$^{-5}$</td>
</tr>
<tr>
<td>10 nm</td>
<td>3.829 ± 0.002</td>
<td>10.2 ± 0.3</td>
<td>4.45x10$^{-5}$</td>
</tr>
<tr>
<td>4 nm</td>
<td>3.827 ± 0.003</td>
<td>4.0 ± 0.1</td>
<td>6.15x10$^{-5}$</td>
</tr>
</tbody>
</table>

Table 4-2. Thickness series of CaVO$_3$ grown on SLAO samples. Lattice parameter and film thickness has been extracted from XRD spectra shown in Fig. 4-2.

<table>
<thead>
<tr>
<th>Nominal film thickness</th>
<th>Lattice parameter (Å)</th>
<th>film thickness (nm)</th>
<th>$\rho$ (300 K) (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 nm</td>
<td>3.822 ± 0.001</td>
<td>45.9 ± 0.2</td>
<td>2.90x10$^{-5}$</td>
</tr>
<tr>
<td>20 nm</td>
<td>3.824 ± 0.001</td>
<td>20.1 ± 0.1</td>
<td>2.84x10$^{-5}$</td>
</tr>
<tr>
<td>15 nm</td>
<td>3.825 ± 0.001</td>
<td>14.9 ± 0.3</td>
<td>3.28x10$^{-5}$</td>
</tr>
<tr>
<td>12 nm</td>
<td>3.828 ± 0.002</td>
<td>12.0 ± 0.3</td>
<td>4.15x10$^{-5}$</td>
</tr>
</tbody>
</table>
All surfaces of thin films were atomically smooth, exhibiting a terrace structure, see Fig. 4-3. The root mean square (RMS) roughness of 4, 10, 12, 15, 20 and 45 nm thick SrVO$_3$ films were determined to 6.5, 1.8, 1.8, 2.5, 1.5, and 2.0 Å, respectively. RMS roughness of 4, 9, 14, 18, and 38 nm thick CaVO$_3$ films were determined to 2.2, 5.2, 2.1, 2.2 and 2.3 Å, respectively.
4.3 Electrical properties of SrVO$_3$ and CaVO$_3$

Figure 4-4. Structure and electrical transport properties of vanadate films. (a) Crystal structure of SrVO$_3$ and CaVO$_3$. (b) Temperature dependent sheet resistance of SrVO$_3$ and CaVO$_3$ films. (c) Carrier concentration and (d) Carrier mobility of SrVO$_3$ and CaVO$_3$ films at room temperature. (e) Thickness dependent conductivity of Ag (gray triangles)$^{18}$ and Au (orange triangles)$^{19}$, polycrystalline ITO (light green rhombus)$^{19}$, PLD-grown ITO (light green squares)$^{107}$ and epi-ITO
Temperature-dependent sheet resistance is shown in Fig. 4-4 (b). All films were metallic. For the 45 and 4 nm thick SrVO₃ films room-temperature sheet resistances of about 6 and 150 Ω/sq, i.e. electrical conductivities of 3.5×10⁴ S/cm and 1.6×10⁴ S/cm were determined, respectively. Similarly, for the 38 and 4 nm thick CaVO₃ films room-temperature sheet resistances of about 10 Ω/sq and 205 Ω/sq, i.e. electrical conductivities of 2.6×10⁴ S/cm and 1.3×10⁴ S/cm were determined, respectively. The conductivity of vanadate films largely exceeded values typically reported for ITO⁹⁵, demonstrating excellent electrical properties. The carrier concentration is shown in Fig. 4-4 (c). The average value of 2.26×10²² cm⁻³ (2.40×10²² cm⁻³) was slightly higher than the nominal concentration of 1.76×10²² cm⁻³ (1.87×10²² cm⁻³) for one electron per unit cell of SrVO₃ (CaVO₃), but one order of magnitude higher compared to conventional TCOs. The room temperature carrier mobility shown in Fig. 4-4 (d) was found in good comparison with other transition metal perovskite oxides, such as SrTiO₃, one order of magnitude smaller than those achieved in conventional high performance TCOs. This is a direct consequence of the smaller conduction band width originating from the strongly localized and directed nature of transition metal 3d orbitals, leading to a high m*. The lower carrier mobility is compensated by the high carrier concentration, resulting in a competitive electrical conductivity.

Enhanced surface scattering adversely affected room temperature mobility of the vanadate films only for thicknesses less than 10 nm. This is a remarkable difference in contrast to conventional metals, as shown in Fig. 4-4 (e). Calculating EMFP and comparing to conventional conductors, such as Ag ( =52 nm)¹⁹ or Au ( =50 nm)¹⁹, the much smaller EMFP of SrVO₃ ( =5.6 nm) and CaVO₃ ( =3.9 nm) allows for a more aggressive thickness scaling without suffering from surface and interface scattering²⁸, enabled by carrier mass renormalization due to strong electron correlation. The thickness dependent resistivity of SrVO₃ and CaVO₃ is much smaller.
compared to conventional metals\textsuperscript{19} while the resistivity is lower compared to ITO. The trade-offs in electrical properties of vanadates were found to be better balanced compared to conventional transparent conductors.

Figure 4-5. (a) Schematic and (b) optical photograph of Hall bar devices, here for CaVO\textsubscript{3}. Temperature dependent resistivity of (c) 45-nm-thick SrVO\textsubscript{3} and (d) 38-nm-thick CaVO\textsubscript{3} films along the different directions. The scale bar indicates 500 µm. (Adapted from ref\textsuperscript{106})

In order to verify the independence of electrical conductivity on different in-plane orientations of SrVO\textsubscript{3} and CaVO\textsubscript{3}, we have fabricated Hall bar devices on 45-nm SrVO\textsubscript{3} and 38-nm CaVO\textsubscript{3} thin films and measured resistivity along three different directions: \textlangle 100\rangle, \textlangle 110\rangle and \textlangle 010\rangle. The resistivity at room temperature and residual-resistance ratio (300K/5K) are almost identical and independent of the transport directions, as shown in Fig. 4-5.
The deposition of polycrystalline films from correlated metals with a sizeable anisotropy in electrical resistivity can affect the overall sheet resistance. While in cubic and pseudo-cubic crystal structures, such as SrVO$_3$, CaVO$_3$, but also SrNbO$_3$, SrMoO$_3$, CaMoO$_3$, SrRuO$_3$ and LaNiO$_3$, the anisotropy ratio of resistivity $\rho_\perp:\rho_\parallel$ is expected to be small. However, the anisotropies in correlated metals with layered structure, or uniaxial symmetry might be larger, and should be taken into consideration. MgB$_2$ $\rho_\perp:\rho_\parallel \sim 3$, Sr$_2$RuO$_4$ $\rho_\perp:\rho_\parallel \sim 23$, PdCoO$_2$ $\rho_\perp:\rho_\parallel \sim 123$ and LaFePO$_3$ $\rho_\perp:\rho_\parallel \sim 21$.

4.4 Optical properties of SrVO$_3$ and CaVO$_3$

Figure 4-6. (a) Optical properties of vanadates. (a) Transmission spectrum of SrVO$_3$ films (top) and CaVO$_3$ (bottom) with varying thicknesses on LSAT and SLAO substrates. The range of the
visible spectrum is indicated. (b) Photographs of 4 nm and 12 nm SrVO\textsubscript{3} and CaVO\textsubscript{3} films on LSAT and SLAO substrates, respectively. (c) Complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra of SrVO\textsubscript{3} extracted from room temperature spectroscopic ellipsometry measurements and calculated from first principles calculations. Note the different scale for low energy $\varepsilon$. (Adapted from ref\textsuperscript{92})

The optical properties are discussed next. Figure 4-6 (a) shows the normal incidence transmission spectrum of SrVO\textsubscript{3} (CaVO\textsubscript{3}) films with varying thicknesses on 0.5 mm thick 001 (LaAlO\textsubscript{3})\textsubscript{0.3}(Sr\textsubscript{2}AlTaO\textsubscript{6})\textsubscript{0.7} (LSAT) (001 SrLaAlO\textsubscript{4} (SLAO)) substrates from infrared (0.5 eV) to ultraviolet (6.2 eV) by using a Perkin-Elmer Lambda 950 UV–Vis–NIR spectrophotometer. Photographs of the samples (corners covered during growth) on a colored background are shown in Fig. 4-6 (b). With increasing thickness, transmission was suppressed for energies above \~3.3 eV, marking the onset of strong interband optical transitions. Additionally, a broad feature of reduced transmission around 1.8 eV (1.6 eV) for SrVO\textsubscript{3} (CaVO\textsubscript{3}) evolved with increasing thickness. Since the optical properties of SrVO\textsubscript{3} and CaVO\textsubscript{3} are similar, we limit the detailed discussion to SrVO\textsubscript{3}. Figure 4-6 (c) shows the complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) determined from room temperature ellipsometric spectra obtained from 10, 20, and 45 nm thick SrVO\textsubscript{3} films. Experimental and modeling details are given in the supplement. A screened plasma energy of 1.33 eV was experimentally determined for SrVO\textsubscript{3} by setting $\varepsilon_1$ to zero, higher than the highest plasma energies of TCOs but below 1.75 eV. Spectra in $\varepsilon_2$ were near-zero throughout the visible range and increased in the infrared region due to free carrier reflection. The dielectric function obtained from first principles band structure calculations of SrVO\textsubscript{3} at zero temperature is also shown. All main interband transition peaks were adequately predicted with only slight overestimation in amplitude and peak position, attributed to the intrinsic inaccuracies in calculating the unoccupied electronics states of the density functional theory (DFT) method.
4.5 Determination of the correlation strength

To highlight the beneficial role of strong electron correlation, experimental results were compared to calculation neglecting electron correlation effects, which gave rise to an intended discrepancy. The calculated spectrum of $\varepsilon_1$ crosses zero at $E = 1.58$ eV, ignoring the effective mass enhancement due to strong electron correlation, and therefore a reduced oscillator strength. The computed screened plasma frequency is shifted by 0.25 eV to higher energies. The shift is expected to underestimate the electron correlation, because the screened plasma frequency invokes the dielectric function, being plagued by the systematic overestimation of the interband absorption features. The overestimation of the free carrier response in DFT by neglecting electron correlation effects is better seen by comparing $\varepsilon_2$ from experiment and calculation at low energies in Fig. 4-6 (c). Finally, the wide, but weak absorption feature in $\varepsilon_2$ measured around 1.8 eV is attributed to the spectral weight transfer to higher energies caused by the strong electron correlation present in the films, which overlaps with a weak interband transition from $t_{2g}$ to $e_g$ bands, the only interband optical absorption feature predicted by the density function theory (DFT), see below.

The pronounced electron correlation effect lies at the heart of the proposed design paradigm for transparent conductors, where correlation effects suppress optical absorption of the free carriers, extending the transparent window to lower energies despite a high, metal-like carrier concentration. In order to quantify the electron correlation strength for SrVO$_3$, the effective band mass for non-interacting free electrons, predicted by DFT, is compared to the experimentally determined renormalized effective mass. The reduction in reflectivity of an itinerant electron liquid compared to the free electron gas can be used to determine the degree of correlation using the quasiparticle renormalization constant by considering the unscreened plasma frequencies from DFT calculations and experiment, the latter being determined from optical
conductivity$^{82,112}$. The use of unscreened plasma frequencies avoids potential convolution of interband transition into the determination of the correlation strength. While the screened plasma frequency determines the reflection edge of the carriers, the unscreened plasma frequency is used to determine $Z_k$. An unscreened plasma energy of 3.66 eV was calculated from DFT$^{113}$. The unscreened plasma frequency $\omega_p$ was calculated from the real part of $\sigma$ using$^{82,112}$:

$$\frac{\omega_p^2}{8} = \int_0^{\omega_c} \sigma_1(\omega) d\omega.$$

where Spectra in $\varepsilon$ are related to the complex optical conductivity ($\sigma = \sigma_1 + i\sigma_2$) by$^{114}$:

$$\sigma(\omega) = -i\varepsilon_0\varepsilon[\varepsilon(\omega) - 1]$$

Figure 4-7. (a) Optical conductivity as a function of frequency. (b) Sum-rule plasma frequency as a function of cut-off frequency.

The optical conductivity as a function of frequency for SrVO$_3$ is shown as Fig. 4-7 (a). Systematic errors determining the plasma frequency arise from the choice of the upper integration limit $\omega_c$, the approximation of optical conductivity contribution below the lowest frequency measured (282 cm$^{-1}$), and interband contribution to $\sigma_1$ from transition between the $t_{2g}$ bands. A cut-off frequency $\omega_c$ of 3000 cm$^{-1}$ was used and values of optical conductivity for frequencies below 282 cm$^{-1}$ were omitted. The choice of $\omega_c$ is to include all contribution from free carriers
and to exclude contribution from interband transition. Doubling \( \omega_c \) to 6000 cm\(^{-1} \) increased \( \omega_p \) by less than 10\%, while the contribution from \( t_{2g} \) to \( t_{2g} \) interband transition calculated by DFT contributed less than 4\% of the total Drude peak. With sample-to-sample deviations less than 3\% the total error in \( \omega_p \) was estimated to 10\%. The plasma frequency of SrVO\(_3\) was estimated to be \( \omega_p = (2.1 \pm 0.2) \) eV. The sum-rule plasma frequency as a function of cut-off frequency is shown in Fig. 4-7 (b). A renormalization constant of \( Z_k = 0.33 \pm 0.03 \) was found for SrVO\(_3\), a much reduced value compared to conventional metals (\( Z_k \approx 1 \)), revealing pronounced correlation effects without complete carrier localization.
4.6 DFT calculation

Figure 4-8. First principle calculation results of SrVO$_3$. (a) Band structure of SrVO$_3$ in the vicinity of the Fermi level EF (dotted line), comprised of nine bands originating from O 2$p$ orbitals, three bands from V 3$d$ $t_{2g}$, and two bands from V 3$d$ $e_g$ orbitals. Interband transition (I) through (III) are indicated. (b) Brillouin zone of SrVO$_3$ containing the Fermi surfaces of the three $t_{2g}$ bands. Isosurface representation of the dipole matrix element $M^2$ for electronic states in the Brillouin zone for the interband transitions (c) (I): $t_{2g}^2$ to $e_g^1$, (d) (II): 2$p^1$ to $t_{2g}^1$, (e) (III): 2$p^1$ to $t_{2g}^3$ with 2$p^1$ the highest lying valence band, $t_{2g}^1$, $t_{2g}^2$, $t_{2g}^3$ the lowest middle and highest lying $t_{2g}$ bands, and $e_g^1$, $e_g^2$ the lowest, highest lying $e_g$ bands, respectively. The Fermi surface of the $t_{2g}$ band involved in the transition is indicated in c-e as well. (Adapted from ref$^{92}$)
The interband transitions in SrVO$_3$ through first principles calculations of the band structure and the dipole transition matrix element for interband optical transitions was done by Zhou and coworker$^{92,113}$. First principle calculations of SrVO$_3$ were performed using the generalized gradient approximation (GGA) with the Perdew-Becke-Erzenhof parameterization$^{115}$ as implemented in the Vienna Ab initio Simulation Package (VASP-5.2.12)$^{116,117}$. The projector augmented wave (PAW) potentials used contained 10 valence electrons for Sr (4s$^2$4p$^6$5s$^2$), 13 for V (2s$^2$2p$^6$3d$^3$4s$^2$) and 6 for O (2s$^2$2p$^4$)$^{115,118}$. We used 500 eV as the energy cutoff. An 8x8x8 Monkhorst-Pack k-point mesh was used for the structural relaxation, and a 31x31x31 $\Gamma$ centered k-mesh was used for the interband transition calculation. Extensive testing with the GGA+U method with nonzero $U$ and ferromagnetic, G-type antiferromagnetic and nonmagnetic configurations showed that the relevant features of the band structures and interband transitions are not sensitive to $U$ or the magnetic ordering. For $U=0$, the ground state was found to be nonmagnetic. Since SrVO$_3$ is paramagnetic at room temperature$^{119-121}$, we performed the analysis for the nonmagnetic state with $U=0$. The c lattice parameter of the tetragonal five-atom unit cell was relaxed with in-plane lattice constant fixed to the experimental value 3.868 Å, preserving P4/mmm symmetry, yielding a c/a ratio of 0.979.

The unscreened plasma frequency was calculated from the band structure using$^{112,122}$:

$$\omega^2_{p,\alpha\beta} = \frac{4\pi e^2}{\hbar^2} \sum_{n,k} 2 g_k f(E_{\alpha k}) \left( e_\alpha \frac{\partial E_{\beta k}}{\partial k} \right) \left( e_\beta \frac{\partial E_{\alpha k}}{\partial k} \right),$$

Where $\alpha, \beta$ denote the direction, $V$ denotes the volume of the unit cell, $f$ is the occupancy, $E$ is the band energy, $e$ is the unit vector, and $g$ is the weight of k point. For SrVO$_3$, the plasma frequency is determined by the $t_{2g}$ bands that cross the Fermi level. Since the $t_{2g}$ band structure is relatively simple, the uncertainty in the plasma frequency is determined by the uncertainty in the $t_{2g}$ bandwidth. We have computed band structures for different $U$ and k-meshes,
and the $t_{2g}$ bandwidth is found to vary by less than 2%. The uncertainty in $\omega_p^2$ can thus be estimated to be about 4% of the computed value.

The intraband contribution to the dielectric function was obtained empirically from the Drude model

$$
\varepsilon_{\text{intra}}^{(1)}(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2}, \quad \varepsilon_{\text{intra}}^{(2)}(\omega) = \frac{\gamma \omega_p^2}{\omega^3 + \omega \gamma}, \quad \text{and} \quad \gamma = \frac{ne^2 \rho}{m_e};
$$

Where $\rho = 2 \times 10^{-5} \Omega \times \text{cm}$, $n = 2 \times 10^{22} \text{ cm}^{-3}$, to estimate $\gamma = 0.1 \text{eV}$ and $m_e = 4.5m_0$. The interband contribution $\varepsilon_{\text{inter}}^{(1)}$, $\varepsilon_{\text{inter}}^{(2)}$, to the dielectric function was calculated using the VASP implementation, in the approximation that the local field effects are neglected$^{123}$. The imaginary part was determined by

$$
\varepsilon_{\text{inter}, \alpha\beta}^{(2)}(\omega) = \frac{4\pi^2 e^2}{V} \lim_{\omega \to 0} \frac{1}{q} \sum_{c,v,k} 2\pi \delta(E_{c,k} - E_{v,k} - \omega) \times \langle u_{c,k+e_{\alpha,q}} | u_{v,k} \rangle \langle u_{v,k} | u_{c,k+e_{\beta,q}} \rangle
$$

Where $V$ is the volume of the unit cell, the index $c$ and $v$ refer to conduction and valence bands, respectively, and $u_{c,k}$ is the cell periodic part of the wavefunction at $k$-point $k$. $e_{\alpha}$ and $e_{\beta}$ denote unit vector in Cartesian directions. $\lim_{q \to 0} \langle u_{c,k+e_{\alpha,q}} | u_{c,k} \rangle$ gives the $\alpha$ component of the dipole matrix element between two bands.

The real part of the dielectric function was obtained using the Kramers-Kronig transformation,

$$
\varepsilon_{\text{inter}, \alpha\beta}^{(1)}(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_{\text{inter}, \alpha\beta}^{(2)}(\omega') \omega'}{\omega^2 - \omega'^2 + i \eta} d\omega',
$$

where the $P$ means the principal value, and $\eta$ is a tiny shift.
The three relevant sets of bands yielding interband transitions with energies $\Delta E$ below 3.6 eV are shown in Fig. 4-8 (a) along with the Fermi surfaces in Fig. 4-8 (b). It is remarkable that absorption at lower energy were either absent (Fermi factor, same occupancy), or strongly suppressed due to a small dipole transition matrix element and/or joint density of states. The square of the computed dipole matrix element $M^2$ for three transitions are displayed as an isosurface representation in Fig. 4-8 (c) (higher $t_{2g}$ band to lowest eg band ($\Delta E = 0.3$ to 3.6 eV), marked as I in Fig. 4-8 (a), Fig. 4-8 (d) (highest valence band to lower $t_{2g}$ band ($\Delta E = 1.4$ to 3.5 eV), marked II) and Fig. 4-8 (e) (highest valence band to upper $t_{2g}$ band ($\Delta E = 1.4$ to 4.1 eV), marked III). The detailed analysis is summarized in the supplement. While only states with wave vectors inside the Fermi surface sheet are a filled-to-empty transition in the first case (Fig. 4-8 (c), only states with wave vectors outside the Fermi surface sheets are optically active in the ladder two cases (Figs. 4-8 (d) and 4-8 (e). Note that in Fig. 4-8 (d) the strongest interband transition occurs for states inside the Fermi sheets, while sizeable interband transition strengths just outside the Fermi surface sheet are found in Figs. 4-8 (d) and 4-8 (e). The exact Fermi level position in the $t_{2g}$ bands is critical to further reduce optical interband absorption.

4.7 Figure-of-merit calculation for transparent conductors

The alternative paradigm to utilize the mass enhancement of carriers in correlated metals rather than doping wide-band-gap semiconductors constitutes another class of transparent conductors, represented by SrVO$_3$ and CaVO$_3$. We benchmarked them against conventional transparent conducting materials based on the figure of merit (FOM) proposed by Haacke$^{124}$ with transmission coefficient $T$ and sheet resistance $R_s$. The exponent of $T$ ensures 90% optical transmittance at maximum. The FOM was calculated as a function of thickness assuming free-
standing films, using electrical conductivity and absorption coefficient $\alpha$ determined from $\varepsilon$ for Ag, Au, ITO, SrVO$_3$ and CaVO$_3$.

A free standing film of thickness $t$, situated between two dielectric media (air) and forming an abrupt upper and lower interface was considered. The absorption coefficient $\alpha$ of the film is given by:

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

with $k$ extinction coefficient and $\lambda$ the wavelength in the film. For normal incidence and monochromatic radiation the transmission coefficient $T$, i.e. the ratio of incident intensity at the upper interface and the transmitted intensity at the lower interface is given by

$$T = \frac{I}{I_0} = \frac{(1 - R)^2 + 4R \sin^2 \psi}{e^{\alpha t} + R^2 e^{-\alpha t} - 2R \cos(\phi + \psi)}$$

with the reflectivity $R$:

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

the refractive index $n$ and

$$\phi = \frac{2\pi nt}{\lambda}; \quad \psi = \tan^{-1} \frac{2k}{n^2 + k^2 - 1}.$$ 

The term $2R \cos 2(\phi + \psi)$ takes into account the interference effect arising from the upper and lower film interface. The refractive index $n$ and extinction coefficient $k$ are intimately coupled to the dielectric function.
\[ \varepsilon = \varepsilon_1 + i \varepsilon_2 = n^2 - k^2 + i2nk \]

Figure 4-9. Optical transmission of free standing films, accounting for reflection and interference, at a wavelength \( \lambda = 550 \text{nm} \) [Eqns. (H), (I), (K), (L)], and averaged over the range of the visible spectra [Eqn. (N)]. Data of the complex refractive index of Ag, ITO, SrVO\(_3\) and CaVO\(_3\) were taken from Refs.\(^\text{126,127}\) and this work. (Adapted from ref\(^\text{106}\))

The thickness dependent transmission at 550 nm wavelength for freestanding conducting films Ag, ITO, SrVO\(_3\) and CaVO\(_3\) were calculated and are shown in Fig. 4-9. Since the choice of a specific wavelength can change \( \alpha \) and \( R \) quite significantly, \( T \) averaged over the visible spectrum from 400 to 800 nm:

\[ T_{\text{ave}} = \frac{\int_{400\text{nm}}^{800\text{nm}} T(\lambda) d\lambda}{\int_{400\text{nm}}^{800\text{nm}} d\lambda} \]

was calculated and is shown as well.
Thickness dependent effects, such as multiple reflection and interference at film surfaces, as well as decreasing electrical conductivity due to enhanced surface scattering, as described by Fuchs and Sondheimer\textsuperscript{128,129}, have also been taken into consideration.

The electron mean free path (EMFP) $\Lambda$ considered here is calculated from the Sommerfeld model\textsuperscript{130}:

$$\Lambda = \tau \cdot v_F = \frac{\hbar}{e} \frac{\mu}{n} \left(\frac{3\pi^2}{2}\right)^{\frac{1}{3}}$$

Where $\tau$ is the relaxation time, $v_F$ the Fermi velocity, $\mu$ the carrier mobility, $n$ the carrier concentration, and $e$ the elemental charge. Values for the EMFP of selected materials considered here, including conventional metals, degenerately doped semiconductors, and SrVO$_3$ and CaVO$_3$ are given in Table 4-3.

Table 4-3. Calculation of the electron mean free path (EMFP) for selected materials at room temperature. Data for Cu, Ag and Al were taken from Ref.\textsuperscript{19}, ITO from Ref.\textsuperscript{131} and SrVO$_3$ from this work.

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity ($\Omega \text{ cm}$)</th>
<th>Carrier Concentration ($m^3$)</th>
<th>EMFP (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.70x10$^{-6}$</td>
<td>8.45x10$^{28}$</td>
<td>39</td>
</tr>
<tr>
<td>Ag</td>
<td>1.61x10$^{-6}$</td>
<td>5.85x10$^{28}$</td>
<td>52</td>
</tr>
<tr>
<td>Al</td>
<td>2.74x10$^{-6}$</td>
<td>1.81x10$^{29}$</td>
<td>15</td>
</tr>
<tr>
<td>ITO</td>
<td>2.70x10$^{-4}$</td>
<td>4.50x10$^{20}$</td>
<td>8.0</td>
</tr>
<tr>
<td>SrVO$_3$</td>
<td>2.83x10$^{-5}$</td>
<td>2.26x10$^{28}$</td>
<td>5.6</td>
</tr>
<tr>
<td>CaVO$_3$</td>
<td>3.87x10$^{-5}$</td>
<td>2.40x10$^{28}$</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Fuchs\textsuperscript{128} and Sondheimer\textsuperscript{129} attributed the pronounced conductivity decrease in ultrathin films to enhanced surface scattering, if film thickness is on the order of the EMFP or below:

$$\sigma_{FS} = \sigma_0 \left[ 1 - \frac{3(1-p)}{2\kappa} \int_{1}^{\infty} \left( \frac{1}{\zeta^3} - \frac{1}{\zeta^5} \right) \frac{1-e^{-\kappa\zeta}}{1-pe^{-\kappa\zeta}} \, d\zeta \right]$$
Where \( \sigma_0 \) is the bulk conductivity, \( \kappa = t/\Lambda \) is the normalized length with \( t \) referring to the film thickness and \( \Lambda \) the EMFP and \( p \) the reflection coefficient \((0 \leq p \leq 1, p=0 \text{ diffuse}; \text{ random direction and magnitude of velocity after surface scattering event, } p=1 \text{ specular: elastic scattering at the surface with reversal of the normal component})\). Mayadas and Shatzkes\(^{132}\) have expanded the Fuchs Sondheimer model by considering the following three main mechanisms: background scattering, grain boundary scattering and external surface scattering.

\[
\sigma_{MS} = \sigma_0 \left[ 1 - \frac{3}{2} \zeta^2 + 3 \zeta^2 - 3 \zeta^3 \ln \left( 1 + \frac{1}{\zeta} \right) \right]
\]

\[
\zeta = \frac{\Lambda}{D} \frac{R}{1 - R}
\]

Where \( \Lambda \) is the EMFP, \( D \) the average grain size and \( R \) the reflection coefficient.

---

**Figure 4-10.** Thickness dependence of the sheet resistance \( R_s \) for (a) SrVO\(_3\) (b) CaVO\(_3\) (c) ITO, and (d), Ag taking the thickness dependent resistivity into account. The increase in resistivity \( \Delta \rho \) normalized to the bulk resistivity \( \rho_0 \) is shown below. Data for Ag, ITO, SrVO\(_3\) and CaVO\(_3\) were taken from Refs\(^{19,133}\) and this work, respectively. (Adapted from ref\(^{106}\))
The total resistivity \( \rho = \sigma^{-1} \) of SrVO\(_3\), CaVO\(_3\), Ag and ITO thin films have been calculated as a function of thickness and the resistivity increase \( \Delta \rho \) due to enhanced carrier scattering in the films was calculated\(^{10} \) using \( \Delta \rho = \rho_{FS} + \rho_{MS} - \rho_0 \) and the experimental data and fitting for SrVO\(_3\), CaVO\(_3\), Ag and ITO are shown in Fig. 4-10.

Two parameters determine the performance of a transparent conducting film: optical transmission \( T \), and sheet resistance \( R_s \). Both are connected via the film thickness \( t \) to the material specific parameters optical absorption \( \alpha \) and electrical conductivity \( \sigma \). The best performance is achieved for simultaneously high electrical conductivity and optical transmission. The figure of merit (FOM) \( \Phi_{TC} \) used is based on the metric proposed by Haacke\(^{124} \):

\[
\Phi_{TC}(t) = \frac{T^{10}}{\frac{\rho_0 + \Delta \rho}{t}}.
\]

Where \( T \) is the optical transmission and \( (\rho_0 + \Delta \rho)/t \) represents the sheet resistance \( R_s \) that takes into account surface scattering effects. The exponent of the transmission balances the relative weights of \( T \) and \( (\rho_0 + \Delta \rho)/t \) contributing to \( \Phi_{TC} \) and determines the transmission for the thickness at maximum \( \Phi_{TC} \). Using an exponent of 10 stipulates a transmission close to 90% at maximum \( \Phi_{TC} \). As discussed earlier, the choice of a specific wavelength affects \( T \), which can dramatically alter \( \Phi_{TC} \) due to the large exponent. Therefore, rather than performing the calculation at a selected wavelength (550 nm was chosen by Haacke\(^{124} \), close to the maximum spectral sensitivity of the human eye) the average transmission was used instead.

To ensure a meaningful comparison across the different material options considered, namely conventional metals, represented by Ag, degenerately doped wide band gap semiconductors, represented by ITO, and the proposed correlated metals, represented by SrVO\(_3\),
and CaVO$_3$, the FOM has been modified to incorporate effects of enhanced carrier scattering, relevant for films with thicknesses smaller than the electron mean free path, and changes in the transmission from multiple reflection at the top and bottom surface and the interference effects arising from it for the free standing film, relevant for film thicknesses with optical path length on the order of $\lambda/4$. Taking into account both effects caused a sizable overall reduction of $\Phi_{TC}$ compared to the uncorrected FOM.

Figure 4-11. Consideration for the figure of merit (FOM) for transparent conductors. Solid black line: FOM defined after Haacke$^{124}$, calculated for light at wavelength $\lambda=550$ nm. Dashed gray line: FOM using transmission value taken as average across the visible spectrum. Dotted blue line: Averaged transmission incorporating multiple reflection and interference effects from top and bottom interface of a free standing film by calculating the transmission averaging over the visible range, see Fig. 4-9. Thick solid green line. Figure of merit includes thickness dependent increase of electrical conductivity due to enhanced surface scattering for films with thicknesses below the electron mean free path, see Fig. 4-10. (a) Example of Ag representing ultrathin metal films. (b) Example of ITO representing degenerately doped wide band gap semiconductors. (Adapted from ref$^{106}$)
Figure 4-11 shows the impact of the different corrections to $\Phi_{TC}$ for the case of Ag and ITO. In the first case, averaging the transmission over the entire visible spectrum compared to the transmission at 550 nm resulted in a small $\Phi_{TC}$ increase, attributed to the strong interband transition of Ag around 360 nm. Taking reflection into account the transmission increased from interference and multiple reflection within the film. The effect of enhanced surface scattering of electrons is rather strong. Although FOM only scales linearly with this effect, the electron mean free path (EMFP) in Ag is rather large (52 nm, see Table 4-3) The maximum $\Phi_{TC}$ for a film thickness around 4 nm is only a small fraction of the EMFP, resulting in a more than one order of magnitude increase in the conductivity compared to the bulk value, see Fig. 4-11 (a)\textsuperscript{93,124}. Much more dramatic is the effect of reflection for thicker films, i.e. in the case of degenerately doped wide band gap semiconductors, where low electrical conductivity is compensated by low optical absorption allowing a larger film thickness. In case of ITO, averaging $T$ over the entire visible spectrum resulted in a reduction of the average $T$, which is further reduced by taking reflection into account, showing pronounced interference effects in $\Phi_{TC}$ with a local minimum at a film thickness of 60 nm. Taking surface scattering effects into consideration $\Phi_{TC}$ only marginally decreased at the maximum around 150 nm, but was reduced at the second local maxima at 10 nm, see Fig. 4-11 (b).

It is noted that simplifying assumptions in either the transmission of a free standing conducting film, or limiting the model to only one wavelength, or ignoring the thickness dependence of conductivity, can result in significant overestimation of $\Phi_{TC}$ with dramatic implications using it as a metric to benchmark the performance of transparent conductors. Careful consideration of all relevant effects and using a complete set of experimental data, i.e. the $\varepsilon$ in the
entire range of wavelengths considered and thickness dependent electrical conductivity for the material to benchmark, are mandatory for a meaningful comparison.

Figure 4-12. Figure of merit $\Phi_{TC}$ for transparent conducting materials. Experimental data compiled for Au (orange circles), Ag (grey circles), polycrystalline ITO (green circles), epi-ITO (solid triangle, empty triangle, cross triangle) and SrVO$_3$ (red circles) and CaVO$_3$ (blue rhombus) from this work. Lines are from $\Phi_{TC}$ calculations (see supplement). Deviations between experiment and calculation for Au and missing experimental data of Ag for thicknesses less than 10 nm are due to inferior percolation behavior of ultrathin metal films. (Adapted from ref 92)

The results of overall $\Phi_{TC}$ as a function of thickness are shown in Fig. 4-12. Note that the maximum occurs for SrVO$_3$ and CaVO$_3$ for much thinner films compared to epi-ITO, a big advantage for device manufacturing (reduced deposition time and higher throughput) for ITO benefits from excellent optical transmittance, but suffers from low electrical conductivity, resulting in a large film thickness (> 100 nm) at maximum. A maximum $\Phi_{TC}$ of $4 \times 10^{-3} \Omega^{-1}$ was obtained for a single crystalline epi-ITO film, about 2.5 times higher compared to polycrystalline ITO films. For ultrathin metals the film thickness for optimal $\Phi_{TC}$ is well below 10 nm, posing a
tremendous challenge for depositing smooth and coalesced films due to their preference to Vollmer-Weber growth with percolation thicknesses typically above 10 nm\textsuperscript{129,136}. Recent efforts are geared towards improving nucleation behavior using seeding or wetting layers\textsuperscript{137} to reduce percolation thresholds and suppress film dewetting, which, if successful, would allow $\Phi_{TC}$ similar to epi-ITO. $\Phi_{TC}$ of correlated vanadates is striking. While conventional conductors were largely outperformed by the highest FOM achieved for 12-nm-thick SrVO$_3$ and 10-nm-thick CaVO$_3$ only one data point, experimentally demonstrated for epi-ITO, is on par with SrVO$_3$ and CaVO$_3$, albeit at much larger film thicknesses. While the mass enhancement through electron correlation restrains the free carrier reflection to the IR range, it also allows a more favorable thickness scaling and thus thinner films due to the small. High electrical conductivity and good optical transparency in combination with favorable thickness scaling of SrVO$_3$ and CaVO$_3$ films result in a high $\Phi_{TC}$.

4.8 Conclusion

Strategies to optimize transparent conducting materials, whose fundamental properties are well described by a free electrons gas with $n$ and $m^*$ have been exhausted during the past decades. The rise in costs of ITO due to indium scarcity is expected to continue and the growing demand for transparent conductors makes it highly desirable to find alternative solutions. Improvements in the performance of transparent conducting materials are within reach, if additional opportunities and materials choices become available. The approach proposed here dramatically expands the palette of potential “TCO cations” beyond conventional candidates towards transition metal elements. Rather than tuning the carrier concentration through doping, controlling the carrier effective mass by tailoring the electron correlation strength represents an
alternative paradigm for the design of transparent conductors. Positioning the correlated metal close to the metal-to-insulator transition, so that pronounced correlation effects occur while the carriers maintain sufficient itinerant character, manipulating band position, band dispersion and thus Fermi surface size and shape to suppress interband transitions are materials design strategies to discover transparent conductors in the class of correlated metals beyond SrVO$_3$ and CaVO$_3$. Given the short EMFP of correlated metals, a much higher “tolerance” to grain boundary scattering of polycrystalline film compared to conventional metals and ITO is expected, rendering the transport properties less vulnerable to economic, large scale deposition techniques on industry relevant substrates. Combining the excellent intrinsic materials performance of correlated metals with extrinsic optimization strategies, such as geometric optimization used in metal networks$^{138}$, a tandem approach towards correlated metal networks will likely boost the performance even further. First principles calculations will help rapid screening of potential candidates in the wide class of correlated metals, predicting $\epsilon$ to down-select materials with sufficiently high interband transition energies and low probability of dipole-allowed transition in the optical spectrum. Radically different approaches to optimize the optoelectronic properties of targeted correlated metals, such as changes in the band width to control carrier effective mass or remolding the Fermi surface to suppress optically active interband transition through identical occupation, will open up an unexplored field to develop the next generation of high performance transparent conductors.
Chapter 5
Enhancing the performance of correlated metals as transparent conductors via A-site aliovalent substitution

[L. Zhang et al. Submitted]

5.1 Introduction

Transparent conductors are key materials in current technologies due to their essential roles in display (flat-panel display and touchscreen devices), solid state lighting, as well as active energy generation (photovoltaics) and passive energy preservation (architectural low-emissivity glass, smart windows). With the steadily increasing price of indium, intensive research efforts have been made to find a replacement for tin-doped indium oxide (ITO), which is currently used in most applications. The material performance of degenerately doped wide band gap semiconductors in general and ITO in particular have been pushed to their intrinsic limits, and further improvements in the electrical conductivity are hampered by the solid solution limit of dopants and sizeable contributions from charged impurity scattering at high dopant concentrations. While conventional metals are ideal conductors and were considered as transparent conductors if deposited as ultrathin films, they are not ideal material choices compared to ITO due to the much lower optical transparency. Metals have high plasma frequencies and are thus highly reflective in the visible range (1.75-3.25 eV); and some metals have strong interband transitions in the visible range leading to absorption.

Recently, metals exhibiting strong electron-electron correlation effects have been proposed and experimentally demonstrated to exhibit a higher optical transparency while largely
maintain their high electrical conductivity, rendering them highly suitable for transparent conductor application\textsuperscript{92}. In the transition metal oxides SrVO\textsubscript{3} and CaVO\textsubscript{3} it was found that despite the large carrier densities, the large carrier effective masses originated from strong electron-electron correlation red-shift the free carrier reflection edge into the infrared range. Their favorable band structure, characterized by isolated and narrow bands around the Fermi level suppresses the direct interband transitions resulting in a good transparency in the visible range\textsuperscript{92}. The figure of merit $\Phi_{TC}$ of SrVO\textsubscript{3} and CaVO\textsubscript{3} films compared favorably to epitaxial ITO at only one tenth of the film thickness, making correlated metals a relevant contender to potentially replace ITO as transparent electrode\textsuperscript{92}.

While the electrical conductivity in SrVO\textsubscript{3} is much larger than that of ITO, a broad absorption peak centered around 3.33 eV, which corresponds to an interband transition between oxygen (O) 2$p$ to vanadium (V) $t_{2g}$ band with a full width at half-maximum of $\sim$0.79 eV infringes on the optical transmittance in the blue regime\textsuperscript{92,113}. Consequently, there is a need to explore material optimization strategies within the class of correlated metals to expand the high optical transparency towards shorter wavelengths. Inspired by the Burstein-Moss effect\textsuperscript{130}, a blue-shift of the absorption edge in degenerately doped semiconductors by blocking the lowest states in the conduction band with an occupation of carriers from the activated dopants, the proposed strategy here is to raise the Fermi level of SrVO\textsubscript{3} by substituting the divalent element, Sr, that occupies the $A$-site in the perovskite structure with the trivalent element La. Therefore, the onset of photon energy of absorption corresponding to O 2$p$ to V $t_{2g}$ could possibly be increased. Even though blue-shifting the absorption peak by up-shifting the Fermi level in oxides has not been realized, an opposite change of the Fermi level in hole-doped ($x$) La\textsubscript{1-x}Sr\textsubscript{x}MO\textsubscript{3} ($M$=Mn, Fe, Co and Ni) by substituting $A$-site element La with Sr was reported\textsuperscript{140}. The Fermi level did down-shift $\sim$0.9 eV as $x$ increased from 0.1 to 0.9, which was in a good agreement with results from photoemission spectroscopy measurements\textsuperscript{141–143}. 
SrVO$_3$ is a perovskite oxide with the electronic configuration $d^1$. V has a valence state of V$^{4+}$ possessing one unpaired 3d electron per unit cell, and the Fermi level intersects with narrow bands derived from V 3d $t_{2g}$ orbitals forming a correlated metal. In contrast, LaVO$_3$ is a $d^2$ Mott insulator where the strong correlation effects split the V 3d $t_{2g}$ bands into a fully occupied lower and an empty upper Hubbard band$^{144}$.

The difference of ionic radii of 12-fold coordinated Sr (1.44 Å) and La (1.36 Å) at the A-site is ~6%, which is much smaller than 15% in the Hume-Rothery rule$^{145}$. The electronegativity of Sr (0.95) and La (1.10) is also similar to avoid the formation of any intermetallic compounds. Though La (3+) and Sr (2+) exhibit different valence states in the perovskite structures, it is believed that an electronic reconstruction of V (4+ → 3+) enables a complete solid solution in La$_x$Sr$_{1-x}$VO$_3$ thin films.

Previous studies of La$_x$Sr$_{1-x}$VO$_3$ mainly focused on band-filling-driven metal-to-insulator transition that occurred at a La composition of ~0.80$^{146-148}$. Here we explore the effect of aliovalent substitution in the dilute limit of La composition which was restricted to less than ~0.20 to ensure a highly metallic phase. This enables us to gain a fundamental understanding how the up-shift of the Fermi level with increasing La composition affects the optical and electrical properties of the correlated metal La$_x$Sr$_{1-x}$VO$_3$, providing insights about the effectiveness of this material optimization strategy to further improve the performance of correlated metals for the application as transparent conductors.

5.2 Growth of La$_x$Sr$_{1-x}$VO$_3$
La$_{x}$Sr$_{1-x}$VO$_3$ films with various La compositions ($x=0.00$ or no doping, 0.01, 0.02, 0.03, 0.11 and 0.18) were grown on (LaAlO)$_{3.3}$(Sr$_{2}$AlTaO$_{6.7}$) (LSAT) substrates by hybrid molecular beam epitaxy (hybrid MBE) using an adsorption-controlled growth mode. The growth is self-regulated within a wide range of V flux, resulting in an ideal cation stoichiometry for ternary
SrVO$_3$\textsuperscript{149} and LaVO$_3$\textsuperscript{150}, which has been experimentally interpolated for the growth of quaternary La$_x$Sr$_{1-x}$VO$_3$ system, as confirmed using high-resolution x-ray diffraction (XRD) and Rutherford backscattering spectrometry (RBS) measurements\textsuperscript{151}. Accessing a growth window for the solid solution system La$_x$Sr$_{1-x}$VO$_3$ is key to explore the intrinsic properties and to avoid confusion from unintentional sources, such as defect formation in the film to accommodate a nonstoichiometric composition\textsuperscript{49,152}. High-resolution XRD 2$\theta$-$\omega$ scans of La$_x$Sr$_{1-x}$VO$_3$ films are shown in Fig. 5-1 (a). The pronounced thickness fringes observed with substrate and film peaks indicate a high crystalline quality. Film thickness and film lattice parameters were extracted from fits and are included in the Supplementary Information\textsuperscript{153}. On-axis 2$\theta$-$\omega$ scans and fitting of all La$_x$Sr$_{1-x}$VO$_3$ films are shown in Fig. 5-2 (a)–(f). The pronounced thickness fringes indicated the high quality of the thin films, and was fit by considering both film lattice parameters and film thickness by GenX, and further details elsewhere\textsuperscript{154}. The results are summarized in Table 5-1.

Table 5-1. Thickness series of La$_x$Sr$_{1-x}$VO$_3$ grown on LSAT samples. Lattice parameter and film thickness has been extracted from XRD spectra shown in Fig. 5-1.

<table>
<thead>
<tr>
<th>La content (x)</th>
<th>0.00</th>
<th>0.01</th>
<th>0.02</th>
<th>0.03</th>
<th>0.11</th>
<th>0.18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness</td>
<td>nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 49.30±0.40    | 34.05±0.40 | 35.59±0.40 | 50.15±0.40 | 53.72± &nbsp;32.26±0.40
| Lattice parameter | Å     |      |      |      |      |      |
| 3.825±0.0005 | 3.826±0.005 | 3.827±0.005 | 3.282±0.005 | 3.837±0.005 | 3.841±0.005 |
Figure 5-2. 2θ-ω scans (red dots) around the 002 LSAT substrate peak for La$_x$Sr$_{1-x}$VO$_3$ films and their fitting results (solid black line) with La compositions (a) $x=0.18$; (b) $x=0.11$; (a) $x=0.03$; (a) $x=0.02$; (a) $x=0.01$; (e) $x=0.00$;

Out-of-plane (OOP) lattice parameters are calculated from the 2θ positions of La$_x$Sr$_{1-x}$VO$_3$ 002 peak, which increased from 3.825Å for SrVO$_3$ to 3.843Å for La$_{0.18}$Sr$_{0.82}$VO$_3$. Since the cation stoichiometry was maintained by employing the self-regulated growth, the lattice expansion was solely attributed to the increase of La incorporation into the film$^{151,155}$. La composition extracted from the OOP lattice parameter expansion with respect to that of intrinsic SrVO$_3$ films are shown in Fig. 5-1 (b)$^{151}$. Reciprocal space mapping (RSM) was performed on La$_x$Sr$_{1-x}$VO$_3$ films with $x=0.11$ and 0.03, as shown in Fig. 5-1 (c) and (d), respectively. The identical in-plane lattice parameters of substrate and film and absence of film peak broadening indicated coherently strained La$_x$Sr$_{1-x}$VO$_3$ films.
5.3 Optical properties of La$_x$Sr$_{1-x}$VO$_3$

Figure 5-3. (a) The schematic of optical absorption between O 2$p$ and V $t_{2g}$ band for SrVO$_3$ and La$_x$Sr$_{1-x}$VO$_3$. (b) Real (top panel) and imagery (bottom panel) part of the dielectric function of La$_x$Sr$_{1-x}$VO$_3$ films extracted from spectroscopic ellipsometry measurements. (c) The calculated transmission as a function of photon energy for 10-nm-thick La$_x$Sr$_{1-x}$VO$_3$ films with $x=0$, 0.03, 0.11 and 0.18. The 80% transmission is drawn by a dash line. The inset shows the photon energy at which the dash line crossed the transmission curves as a function of La compositions.

The effect of La aliovalent substitution on the Fermi level position is schematically shown in Fig. 5-3 (a). The Fermi level of SrVO$_3$ lies in the partially filled V $t_{2g}$ band, while the valence band originated from O 2$p$ band. Increasing La incorporation $x$ up-shifts the Fermi level and the blue-shifts the interband absorption edge in La$_x$Sr$_{1-x}$VO$_3$ for excitation from the O 2$p$ to the V $t_{2g}$ band, resulting in a reduction in optical absorption and an increase of optical transmission at short wavelengths. At the same time the states populating V $t_{2g}$ band may cause an unwanted increase in
the interband transition from the V $t_{2g}$ into the higher lying V $e_g$ conduction band. To investigate the trends in optical properties with La substitution, the complex dielectric constant of La$_x$Sr$_{1-x}$VO$_3$ films at room temperature was characterized using spectroscopic ellipsometry (SE) measurements. Figure 5-3 (b) shows the real part $\varepsilon_1$ (top panel) and imaginary part $\varepsilon_2$ (bottom panel) of the dielectric function of La$_x$Sr$_{1-x}$VO$_3$ films. Shifts of the screened plasma frequencies $\omega_p$, obtained from the real part $\varepsilon_1(\omega_p) = 0$, were small ($\omega_p = 1.34$ eV for SrVO$_3$, $\omega_p = 1.31$ eV for La$_{0.18}$Sr$_{0.82}$VO$_3$, as shown in the inset of Fig. 5-3 (b)). All plasma frequencies were well below the minimum of visible spectrum (1.75 eV), ensuring a low reflectance in the visible spectrum irrespective of La incorporations. The bottom panel of Fig. 5-3 (b) shows the imaginary part of the dielectric constant as a function of La compositions, which is directly linked to interband transitions. The upturn of $\varepsilon_2$ below 1 eV is due to the free carrier concentration, indicating the metallic nature of all films. The small but nonzero dielectric constant between 1 to 2 eV is attributed to weak interband transitions between V $t_{2g}$ to V $e_g$. The slight increase of $\varepsilon_2$ between 1 to 2 eV for the films with $x=0.11$ and 0.18 was attributed to the up-shift of the Fermi level, filling more states in the V $t_{2g}$ band that can contribute to V $t_{2g}$ to V $e_g$ interband transition. Since the increase of $\varepsilon_2$ occurred for energies below 1.75 eV, the transmittance in the visible range was therefore not affected.

The most pronounced change in the imaginary part of the dielectric constant was found for the absorption peak at ~3.33 eV, originating from the interband transitions from O 2p to V 3d $t_{2g}$ band$^{92}$. While for smaller La composition up to $x=0.03$ a pronounced blue-shift of interband transition was observed, as indicated by an arrow in Figure 2b (bottom panel), for large La compositions ($x=0.11$ to 0.18) the shape of the absorption peak was altered as well. The shift of the
dominant interband transition is attributed to the Fermi level raise originated by an increase of the free carrier concentration donated from La substituting Sr at the A-site.

The effect of the Fermi level position on the optical transmission properties of $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ is shown in Fig. 5-3 (c). The optical transmission for 10-nm-thick films with varying La compositions was calculated using the dielectric constant determined from SE experiments; the details are given in the Supplementary Information $^{92,125}$. A pronounced expansion of the optical transmission window (>80%) towards shorter wavelength is found. The inset of Fig. 5-3 (c) shows the cut-off photon energies for a transmission >80%, which increased from 2.56 eV for SrVO$_3$ to 2.77 eV (2.76 eV) for $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ with $x=0.11$ (0.18). The average transmission in the infrared (0.75~1.75 eV) decreases from 91.4% of SrVO$_3$ to 90.0% (90.6%) for the film with $x=0.11$ (0.18), which is quite small considering the gain in the short wavelength.
5.4 Electrical properties of La$_x$Sr$_{1-x}$VO$_3$

Figure 5-4. (a) Temperature-dependent resistivity of La$_x$Sr$_{1-x}$VO$_3$ films. (b) RRR ($\rho_{300K}/\rho_{2K}$) of La$_x$Sr$_{1-x}$VO$_3$ films as a function of La compositions. (c) Room temperature carrier concentration (top panel), mobility (middle panel) and resistivity (bottom panel) as a function of La compositions, respectively.

Figure 5-4 (a) shows the electrical resistivity of La$_x$Sr$_{1-x}$VO$_3$ films as a function of temperature, measured in the van der Pauw geometry. The resistivity increased with temperature, which confirmed the metallic transport character of the films irrespective of La incorporation $x$. All films showed a room temperature resistivity below $4\times10^{-5}$ $\Omega$-cm, while La$_x$Sr$_{1-x}$VO$_3$ with higher La substitution levels had slightly higher values. Consistent trend with increasing La substitution was found at low temperature, where resistivity is limited by scattering occurring from defects, such as impurities or disorder. To better elucidate the temperature-dependence, Figure 5-4 (b) shows the residual-resistivity ratio (RRR) between the resistivity at 300K and at 2K, which
decreased from 127 down to 3.5 with increasing La from $x=0$ to $x=0.18$ attributed to the increased impurity scattering from La. Given the order of magnitude difference in residual-resistivity at 2 K for films with different La compositions ($\rho_{2K}= 2.29\times 10^{-7} \, \Omega \cdot \text{cm}$ for $x=0$, $\rho_{2K}= 4.20\times 10^{-5} \, \Omega \cdot \text{cm}$ for $x=0.18$), it is remarkable that film resistivity at room temperature remained largely unaffected. This indicates that the room temperature resistivity of correlated metals is quite robust against extrinsic charged defects, effectively screened by a high carrier concentration present. This could be understood by the extremely small Thomas-Fermi screening length in metals, or $\lambda_{TF}$, which is used to describe how effectively the metals screen the external electrical field, as defined by $^{156}$:

$$\lambda_{TF} = \left[ \frac{\hbar^2 \varepsilon}{4m^* e^2} \left( \frac{\pi}{3N} \right)^{1/3} \right]^{1/2}$$

Where $\hbar = h/2\pi$ is the reduced Planck’s constant, $\varepsilon$ is the dielectric constant, $n$ is carrier density, and $m^*$ is the effective mass. For copper, a normal metal, with a carrier density of $8.5\times 10^{22} \, \text{cm}^{-3}$, $\lambda_{TF}$ is $\sim 0.55 \, \text{Å}$. $^{157}$ By assuming $\varepsilon = 4 \pm 1$, $n = 2.2\times 10^{22} \, \text{cm}^{-3}$ and $m^* = 3 \pm 1 \, m_0$ of SrVO$_3$, where $m_0$ is the rest mass for electron, $\lambda_{TF}$ of SrVO$_3$ is only $0.8 \pm 0.3 \, \text{Å}$.

The free carrier density and type at room temperature was obtained from Hall measurements. Despite the presence of multiple Fermi surfaces the Hall voltage changed linearly with applied magnetic field. Assuming a single band conduction model the free carrier concentration was extracted as a function of La composition and is shown in Fig. 5-4 (c) (top panel). The free carriers were n-type, all carrier densities were above $\sim 2\times 10^{22} \, \text{cm}^{-3}$, consistent with the metallic nature of La$_x$Sr$_{1-x}$VO$_3$ films. An increase in carrier concentration with increasing La substitution was found for small $x$, while it was $\sim 3\times 10^{22} \, \text{cm}^{-3}$ for larger La substitution irrespective of composition $x$. The Fermi surface of the dominant transport channel increased only in the regime of small $x$. The middle panel of Fig. 5-4 (c) shows the change in electron mobility at room temperature as a function of La incorporation. The highest mobility was found for SrVO$_3$ (9 cm$^2$ V$^{-1}$...
1 s⁻¹). With increasing La content the mobility slightly reduced to about 7 cm² V⁻¹ s⁻¹ for \( x = 0.11 \), to below 4 cm² V⁻¹ s⁻¹ for \( x = 0.18 \). In Fig. 5-4 (c) (bottom panel), the room temperature resistivity monotonically decreased from \( x = 0.00 \) to 0.03, indicating that the increase of carrier concentration overcompensated the slight loss of electron mobility in La-substituted films in the dilute La substitution limit (\( x < 0.11 \)). For higher \( x \), the reduction in carrier mobility outweighed the increase in carrier concentration, and electrical resistivity increased.

5.5 Figure-of-merit calculation for transparent conductors

We consider a free standing film with a thickness of \( t \), which is situated between air and a highly insulting LSAT substrate and forms an abrupt upper and lower interface. The absorption coefficient \( \alpha \) of the film is given by:

\[
\alpha = \frac{4 \pi k(\lambda)}{\lambda}
\]

where \( k \) is the extinction coefficient and \( \lambda \) is the wavelength in the film. For a normal incidence condition, the transmission coefficient \( T(\lambda) \), which is the ratio of incident intensity at the air/film interface and the transmitted intensity at the film/substrate interface is given by:

\[
T = \frac{(1 - R(\lambda))^2 + 4R \sin^2 \Psi}{e^{\alpha t} + R(\lambda)^2 e^{-\alpha t} - 2R(\lambda) \cos 2(\Phi + \Psi)}
\]

\[
R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}
\]

\[
\phi = \frac{2 \pi n t}{\lambda}
\]
\[ \psi = \tan^{-1} \frac{2k}{n^2 + k^2 - 1} \]

The term \(2R(\lambda) \cos 2(\varphi + \psi')\) originates from the interference effect between two different interfaces and three different media. The refractive index \(n\) and extinction coefficient \(k\) are extracted from the measured dielectric function:

\[ \varepsilon = \varepsilon_1 + i\varepsilon_2 = n^2 - k^2 + i2nk \]

Figure 5-5. The optical transmission integrated from 400 to 800 nm (solid line) and optical transmission at a fixed wavelength of 550 nm (dash line) for La\(_x\)Sr\(_{1-x}\)VO\(_3\) films with \(x=0.18\), \(x=0.03\) and \(x=0.00\).

The transmission coefficient \(T(\lambda)\) is a function of photo energy (0.73~5.04 eV). Since \(\alpha\) and \(R\) significantly depends on the choice of the specific wavelength, \(T\) averaged over the visible spectrum from 400 to 800 nm will be more related to practical applications, as defined by:
The thickness-dependent optical transmission of La$_{x}$Sr$_{1-x}$VO$_3$ films is shown in Fig. 5-5 (solid line: the transmission integrated from 400-800 nm; dash line: the transmission at a wavelength of 550 nm).

Finally, the overall performance trends of La$_{x}$Sr$_{1-x}$VO$_3$ as function of thickness with increasing La substitution $x$ was evaluated using the figure of merit (FOM) $\Phi_{TC}$ for transparent conductors. Considering both electrical and optical properties, $\Phi_{TC}$ is suggested by Haacke et al.$^{124}$

$$\Phi_{TC} = \frac{T^{10}}{R_s}$$

where $T$ is the transmission coefficient and $R_s$ is the sheet resistance of the films and the exponent is chosen to ensure that the highest FOM occurs for an optical transmission coefficient of 90%. The figure of merit (FOM) is calculated on the metric proposed by Haacke$^{124}$

$$\Phi_{TC}(t) = \frac{T^{10}}{\bar{R}_s} = \frac{T^{10}}{(\rho_0 + \Delta \rho)/t}$$

where $T$ is the optical transmission and $(\rho_0 + \Delta \rho)/t$ represents the sheet resistance $R_s$ which takes surface scattering effects into account. Fuchs and Sondheimer attributed the pronounced conductivity, $\sigma = 1/\rho$, to the enhanced surface scattering in ultrathin film with the following equation$^{124,129}$:

$$\sigma_{FS} = \sigma_0 [1 - \frac{3(1 - p)}{2\kappa} \int [\frac{1}{\bar{\xi}^5} - \frac{1}{\bar{\xi}^5} \frac{1 - e^{-\bar{\xi}^2}}{1 - p e^{-\bar{\xi}^2}} d\bar{\xi}]]; \Lambda = \frac{\hbar \mu}{e} (3\pi^2 n^3)^{\frac{1}{3}}$$
Where $\sigma_0$ is the bulk conductivity, $\Lambda$ is the electron mean free path, $\kappa = t / \Lambda$ the normalized thickness to EMFP, $p$ the reflection coefficient ($0 \leq p \leq 1$, $p = 0$ diffuse: random direction and magnitude of velocity after the surface scattering event, $p = 1$ specular: elastic scattering at the surface with reversal of the normal component). Mayadas and Shatzkes further expanded the conductivity model of ultrathin films considering three main mechanisms: background scattering, grain boundary and external surface scattering:

$$\sigma_{ds} = \sigma_0 [1 - \frac{3}{2} \zeta + 3\zeta^2 - 3\zeta^3 \ln(1 + \frac{1}{\zeta})], \quad \zeta = \frac{\Lambda}{D} \cdot \frac{R}{1 - R}$$

where $R$ is the reflection coefficient and $D$ is the average grain size. The fitting results of SrVO$_3$ matched quite well with the experimental data.

![Figure 5-6](image)

Figure 5-6. (a) Figure of merit $\Phi_{TC}$ of La$_x$Sr$_{1-x}$VO$_3$ films as a function of film thickness. (b) The highest figure of merit $\Phi_{TC}$ of La$_x$Sr$_{1-x}$VO$_3$ films as a function of La compositions $x$. The film thickness at which the highest figure of merit is acquired is displaced next to the symbol. Figure of merit of epitaxial ITO$^{92}$ (red dashed line) and polycrystalline ITO$^{92}$ (blue dashed line) is included as references.

In this work, since the motilities of all La$_x$Sr$_{1-x}$VO$_3$ are either equal or less than those of SrVO$_3$ due to the substitution of La, which could also be seen by the measured mobility, as shown
in Fig. 5-4 (c), the same fitting parameters will be used for all La$_x$Sr$_{1-x}$VO$_3$ films, probably with a minor underestimation of FOM of La$_x$Sr$_{1-x}$VO$_3$ films, by the following equations:

\[
\Phi_{TC,LSVO}(t) = \frac{T_{LSVO}^{10}}{\rho_{LSVO}(t) / t} = \frac{T_{SVO}^{10}}{\rho_{SVO}(t) / t} \cdot \frac{\rho_{SVO}(bulk)}{\rho_{LSVO}(bulk)}
\]

where \( T \) is the optical transmission integrated from 400 to 800nm, \( \rho_{SVO}(bulk) \) is the resistivity for SrVO$_3$ films in previous study \(^{92} \), and \( \rho_{LSVO}(bulk) \) is the resistivity for La$_x$Sr$_{1-x}$VO$_3$ films in the study with thicknesses ranging from 33 to 54 nm.

Owing to the reduction of resistivity and the increase of the optical transmission, all La-substituted films \((x=0.01, 0.02, 0.03 \text{ and } 0.11)\) exhibit higher FOM than that of the intrinsic correlated metal SrVO$_3$, as shown in Fig. 5-6 (a). This confirms the overall benefit of aliovalent substitution strategy to further enhance the performance of correlated metals as transparent electrodes. While SrVO$_3$ had a \( \Phi_{TC} =3.96\times10^{-3} \Omega^{-1} \), La$_{0.03}$Sr$_{0.97}$VO$_3$ with \( x=0.03 \) had a \( \Phi_{TC} =4.74\times10^{-3} \Omega^{-1} \). This increase in performance by \(~20\%\) pushed the \( \Phi_{TC} \) of La$_{0.03}$Sr$_{0.97}$VO$_3$ above the highest FOM reported for epitaxial ITO in the literature \(^{92,108} \), as indicated in Fig. 5-4 (b). FOM of La$_x$Sr$_{1-x}$VO$_3$ \((x=0.02, 0.03 \text{ and } 0.11)\) in this work also outperforms the highest FOM of epitaxial ITO, albeit with a smaller margin. At \( x=0.18 \), a decrease in FOM was observed attributed to the decreased electrical conductivity of La$_x$Sr$_{1-x}$VO$_3$. Here, the FOM for La$_x$Sr$_{1-x}$VO$_3$ was below that of SrVO$_3$, marking the limit to enhance FOM through aliovalent substitution.

5.6 Conclusion

Aliovalent substitution has been demonstrated as successful strategy to enhance the performance of correlated metals as transparent conductors. The figure of merit of SrVO$_3$ was
markedly improved by ~20% upon aliovalent substitution of Sr with La in the dilute limit of $x=0.03$ in $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$, attributed to the improvement in both, the optical and electrical properties. A blue-shift of interband transitions in the UV range in $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ up to 0.21 eV was found for La composition of $x=0.11$ and $x=0.18$, attributed to a raise in the Fermi level. Improvements in the electrical properties were found in the dilute limit of $\text{La}_x\text{Sr}_{1-x}\text{VO}_3$ up to $x=0.03$, where increase in carrier concentration outweighed reduction in electron mobility at room temperature. Further increasing the La composition beyond the dilute limit resulted in a decrease of electrical conductivity and therefore decreases of the figure of merit.

The abundant choices of chemical elements and robustness of perovskite structures towards aliovalent substitution renders the proposed strategy a general scheme for perovskite-based correlated metals\textsuperscript{158-160}. The controlled positioning of the Fermi level leads to a ‘reshaping’ of the Fermi surface, therefore affecting interband transition and carrier concentration, offering an additional materials design knob for tuning the balance between electrical conductivity and optical transparency in correlated metals. We believed that aliovalent substitution in correlated metals will provide a new perspective to search for materials that go beyond the intrinsic correlated metals for transparent conducting applications.
Chapter 6

Growth of SrTiO$_3$ on Si (001) by hybrid molecular beam epitaxy


[L Zhang et al. Submitted]

6.1 Introduction

Successful heteroepitaxy of perovskite oxide thin films on silicon is of great interest for adding unique functionalities inherent to this class of materials, such as ferroelectricity, piezoelectricity or multiferroicity, to Si-based electronic devices and circuits$^{161-165}$. Benefiting from its relatively small lattice mismatch, SrTiO$_3$ was considered as a template for heterogeneous integration of complex oxides on Si$^{166,167}$ as well as a viable method towards monolithic integration of GaAs with Si$^{168}$. Following the pioneering work of McKee et al. various groups have studied the heteroepitaxial growth of SrTiO$_3$ on Si by molecular beam epitaxy (MBE) employing a SrSi$_2$ buffered Si surface$^{24,167,169-174}$. However, the structural disparities between SrTiO$_3$ and Si, reflected in their different crystal structures, lattice parameter and thermal expansion coefficients, result in relatively high structural defect densities of the grown films. This situation is further aggravated by the limited control over the film stoichiometry during MBE growth of SrTiO$_3$ due to the absence of a self-regulated growth mechanism. Although structural quality of the films can be improved using post growth anneals$^{171}$, the growth of thicker films and excellent control over the film’s stoichiometry are mandatory steps towards the development of a growth template for the monolithic integration of functional perovskite oxides with high
structural perfection on Si. However, Ti is a low vapor pressure element and Ti fluxes are low if supplied from a high temperature effusion cell. The cell temperature has to be kept below the melting point of Ti to avoid fatal failure due to alloying of the Ti charge with the crucible material (typically W or Ta). Alternative growth methods have been considered to integrate SrTiO$_3$ on Si (001), namely atomic layer deposition (ALD) and metal-organic chemical vapor deposition (MOCVD). Besides the potential economic advantages that both growth approaches might offer, their different growth mechanisms could provide a better stoichiometry control. However, the inherently small deposition rate of ALD excludes this approach for the growth of thick SrTiO$_3$ buffer layers. Furthermore, films grown by ALD required a growth template of 6 monolayers (ML) of SrTiO$_3$ on Si by MBE as well as a post deposition crystallization step. MOCVD experiments to nucleate and grow SrTiO$_3$ directly on Si have resulted in polycrystalline films and contained substantial amounts of carbon and hydrogen.

The hybrid MBE approach, where conventional MBE and chemical beam epitaxy (CBE) are combined by co-supplying elemental Sr and an alkoxide precursor, titanium tetraisopropoxide [TTIP or Ti(OC$_3$H$_7$)$_4$] for Ti and O, ideally complements the merits of the two growth techniques and is ideally suited for the growth of thick SrTiO$_3$ films. The high vapor pressure of TTIP allows to easily scale up growth rates. Moreover, each Ti is fourfold coordinated with oxygen in the TTIP molecule, which is beneficial to keep the exposure of Si to reactive oxygen to a minimum. Superior stoichiometric control of SrTiO$_3$ films grown by hybrid MBE has been demonstrated, and the existence of a self-regulated growth window has lifted the stringent requirements of cation flux control during growth. Excellent doping control down to the parts per million level and record high electron mobilities >30,000 cm$^2$V$^{-1}$s$^{-1}$ are further evidence of the excellent material quality achieved by this approach. In this paper we demonstrate that nucleation and growth of SrTiO$_3$ on Si (001) is possible using hybrid MBE and
that crystalline SrTiO$_3$ thin films can be grown with excellent control over stoichiometry by co-supplying elemental Sr and TTIP in the absence of additional oxygen.

6.2 Experimental section

Thin film growth: Epitaxial SrTiO$_3$ films were grown on 3 inch p-type Si (001) substrates (1–10 $\Omega$×cm, 380 µm, University Wafer Inc.) using an oxide MBE system (DCA Instruments), equipped with a heated gas inlet system to supply the metalorganic precursor through a gas injector. The gas inlet system has a capacitance manometer to regulate the conductance through an upstream linear leak valve, allowing to precisely maintain a constant gas inlet pressure $P_{\text{TTIP}}$. The TTIP container vessel was held at 70 °C to ensure sufficient vapor pressure. No carrier gas was used. The relatively high gas load on the hybrid MBE system was accommodated using a turbomolecular pump and a cryo pump (combined pump speed ~3500 l/s) keeping the background pressure below 5×10$^{-7}$ Torr during the growth. RHEED was employed for real-time growth monitoring. A residual gas analyzer (RGA, Stanford Research System 200) equipped with an electron impact ionization source and a quadrupole mass spectrometer was connected to the reactor for identifying residual gas species.

The Si substrates were first exposed to ultraviolet (UV)-ozone for 12 minutes to remove carbon contamination, and then dipped into 2% HF solution for 30 seconds. All substrates were ensured hydrophobic before rinsing them in deionized (DI) water for 2 minutes. The Si wafers were loaded into the MBE system within 10 minutes and baked at 150 °C for about 2 hours in the load lock at a pressure below 5×10$^{-8}$ Torr. After that, Si substrates were transferred into the hybrid MBE reactor chamber. The remaining native oxide on the Si wafer was removed by adapting a Sr-assisted low temperature native oxide removal process$^{180}$. Here, 2 ML of Sr were...
deposited at 600 °C and the sample temperature was subsequently ramped up to 720 °C and maintained for 10 minutes. Additional Sr was deposited until a sharp 2×1 reconstruction was seen in RHEED taken along Si (110) azimuth, which indicated the complete removal of the native oxide. The substrate temperature was then lowered to 400 °C and the surface was exposed to an oxygen partial pressure of 1×10⁻⁸ Torr for about 1 minute to oxidize Sr. The lower substrate temperature and low oxygen partial pressure, which is about the minimum oxygen partial pressure needed to oxidize Sr, was chosen to minimize unintentional oxidation of Si underneath the ½ ML SrSi₂. A 5 ML thick buffer layer of SrTiO₃ was then deposited at 400 °C by co-supplying Sr and TTIP in the absence of additional oxygen followed by an in situ anneal at 600 °C for 10 minutes. After buffer layer formation SrTiO₃ film growth was carried out at 600 °C with different TTIP/Sr flux ratios. The Sr flux rate, measured using quartz crystal monitor (QCM), was kept at a constant value of 2.5×10¹³ cm⁻² s⁻¹ for all growths, whereas the flux of TTIP molecules was varied by changing the TTIP gas inlet pressure in the range from 48 to 64 mTorr. Films were grown for about 50 min, and the nominal thickness was estimated to about 46 nm assuming a Sr sticking coefficient of 100 %.

HRXRD was performed using a PANalytical XPert Pro MRD 4-circle diffractometer equipped with a duMond-Hart-Partels Ge (440) incident beam monochromator using Cu Kα₁ radiation with a wavelength λ=1.5406 Å. On-axis 2θ-ω as well as reciprocal space maps around the SrTiO₃ off-axis diffraction spots 103 and 103 were taken. The surface morphology was investigated by a Bruker Dimension Icon atomic force microscope (AFM) operated in peak force tapping mode. High-resolution transmission electron microscopy (HRTEM) of the SrTiO₃/Si interface was taken in cross-section along the [110] zone axis of Si using a JEOL 2010F operated at 200 kV. TEM samples were prepared using standard mechanical polish followed by 3 kV Ar ion milling on a cold stage.
6.3 Buffer layer growth

The commonly employed approach to nucleate single crystalline SrTiO$_3$ films on Si is to first deposit a few ML of SrTiO$_3$ at low temperature and low oxygen flux to avoid SiO$_2$ formation, and subsequently crystallize it at a higher temperature in vacuum$^{166,170,181,182}$. Once this buffer layer is formed, SrTiO$_3$ growth is continued at higher temperatures and in the presence of a higher oxygen flux$^{181,182}$. Adopting this strategy to the hybrid MBE growth approach, two main challenges needed to be addressed: (1) Finding an optimized temperature for the nucleation and formation of the SrTiO$_3$ buffer layer; i.e. sufficiently high for the thermal decomposition of TTIP, but not too high to limit the potential formation of an amorphous SiO$_2$ interlayer, which might impede a good epitaxy; (2) Avoiding carbonization of the Si (001) surface during in-situ native oxide removal. In-situ SiO$_2$ desorption in ultrahigh vacuum requires a high temperature heat flush ($>1000 \, ^\circ\text{C}$)$^{183}$ during which SiC could very easily form on the Si surface in the hybrid MBE chamber, given these high temperatures and the relatively high background pressure of hydrocarbons in the reactor$^{184}$. 
Figure 6-1. (a) The residual gas spectrum of the hybrid MBE reactor chamber before and after Sr getter deposition. RHEED pattern of Si (001) surface along the (110) azimuth after (b) a heat flash at 900 °C containing diffraction spot from the 3C-SiC overlayer encircled by a dotted line, (c) Sr getter step and Sr-promoted SiO₂ desorption revealing a (2×1) reconstruction and no 3C-SiC features, indicating a clean and oxygen-free surface. (d) 5ML SrTiO₃ buffer layer deposition and subsequent anneal (e) SrTiO₃ film after growth.

Figure 6-1 (a) shows a mass spectrum of the residual gas species present in the hybrid MBE reactor. The background pressure of $3 \times 10^{-9}$ Torr was recorded by an ion gauge. Pronounced peaks at atomic mass unit (AMU) values around 2, 17, 27, 42 and 59 were observed and assigned
to hydrogen (2), water, methane and oxygen (17), ethylene (27), propene (42) and isopropanol (59) species by comparing them to their individual fragmentation pattern\textsuperscript{183}. These hydrocarbons are volatile by-products formed during the thermal decomposition of the TTIP precursor\textsuperscript{185}. Reflection high-energy electron diffraction (RHEED) images taken during native oxide removal at this background pressure revealed additional diffraction spots at larger distance from the specular spot that were observed after heating the Si sample for about 15 minutes at 900 °C [Fig. 6-1 (b)]. They were attributed to the formation a 3C-SiC overlayer. Similar observation have been reported before by intentionally exposing Si (001) surfaces to hydrocarbons C\textsubscript{3}H\textsubscript{8}\textsuperscript{186} and C\textsubscript{2}H\textsubscript{2}\textsuperscript{187} at elevated temperatures. To avoid carbonization of the Si (001) surface the excellent getter properties of Sr were utilized\textsuperscript{188} by freshly evaporating Sr into the hybrid MBE chamber for about 15 minutes prior to growing the films, which resulted in a significant reduction of the total background pressure down to 4×10\textsuperscript{-10} Torr. The improvement in the background pressure was attributed to the enhanced chemisorption of water, oxygen and hydrocarbons on metallic Sr surfaces.\textsuperscript{[32]} Direct comparison of the residual gas spectrum taken after ‘seeding’ the reactor chamber with Sr revealed that the partial pressures of water, oxygen and hydrocarbon gas species were reduced by more than half order of magnitude, see Fig. 6-1 (a). The formation of 3C-SiC was sufficiently suppressed to employ Sr-promoted SiO\textsubscript{2} reduction at a lower sample temperature of 720 °C\textsuperscript{180}. No 3C-SiC formation was observed in RHEED when Si surfaces were prepared in the hybrid MBE chamber with a background pressure of 4×10\textsuperscript{-10} Torr using the native oxide removal method developed by the Motorola lab\textsuperscript{180}, as shown by RHEED in Fig. 6-1 (c). An intense and streaky RHEED pattern with a 2× reconstruction along the \langle110\rangle direction and low background intensity indicated that the Si surface was of high quality, addressing the second challenge in the heterogeneous integration of SrTiO\textsubscript{3} on Si using hybrid MBE.
For the nucleation of SrTiO$_3$ a substrate temperature of 400 °C was found to be a good compromise between sufficiently high TTIP decomposition rate and limiting the reaction with Si. The intensity of the RHEED diffraction rods was reduced during the deposition of the first 5 ML, while the hazy background intensity increased, indicating a partially amorphous layer. The crystallinity of this buffer layer was improved by a subsequent annealing step for 10 minutes at 600 °C. The intensity of the diffraction rods increased while the background intensity reduced, indicating an improved crystallinity of the buffer layer [Fig. 6-1 (d)]. The streakiness of the RHEED pattern indicated a smooth layer and cube-on-cube epitaxy.

6.4 Thin film growth and structural characterization

SrTiO$_3$ films with varying cation flux ratios were grown on the 5 ML SrTiO$_3$/Si template at 600 °C and in the absence of molecular oxygen. Here the Sr flux was kept constant while the Ti flux, represented by the TTIP gas inlet pressure $P_{TTIP}$, was systematically varied from 48 mTorr to 62 mTorr. Figure 6-2 (a) shows the 2θ-ω X-ray scans. All films were found to be crystalline and single phase within the detection limit of XRD. Only 00L peaks of SrTiO$_3$ films were observed providing the out-of-plane epitaxial relationship SrTiO$_3$ (001) || Si (001). A good in-plane alignment was found from the ϕ scan of the Si 202 and the SrTiO$_3$ 101 reflection, shown in Fig. 6-2 (b).
Figure 6-2. (a) 20-ω X-ray diffraction scans of SrTiO$_3$ films grown at various TTIP gas inlet pressures $P_{\text{TTIP}}$ showing only 00L peaks of SrTiO$_3$. (b) XRD φ scans of SrTiO$_3$ 101 and Si 202 reflection. (c) Out-of-plane lattice constant $a_{\perp}$ of SrTiO$_3$ on Si (001) as a function of TTIP gas inlet pressure $P_{\text{TTIP}}$, extracted from 20-ω scans. The lattice constant of bulk SrTiO$_3$ (3.905 Å) and the calculated $a_{\perp}$ value for tensile strained SrTiO$_3$ grown on Si at 600 °C (3.895 Å) are indicated as well. Reciprocal spaces maps (RSMs) around the (d) 103 and (e) 103 reflections of the SrTiO$_3$ film grown on Si (001) at $P_{\text{TTIP}}$=54 mTorr. The maps are given in reciprocal lattice units [r.l.u.] of bulk SrTiO$_3$ with a lattice parameter of 3.905 Å.

The expected in-plane epitaxial relationship SrTiO$_3$ [100] || Si [110] was obtained, where SrTiO$_3$ is rotated by 45° with respect to the Si crystal about the film normal$^{164}$. A rocking curve scan was performed around SrTiO$_3$ 200 peak, and a FWHM of 0.65° was acquired for 54mTorr film. Details of the X-ray analysis to further quantify the structural quality of the SrTiO$_3$ films are compiled in Table 6-1.

Table 6-1. Normalized intensity and full width at half maximum (FWHM) of the 002 SrTiO$_3$ peak from the 20-ω scans shown in Fig. 6-2 (a) for films grown at different TTIP gas inlet pressures $P_{\text{TTIP}}$. The peak intensity was normalized to the average background between 55° to 60° of the 20-ω scan.

<table>
<thead>
<tr>
<th>$P_{\text{TTIP}}$ [mTorr]</th>
<th>norm. SrTiO3 002 peak intensity</th>
<th>FWHM of SrTiO3 002 peak [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>25</td>
<td>0.502</td>
</tr>
<tr>
<td>50</td>
<td>106</td>
<td>0.463</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>52</td>
<td>429</td>
<td>0.288</td>
</tr>
<tr>
<td>54</td>
<td>481</td>
<td>0.256</td>
</tr>
<tr>
<td>56</td>
<td>669</td>
<td>0.249</td>
</tr>
<tr>
<td>58</td>
<td>123</td>
<td>0.334</td>
</tr>
<tr>
<td>60</td>
<td>339</td>
<td>0.271</td>
</tr>
<tr>
<td>62</td>
<td>237</td>
<td>0.297</td>
</tr>
</tbody>
</table>

The full width at half maximum (FWHM) of the 002 SrTiO$_3$ peak in the 20-ω X-ray scan had a minimum value $\Delta(2\theta)$ of 0.249º for films grown at $P_{\text{TTIP}}$=56 mTorr. Taking into account the instrumental broadening of 0.012º and calculating the ideal broadening of a 46-nm-thick film using the Scherrer formula$^{189}$:

$$\Delta(2\theta) = K \cdot \lambda / (t \cos \theta)$$

An ideal FWHM of 0.209º was determined in the absence of any additional peak broadening. Here, the Scherrer constant $K$ was assumed to be 0.89$^{190}$, the X-ray wavelength $\lambda$=1.5406 Å, the film thickness $t$=46 nm, and the Bragg angle $\theta$=23.25º. The larger $\Delta(2\theta)$ values indicated the presence of non-uniform lattice distortions in the film induced by local strains, which can either come from structural defects, such as stacking faults, dislocations, antiphase boundaries, or spatial inhomogeneities of the film’s stoichiometry. The FWHM $\Delta(2\theta)$ increased for SrTiO$_3$ films grown at TTIP gas inlet pressures that deviated further from $P_{\text{TTIP}}$=56 mTorr. A similar trend was found for the film’s crystallinity, determined from the peak intensity of the 002 SrTiO$_3$ reflection, normalized to the background signal taken as the average X-ray intensity in the 2θ interval between 55º and 60º. Again, the highest intensity was found for $P_{\text{TTIP}}$=56 mTorr, which sharply dropped for films grown at higher and lower TTIP fluxes.

The position of the 002 SrTiO$_3$ diffraction peak was used to extract the film lattice parameter which is increased to accommodate deviations from ideal cation stoichiometry in the crystal$^{179}$. The trend of the out-of-plane lattice parameter $a_{\perp}$ with TTIP pressure is shown in Fig.
The smallest out of plane lattice parameter of 3.895 Å was found for the film grown at 
P_{TTIP}=54 mTorr. This value is smaller than the SrTiO$_3$ bulk lattice parameter $a_{25^\circ C}^{STO} = 3.905$ Å at room temperature$^{191}$, indicating that the film was tensile strained. The nearest neighbor distance along Si [110] is $a^{Si}_{25^\circ C}/\sqrt{2} = 3.841$ Å$^{192}$, thus lattice mismatch imposes a compressive strain of 1.67% on a coherently strained SrTiO$_3$ film on Si. Another contribution to the strain state of SrTiO$_3$ at room temperature can come from the large thermal expansion mismatch between SrTiO$_3$ (9.3×10$^{-6}$ K$^{-1}$) and Si (2.5×10$^{-6}$ K$^{-1}$), when a partially or completely relaxed film is cooled from growth temperature down to room temperature$^{193}$. Both contributions, lattice and thermal expansion mismatch, have opposite trends giving rise to a complex interplay$^{194}$. The degree of strain relaxation was reported to be strongly dependent on the film thickness below 28 nm, while the out-of-plane lattice parameter was found to be thickness independent above, suggesting that the films were completely relaxed at growth temperature$^{194}$. Thus, thermal expansion mismatch was the governing mechanism of the film’s residual strain at room temperature throughout the entire sample series studied. Therefore an increase of the out-of-plane film lattice parameter was attributed to an increase in intrinsic film lattice parameter due to nonstoichiometric growth conditions$^{195}$. Under the two assumptions that: 1) SrTiO$_3$ films were completely relaxed at the growth temperature of 600 °C $a_{600^\circ C}^{STO} = a_{600^\circ C}^{STO} = 3.929$ Å, and that 2) SrTiO$_3$ completely adopted the changes in the lattice parameter of Si during cool down in the film plane:

$$a_{25^\circ C}^{STO} = a_{600^\circ C}^{STO} + a_{25^\circ C}^{Si} - a_{600^\circ C}^{Si}$$

An ideal out-of-plane lattice parameter of $a_{25^\circ C}^{STO} = 3.895$ Å at room temperature was calculated using:

$$a_{25^\circ C}^{STO} = \frac{2v}{v-1} a_{25^\circ C}^{STO} - \frac{v+1}{v-1} a_{25^\circ C}^{STO}$$
Here, a Poisson’s ratio $v$ for SrTiO$_3$ of 0.232$^{196}$: $a_{\parallel 600^\circ C}^{Si} / \sqrt{2} = 3.848 \, \text{Å}$, $a_{\parallel 25^\circ C}^{Si} / \sqrt{2} = 3.841 \, \text{Å}$, $a_{0 \, 25^\circ C}^{STO} = 3.905 \, \text{Å}$ were used. The ideal out-of-plane lattice parameter was found in very good agreement with the out-of-plane lattice parameter measured for SrTiO$_3$ grown at 54 mTorr, suggesting a near-stoichiometric film. All other films showed a larger out-of-plane lattice parameter, which systematically increased with increasing deviation from the TTIP gas inlet pressure of 54 mTorr. It is therefore concluded that films grown at $P_{\text{TTIP}}$ below 54 mTorr were Sr rich, while films grown at $P_{\text{TTIP}}$ larger than 54 mTorr were Ti-rich.

To confirm this interpretation and to acquire the in-plane lattice constant to calculate the intrinsic film lattice parameter $a_{\perp 25^\circ C}^{STO}$, X-ray diffraction reciprocal space maps (RSM) were performed around the asymmetric 103 and 003 Bragg reflection of SrTiO$_3$ for the film grown at $P_{\text{TTIP}}$=54 mTorr. The in-plane and out-of-plane lattice constants $a_{\parallel}$ and $a_{\perp}$ were determined by projecting the intensity maximum to the in-plane and out-of-plane reciprocal lattice axes H and L, as shown in Figs. 6-2 (d) and 2(e). The intrinsic lattice parameter was calculated using the above equation. From the 103 and the 003 reflections an average value for $a_{\parallel} =$ 3.897 Å and $a_{\perp} =$ 3.929 Å was determined, giving $a_{\perp 25^\circ C}^{STO} =$ 3.909 Å in good agreement with the expected bulk value of 3.905Å. The reciprocal space maps further revealed that the film was neither completely relaxed nor coherently strained, indicating an inhomogeneous strain distribution, presumably due to the presence of structural defects.
Figure 6-3. High resolution transmission electron microscope images of the SrTiO$_3$ film grown at $P_{\text{TTIP}} = 54$ mTorr taken in cross-section along the Si [110] zone axis. (a) Lower magnification image shows only few defects extended throughout the film. (b) High magnification image shows the formation of a ~ 4 nm-thick SiO$_x$ amorphous layer at the SrTiO$_3$/Si interface.

Figure 6-3 shows a high resolution transmission electron microscopy (HRTEM) image of the SrTiO$_3$ film grown at $P_{\text{TTIP}} = 54$ mTorr. A physical film thickness of 43.5 nm was measured in good agreement with the film thickness of 46 nm estimated from the flux density of Sr and growth time. At the interface between Si and SrTiO$_3$ an amorphous layer of around 4 nm thickness was observed. Given the good epitaxial registry between film and substrate it is assumed that this interface layer had been formed after buffer layer nucleation at lower
temperature. Although no extra oxygen was supplied during the buffer layer and film growth, the chemical instability of Si and SrTiO$_3$ caused the formation of the thin SiO$_x$ layer due to the thermodynamic driving force of Si to scavenge oxygen from SrTiO$_3$ $^{170,182,194,197}$. From the HRTEM image a high density of structural defects were found to be present in the film, the majority was confined to the first 15 nm of the film. The comparably lower structural quality of SrTiO$_3$ close to the interface is currently not completely understood. One possible explanation is the temperature dependence of the TTIP decomposition affecting the incorporation of Ti into the film. The TTIP deposition kinetics has been reported to change from the reaction limited to the flux limited regime around 400 °C $^{198}$. This effect has not been factored in for the Sr to TTIP flux ratio of the first 5 ML at lower temperature and may have resulted in Sr-rich growth condition, which is accommodated by accumulation of SrO islands $^{199}$ on the growing surface and the formation of Sr-rich SrTiO$_3$ phases $^{166}$. The pronounced reduction of the defect density with increasing thickness further suggested that an even higher crystalline quality can be achieved if the SrTiO$_3$ film thickness is increased.

6.5 Surface morphology of 600 °C-grown film
Figure 6-4. Atomic force microscopy (AFM) scans of 600°C-grown SrTiO$_3$ films grown on Si grown at different TTIP gas inlet pressures of (a) 52 mTorr, (b) 54 mTorr and (c) 62 mTorr. The sides of square islands in (a) were either parallel or perpendicular to Si [110]. RMS roughness values of the films were taken from the boxes in (b) and (c), as discussed in the text.

Atomic force microscopy images of films grown under Sr-rich (52 mTorr), near-stoichiometric (54 mTorr) and Ti-rich (62 mTorr) conditions were taken to characterize the surface quality, see Fig. 6-4. A markedly different surface morphology was found for the films grown at 52 mTorr, which were dominated by a nanocrystalline texture and a root mean square (RMS) surface roughness of 2.1 nm, Fig. 6-4 (a). Square and rectangular shaped structures with a typical feature size of 20 nm were observed. Their edges were mostly oriented along the Si [110], in agreement with earlier results.$^{166}$ Very smooth surfaces were found for films grown at 54 mTorr that contained only a few localized, round-shaped islands without preferential orientation. These droplet-like features have been attributed to the accumulation of excess SrO on the surface.$^{200}$ The total RMS roughness of 0.65 nm for these films was more than double compared to the surface roughness of the smooth areas between the localized islands, which are indicated by a white box in Fig. 6-4 (b) (RMS=0.29 nm). Number and volume of these islands increased for films grown at $P_{TTIP}$ of 62 mTorr [Fig. 6-4 (c)]. Despite a slight reduction of the RMS roughness of the island free areas (RMS=0.18 nm), the overall RMS values increased to 1.0 nm. The accumulation of irregularly shaped particles for films grown under near-stoichiometric ($P_{TTIP}$=54 mTorr) and even under Sr deficient conditions is a commonly observed feature in SrTiO$_3$ films grown by hybrid MBE.$^{178}$ The formation of the rectangular shaped nanocrystalline texture for films grown at 52 mTorr TTIP at even larger Sr surplus during growth was attributed to the formation of Ruddlesden Popper planar faults by incorporating excess SrO into the growing film. The SrO double layer formed in the {100} planes of SrTiO$_3$ can be oriented perpendicular to the film plane as well, which can break up the lateral coherency of the growth front.
6.6 The emergence of growth window

Figure 6-5. (a) RHEED images captured along the [100], [210] and [110] azimuths for SrTiO$_3$ thin films grown at 850°C at different values of TTIP pressure; (b). Out-of-plane lattice parameters as a function of film thickness for 850°C-grown films; (c) Out-of-plane lattice parameters as a function of TTIP pressure for 850°C-grown films.

Though a stoichiometric SrTiO$_3$ thin film on Si 001 substrate has been demonstrated by hybrid MBE$^{50}$. However, a growth window for SrTiO$_3$ thin film was not found at 600°C. In this
section, the growth temperature has been increased to 725°C and 850°C for accessing growth window.

The stoichiometry control during the growth was characterized by both in-situ RHEED and ex-situ HRXRD 2θ-ω scans. Please note that TTIP pressure (~49.6 mT) required for a stoichiometric SrTiO

3 thin film on Si 001 substrate is different from the previous section (~54 mT) for a Sr flux of 2.5×10^{13} atoms cm⁻² s⁻¹. It could be understood that the metal-organic precursor inlet system and pump station was upgraded in 2016, and thus the conductance of gas inlet system is slightly different from previous design.

Figure 6-5 (a) shows RHEED pattern captured for films grown at 850°C as function of TTIP pressure along [100], [210] and [110] azimuths, and all RHEED patterns are four-fold symmetric. Characteristic surface reconstructions of RHEED patterns are used to monitor stoichiometry during the SrTiO

3 growth. At low TTIP pressure (p_{tip}=46~50 mT), the existence of a 2×reconstruction along [110] azimuth is an indicator of Sr-rich surface, similar to those reported elsewhere. No surface reconstruction appeared at p_{tip}=52~54 mT, indicating an unreconstructed surface. An emergence of a 2×reconstruction along [100] and [210] was found at p_{tip}=56 mT, and an additional 4×reconstruction along [110] were found at p_{tip}=58~68 mT. Such a systematic change of RHEED reconstruction was also found in homoepitaxy growth of SrTiO

3 by hybrid MBE. The onset of multi-domain (1×2) and (2×1) at p_{tip}=56 mT can be related to the expanded region of coherent TiO₂ coverage from unreconstructed surface. Higher-order reconstructions are an indicator of purely TiO₂-terminate surface, where the growing surface is saturated with TiO₂. It is important to form such a TiO₂-saturated surface to bring the growth into an adsorption-controlled regime. A similar study on RHEED reconstruction was also performed on 600°C- and 725°C-grown films (the RHEED images were included in supplementary information). A shrink and shift of RHEED window was found for 725°C-growth.
No evident of RHEED growth window was found for 600°C-growth, and the optimized TTIP pressure was found at 49.5 mTorr where reconstruction-free RHEED patterns were found. These findings can be understood by that the higher desorption rate of TTIP would occur at higher temperature, and an adsorption-control growth could only be activated with sufficient growth temperature.

It was reported that SrTiO$_3$ film would remain coherently strained to Si in the first five MLs and will then start to relax$^{195,202,204}$. The out-of-plane (OOP) lattice parameters of SrTiO$_3$ were calculated from HRXRD 2θ-ω scans as a function of film thickness, as shown in Fig. 6-5 (b). SrTiO$_3$ thin film fully relaxed at a thickness of 15~20 nm since there was no further decrease of lattice parameters. Lattice parameters are a good indicator of defects in perovskite oxides, where cation nonstoichiometry will lead to an expansion of lattice parameters, and thus they are used to identify the evolution of a growth window$^{52,149,153,196}$. The OOP lattice parameters for 50-nm films grown at 800°C as a function to TTIP pressure was shown in Fig. 6-5 (c). The OOP lattice parameters are around ~3.890Å between $p_{\text{tip}}$=53~68 mT, and a rapid increase of OOP lattice parameters is seen at $p_{\text{tip}}$=46 and $p_{\text{tip}}$=74 mT. The XRD growth window overlapped quite well with RHEED growth window, which is consistent with previous study$^{203}$. 
6.7 Continuous strain modulation by thermal strains

Figure 6-6. Schematic of interface structure of SrTiO$_3$/Si interface (a) coherent strained, (b) fully relaxed, (c) cooled down to the ambient temperature; (d) schematic of the in-plane orientation
between SrTiO$_3$ and Si; (e) High-resolution TEM image of SrTiO$_3$/Si interface; (f) XRD phi scans around SrTiO$_3$ 101 and Si 202 diffraction peaks.

In the first few monolayers (ML), SrTiO$_3$ thin film was coherently strained to Si (the schematic is shown in Fig. 6-6 (a), with an in-plane orientation relationship of [100] SrTiO$_3$ $\parallel$ [110] Si and a compressive strain of 1.7% considering a 45° in-plane rotation (the schematic is shown in Fig. 6-6 (d). Then SrTiO$_3$ thin film starts to relax with a formation of an amorphous SiO$_x$, as shown in Fig. 6-6 (b). Once the film is cooled to room temperature, a residual tensile strain originated from thermal expansion-mismatch will build, with the schematic shown in Fig. 6-6 (c).

5ML and 10ML buffer layers were deposited at 400°C and 600°C, respectively, by a codeposition of Sr and TTIP without using molecular oxygen. The growth was then carried out at various temperatures to achieve a thickness of 120 nm. No cracking at the surface was observed at any of the films by atomic force microscopy (the result is not shown here). The out-of-plane lattice parameters of the SrTiO$_3$ thin films were determined from HRXRD 2θ-ω scans. Figure 6-6 (e) shows a HRTEM image of the 850°C-grown thin film, and a crystalline SrTiO$_3$ thin film formed on Si substrate. It is worthwhile to notice that an amorphous SiO$_x$ layer formed between SrTiO$_3$ thin film and Si substrate, which was reported on thick SrTiO$_3$ thin films on Si substrates. This amorphous layer could only by oxygen diffusion through SrTiO$_3$ form during the growth, since clear RHEED images of Si substrate were observed before the growth. The in-plane orientation of [100] SrTiO$_3$ $\parallel$ [110] Si was confirmed by a XRD phi scan, as seen by a separation of 45° in SrTiO$_3$ 101 and Si 202 peaks in Fig. 6-6 (f).
Figure 6-7. (a) Lattice constant of SrTiO$_3$\textsuperscript{191,205} and Si\textsuperscript{206,207} (normalized to [110] direction) and calculated lattice constant of SrTiO$_3$ thin film on Si 001 as a function of temperature. Assume SrTiO$_3$ thin film relaxes at the growth temperature and clamp to Si substrate during cooling process. (b) Tensile strain as a function of growth temperature which is calculated from out-of-plane lattice constant. Solid line is the calculated lattice constant from (a).

Figure 6-7 (a) shows the lattice parameters of SrTiO$_3$\textsuperscript{191,205} and Si\textsuperscript{206,207} (normalized to [110] direction) as a function of temperature, and SrTiO$_3$ undergoes an antiferrodistortive transition from cubic to tetragonal phase at $T_c=105$K. The lattice constant of SrTiO$_3$ at 300K is $\sim$3.905Å, while Si is $\sim$3.482 Å, which account for a compressive strain of $\sim$1.7%. In Fig. 6-7 (a), it could be found that the increase of TCE of SrTiO$_3$ with temperature is much more dramatic than that of Si, which is the key that a tensile strain could form at the interface. At the growth temperature, the lattice parameter of SrTiO$_3$, or $a_{STO}(T)$, is identical to its bulk value since it’s fully relaxed on Si substrate after 20 nm. Once it’s cooled down to the ambient temperature, since the shrink of Si substrate, or $a_{Si}(T) - a_{Si}(RT)$, which is much thicker, is much less than that of SrTiO$_3$ thin film, SrTiO$_3$ thin film will clamped to Si substrate with an in-plane lattice parameter of $a_{STO}(T) - a_{Si}(T) + a_{Si}(RT)$ and retain a residual tensile strain. Such a thermal strain only depends on the difference of growth temperature and ambient temperature, as indicated by a bracket in Fig. 6-7 (a). By varying growth temperature, we could calculate the ideal strain as a
function of growth temperature at 300K, as shown in Fig. 6-7 (b). For instance, if SrTiO$_3$ thin film is grown at 900°C, a tensile strain of 0.65% can be induced. If the growth temperature is 550°C, a tensile strain of 0.37% can be induced.

Finally, the biaxial strain will be converted into stress by the following equations for isotropic materials:

\[
\begin{pmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
\varepsilon_{zz} \\
\varepsilon_{yz} \\
\varepsilon_{zx} \\
\varepsilon_{xy}
\end{pmatrix} = \frac{1}{E} \begin{pmatrix}
1 & -v & -v & 0 & 0 & 0 \\
-v & 1 & -v & 0 & 0 & 0 \\
-v & -v & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 + v & 0 & 0 \\
0 & 0 & 0 & 0 & 1 + v & 0 \\
0 & 0 & 0 & 0 & 0 & 1 + v
\end{pmatrix} \begin{pmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz} \\
\sigma_{yz} \\
\sigma_{zx} \\
\sigma_{xy}
\end{pmatrix}
\]

Where \( E \) is the Young’s modulus of (238 GPa for SrTiO$_3$)\(^{208} \) and \( v \) is the Poisson’s ratio of (0.232 for SrTiO$_3$)\(^{197} \), and strain \( \varepsilon \) and stress \( \sigma \) are both second order tensors. If biaxial strain is 0.65%, the stress can be estimated:

\[
\varepsilon_{xx} = \frac{(1 - v)\sigma_{xx}}{E}
\]

\[
\sigma_{xx} = \frac{E\varepsilon_{xx}}{(1 - v)}
\]

Therefore, the in-plane film stress is \(~2.0\) GPa for a 120 nm SrTiO$_3$ on Si grown at 850°C.

### 6.8 Conclusion

In this section, we successfully demonstrated the nucleation and growth of epitaxial SrTiO$_3$ thin film on Si (001) by hybrid MBE. The cation stoichiometry of the film was controlled by keeping the Sr flux constant and varying the TTIP gas inlet pressure. Crystalline quality, film stoichiometry and surface morphology were found to be the best for SrTiO$_3$ films grown at \( P_{\text{TTIP}} = 54 \) mTorr. An adoption-controlled growth mode with a large growth window was enabled
at higher temperature (725°C and 850°C) which is demonstrated by in-situ RHEED and ex-situ XRD measurements. These results show that a precise flux control throughout the growth is mandatory to achieve an ideal perovskite growth template with atomically smooth surfaces. Meanwhile, it was found that a residual tensile strain would form due to a large discrepancy in coefficient of thermal expansion between SrTiO$_3$ and Si, and such a strain state could be continuously modulated by simply varying the growth temperature. The successful integration of SrTiO$_3$ directly on Si using a thin film growth technique with scalable growth rates and excellent control over stoichiometry represents a promising step towards the development of a growth template for heterogeneous integration of functional perovskite oxides on Si.
Chapter 7

Improving the structural quality and electrical resistance of SrTiO$_3$ thin films on Si (001) via a two-step anneal


7.1 Introduction

Integrating crystalline oxide devices on semiconductors, such as Sr$^{24,209}$, Ge$^{210,211}$ and GaAs$^{212}$, is considered a pathway to augment conventional semiconductor devices by the wealth of unique functionalities inherent to oxide materials. The combination of Si, being the most widely employed semiconductor, and SrTiO$_3$, serving as a substrate for the growth of functional perovskite oxide thin films that exhibit high electrically conductivity$^{213}$, resistive switching behavior$^{25}$, ferroelectric$^{26,163}$, piezoelectric$^{26,27}$, (anti)ferromagnetic$^{28,29}$ and multiferroic$^{30}$ properties, and have been employed as photocathode material for water splitting$^{214}$, renders the monolithic integration of SrTiO$_3$ on Si (001) highly desirable$^{215}$. Since single phase SrTiO$_3$ can be grown epitaxially on silicon its epitaxial integration on Si can serve as virtual substrate for these perovskite oxides. The insulating nature of SrTiO$_3$ (band gap of 3.2 eV)$^{216}$ electrically decouples the oxide layers from the Si substrate, providing a wafer-size platform for all-oxide electronic device technologies. Scaling up the substrate size to reduce manufacturing costs would therefore make novel functionalities emerging at oxide heterointerfaces$^{217-219}$ and oxide thin film properties enhanced by epitaxial strain$^{202,220}$ economically more attractive, providing a path to utilize these phenomena and develop a marketable technology$^{221,222}$. Therefore, epitaxial SrTiO$_3$ thin films with high structural quality
on Si are highly desirable since the crystalline quality will ultimately determine properties of subsequently grown films and heterostructures.

Previous studies have mainly focused on the growth of SrTiO$_3$/Si, such as molecular beam epitaxy (MBE)\textsuperscript{24,50,169,171,182,202,223–226}, hybrid MBE\textsuperscript{50}, pulsed laser deposition (PLD)\textsuperscript{227} and atomic layer deposition (ALD)\textsuperscript{175}, the two latter approaches requiring an MBE-grown buffer layer to facilitate nucleation and crystallization of the film. However, little was reported on \textit{ex-situ} thermal annealing of SrTiO$_3$ films on Si, although it is known to improve the quality of SrTiO$_3$ films\textsuperscript{48,218}. Furthermore, an insulating virtual substrate is required for many applications, which has been proved challenging employing physical vapor deposition techniques. For MBE-grown SrTiO$_3$ films, the reactivity of molecular oxygen is usually insufficient to ensure a low enough oxygen vacancy concentration in the films\textsuperscript{161}. Under oxygen deficient growth conditions, a high concentration of oxygen vacancies - shallow donor levels - form, liberating two electrons per oxygen vacancy site into the conduction band, resulting in a high free carrier concentration with resistivity lower than 0.1 $\Omega \times \text{cm}$\textsuperscript{228}. The utilization of reactive oxygen sources, such as oxygen plasma generated by electron cyclotron resonance (ECR)\textsuperscript{229}, radio-frequency (RF) excitation sources\textsuperscript{230} or ozone\textsuperscript{231} during MBE growth would significantly eliminate the oxygen deficiency. However, to prevent the formation of an amorphous SiO$_2$ during the nucleation of SrTiO$_3$, usually, only molecular oxygen is used when initializing the MBE growth\textsuperscript{225}. Therefore, a post-growth anneal of SrTiO$_3$ in oxygen or air is required to fill oxygen vacancies.

Here we demonstrate how structural and electrical properties of SrTiO$_3$ films grown on Si (001) by hybrid MBE can be optimized using a two-step post-growth annealing process. While high temperatures are required to improve the crystalline quality and reduce the number structural defects formed during the strain relaxation process, a lower temperature anneal in oxygen has been identified to be well-suited to reduce oxygen vacancy levels and increase the resistivity of the film.
Careful optimization of temperature and duration of the high temperature anneal is required to limit surface roughening to a minimum.

7.2 Experimental section

Epitaxial SrTiO$_3$ thin films were grown on 3-inch Si (001) substrates (p-type, 1~10 $\Omega$·cm, 300 µm thick, R$_s$~100 $\Omega$/□, University Wafer Inc.) using an hybrid oxide MBE system (DCA Instruments). In hybrid oxide MBE, Ti was provided using a metalorganic precursor, titanium tetraisopropoxide (TTIP), which was supplied via a heated gas inlet system connected to a gas injector (no carrier gas). A variable leak valve equipped with a capacitance manometer was used to precisely control gas inlet pressure (TTIP pressure) and thus provide a stable TTIP flux. The volatile nature of TTIP allows to significantly increase the growth rate of SrTiO$_3$\textsuperscript{178}. Sr was supplied in elemental form by evaporation from a thermal effusion cell. The Si substrates were prepared using a process reported earlier\textsuperscript{50}. In short, the Si wafer was degreased, etched in 2% HF solution and rinsed in deionized water prior to baking them in the load lock. The remaining native oxide layer was removed using a Sr-assisted desorption process\textsuperscript{180}, and a 5 monolayer (ML) SrTiO$_3$ buffer was grown at 400 °C, followed by another 11 ML buffer deposited at 600 °C. In both cases Sr and TTIP was co-supplied in the absence of additional oxygen. The Sr flux was fixed at 2.5×10$^{13}$ atoms cm$^{-2}$ s$^{-1}$ for all films grown, which was calibrated using a quartz crystal microbalance. TTIP gas inlet pressure was set to 62 mTorr. The second buffer layer was needed to stabilize the template and to enable film growth at a higher temperature. Two sets, 46-nm-thick and 120-nm-thick SrTiO$_3$ films were grown at 850 °C at a growth rate of about 54 nm per hour. A substrate rotation speed of 5 revolutions per minute (RPM) was used. In-situ reflection high-energy electron diffraction (RHEED) was used to monitor the growth. After growth, the wafers were diced into 1×1 cm$^2$ pieces for the subsequent post-growth annealing study. For the high
temperature annealing step, samples were loaded into a quartz tube furnace and annealed in dry air at different temperatures and for varying times, ranging from 800 °C to 1100 °C, and 5 to 15 hours. The low temperature anneal was performed at temperatures between 200 °C to 700 °C for 10 hours. The ramp rate of the furnace was set to 3 °C per minutes. High resolution x-ray diffraction (XRD) was performed using a PANalytical XPer Pro MRD 4-circle diffractometer equipped with a duMond-Hart-Partels Ge (440) incident beam monochromator using Cu Kα₁ radiation with a wavelength λ=1.5406 Å. The surface morphology was investigated using a Bruker Dimension Icon atomic force microscope (AFM) operated in peak force tapping mode. Ohmic Al/Ni/Au (20 nm / 40 nm / 150 nm) contacts were thermally evaporated⁹, and four point probe resistivity measurement was performed at room temperature using van der Pauw-geometry
7.3 Results and discussion

Figure 7-1. Schematic of growing and thermal annealing procedures of SrTiO$_3$ on Si (001) substrate.

The experimental procedure of growth and annealing is shown in Fig. 7-1. Compared to previously reported growth of SrTiO$_3$ on Si by hybrid MBE$^{232}$, here a higher growth temperature was used. RHEED intensity oscillations were observed for a 11 ML buffer layer grown at 600 °C.
and are shown in Fig. 7-2 (a), indicating a layer-by-layer growth. This two-dimensional growth mode was also observed at the actual growth temperature of 850 °C (not shown). Figures 7-2 (b)-(d) show film surface reconstructions of SrTiO₃ observed along different azimuths after cooling down from growth temperature. The observed diffraction pattern are in good agreement with reports of stoichiometric SrTiO₃ films grown by hybrid MBE¹⁷⁸,²⁰³. The occurrence of half order reflections along $\langle 100 \rangle$ and a four-fold reconstruction pattern along the $\langle 110 \rangle$ was attributed to the formation of a c(4×4) reconstructed surface, originating from a TiO₂-saturated surface and a direct indication that the SrTiO₃ film grown by hybrid MBE was stoichiometric²⁰³. It is noted that neither a c(2×2) nor a 2×1 surface reconstruction was observed, which have been obtained for Sr-rich and Ti-rich films grown by hybrid MBE outside the growth window and for films grown by solid source MBE²⁰²,²³³,²³⁴. An XRD 2θ-ω scan of a 120 nm SrTiO₃ thin films on Si is shown in Fig. 7-2(e). Only 00L diffraction peaks were observed, indicating that a single phase and single crystalline SrTiO₃ thin films was grown.
Figure 7-2. (a) RHEED intensity oscillation of the 01 reflection spot taken along the (100) azimuth of an 11-ML-thick SrTiO$_3$/Si buffer layer grown at 600 °C. RHEED pattern of SrTiO$_3$/Si after growth, taken along the (b) (100), (c) (110) and (d) (210) azimuth. (e) Wide range XRD 2θ-ω scan of a 120 nm SrTiO$_3$ film on Si (001).

To quantify the crystalline quality of the films, the full width at half maximum (FWHM) value Δω of the 002 SrTiO$_3$ XRD rocking curve scan was used. Figures 7-3 (a) and (b) show the improvement of the film quality after a post-growth anneal for films with thicknesses of 46 nm and
120 nm, respectively. While the thinner film had $\Delta \omega$ of 0.57 ° prior to the high temperature anneal, the thicker film had a FWHM value of 0.40 ° in the as-grown state. For the optimized post-growth annealing process (details below) employed here, rocking curve FWHM of the 002 SrTiO$_3$ peaks were reduced by a factor for two independent of film thickness, resulting in a FWHM of 0.29 ° and 0.20 ° for the thinner and thicker SrTiO$_3$ film, respectively.
Figure 7-3. Rocking curve FWHM of the 002 SrTiO$_3$ peak of (a) 46-nm-thick SrTiO$_3$ and (b) 120-nm-thick SrTiO$_3$ on Si (001) before and after 1050 °C thermal anneal. (c) Rocking curve FWHM of the 002 SrTiO$_3$ peak as a function of annealing temperature for 5 hours. (d) Rocking curve FWHM of the 002 SrTiO$_3$ peak as a function of annealing duration at 950 °C.
Two sets of experiments were performed to optimize the post growth annealing condition using the 120-nm-thick film: different temperatures at fixed hold-time (5 hours) and different annealing duration at fixed temperature (950 °C). The results are shown in Figs. 7-3 (c) and (d), respectively. The films crystal quality started to considerably improve for temperatures higher than 800 °C, with largest reduction in $\Delta \omega$ was found for anneals around 1050 °C. An annealing time of 5 hours was sufficient to achieve the best quality with no further reduction in $\Delta \omega$ for more prolonged high temperature anneals.

![Graph showing the FWHM values of the 002 SrTiO$_3$ rocking curve scan as a function of film thickness.](image)

Figure 7-4. Comparison of FWHM values of the 002 SrTiO$_3$ rocking curve scan as a function of film thickness (Reference: Gu et al.\textsuperscript{171}, Panomsuwan et al.\textsuperscript{223}, Méchin et al.\textsuperscript{29}, Méchin et al. (1999)\textsuperscript{224}, Lettieri et al.\textsuperscript{225}, Niu et al.\textsuperscript{182}, Gsell et al.\textsuperscript{226}, Yu et al.\textsuperscript{169}, Yong et al.\textsuperscript{227}, McDaniell et al.\textsuperscript{175}, Spreitzer et al.\textsuperscript{235}, Bauer et al.\textsuperscript{236}, and Guo et al.\textsuperscript{237}). Arrows and dashed lines are guide to the eyes.
To compare the crystalline quality of the films grown by hybrid MBE and post-growth annealed at the optimal condition, the 002 SrTiO$_3$ the rocking curve peak widths are plotted in Fig. 7-4 as a function of film thickness for partially or completely relaxed SrTiO$_3$ films on Si (001) reported by Gu et al.$^{171}$, Panomsuwan et al.$^{223}$, Méchin et al.$^{29}$, Méchin et al. (1999)$^{224}$, Lettieri et al.$^{225}$, Niu et al.$^{182}$, Gsell et al.$^{226}$, Yu et al.$^{169}$, Yong et al.$^{227}$, McDaniel et al.$^{175}$, Spreitzer et al.$^{235}$, Bauer et al.$^{236}$, and Guo et al.$^{237}$. Results of coherently strained, ultrathin 5-ML-thick SrTiO$_3$ ($\Delta\omega=0.013^\circ$)$^{202}$ was omitted here. Most reported SrTiO$_3$ films grown on Si (001) had thicknesses between 10 to 100 nm with rocking curve widths in the range of 0.1 to 1$^\circ$. Two main strategies have been employed to improve the film’s crystalline quality: scaling up film thickness, indicated by orange dash line, and improving film nucleation (buffer optimization), indicated by blue arrows. Gu et al.$^{171}$ have systematically studied the thickness dependence of the film quality and achieved a more than fourfold reduction of $\Delta\omega$ by increasing the film thickness from 30 to 120 nm. The minimum FWHM value of 0.06 $^\circ$ for their thickest films (120 nm) is quite close to the bulk crystal quality commonly obtained for single crystalline SrTiO$_3$ substrate grown by Verneuil method ($\Delta\omega\sim0.02$ $^\circ$). The periodic annealing method of buffer layers has also been used to improve the crystalline quality of SrTiO$_3$$^{225,237}$, and a minimum FWHM value of 0.14 $^\circ$ was achieved for 45-nm-thick films by in-situ annealing 360 $^\circ$C-deposited 2 ML SrTiO$_3$ buffer layers at 550 $^\circ$C in the growth chamber for 5 repetitions, a 3x reduction of $\Delta\omega$ compared to a single buffer layer$^{182}$. The lowest FWHM rocking curve value $\Delta\omega$ of 0.20 $^\circ$ achieved by the combination of hybrid MBE and post-growth anneal (120 nm and annealed at 1050 $^\circ$C for 5 hours) was still higher than $\Delta\omega$ of 0.06 $^\circ$ reported by Gu et al.$^{171}$. This might be attributed to the following reasons. The correct TTIP/Sr ratio, critical to ensure a stoichiometric cation ratio in the film, varies with the growth temperature$^{179}$. Since the same TTIP/Sr ratio was used for the first and second buffer layer, as well as for the film growth, and this ratio allowed to grow a stoichiometric film at higher
temperature, the supplied Sr/Ti cation ratio was most likely not adequate during the buffer layer growth. This may have caused a low buffer layer quality and thus a lower film quality\textsuperscript{238}. Carbon incorporation into the SrTiO\textsubscript{3} film from TTIP precursor molecules and the volatile organic by-products formed during the thermal decomposition process is known to be enhanced at lower deposition temperature and might be another origin of a lower buffer layer quality\textsuperscript{239}. Careful optimization of the buffer layer growth will likely improve the crystal quality of SrTiO\textsubscript{3} films grown by hybrid MBE, but require a further study.

![AFM scans](image)

Figure 7-5. AFM scans of (a) as-grown (b) 800 °C annealed (c) 950 °C annealed and (d) 1050 °C annealed 120-nm-thick SrTiO\textsubscript{3} on Si. The scale bar corresponds to 0.5 µm. (e) RMS surface roughness versus different annealing temperatures before and after anneal. (f) Rocking curve FWHM of the 002 SrTiO\textsubscript{3} peak versus RMS roughness values for samples annealed at different temperatures. The lines are guide to the eyes.
Surface morphology change during the post-growth anneal of the 120-nm-thick film was evaluated by root-mean-square (RMS) roughness measured from AFM scans shown in Fig. 7-5 (a)-(d). A smooth surface was observed in as-grown films [Fig. 7-5 (a)], a remarkable improvement over the surface morphology of SrTiO$_3$ films grown at lower temperature (600 °C) on Si, which contained few islands even under stoichiometric growth conditions$^{50}$. The enhanced surface diffusion at higher growth temperature used here (850 °C) enabled a two-dimensional growth mode exhibiting atomically smooth surfaces. Virtually no change in surface roughness were observed for film annealed at 800 °C, while the film surface roughness progressively increased with higher annealing temperatures, as shown in Fig. 7-5 (e). The desired decrease of rocking curve FWHM was accompanied with a slight increase of film surface roughness, shown in Fig. 7-5 (f); however, RMS surface roughness values remained well below 2 nm. It seems counterintuitive that the film surface roughens with increasing temperature, which might be caused by an enhanced SrO desorption$^{237}$. 
Both, as-grown and annealed films were found to be electrically conducting, attributed to a high oxygen vacancy concentration. The carrier concentration was estimated from the resistivity assuming a room temperature mobility of about 10 cm² V⁻¹ s⁻¹. Since Hall mobility in SrTiO₃ has been reported to be almost independent of carrier concentration for oxygen-deficient films in the range from 1×10¹⁷ cm⁻³ to 3×10¹⁹ cm⁻³ (Ref 240) due to the large polar phonon scattering^{240}, it was
further assumed that the room temperature mobility does not change dramatically at even higher carrier concentration. From the low resistivity of around $10^{-3} \, \Omega \times \text{cm}$ in both cases a carrier concentration close to $10^{21} \, \text{cm}^{-3}$ was estimated (see Fig 7-6). The low resistivity of as-grown films was attributed to the oxygen deficient growth condition, while quenching the samples after the high temperature post-growth anneal to room temperature ‘freezes-in’ the higher equilibrium vacancy concentration at higher temperature. Nevertheless it is remarkable that at a similar temperature but orders of magnitude different oxygen partial pressures during growth and post-deposition anneal resulted in a comparable vacancy concentration. Figure 7-6 (a) shows that the film grown on Si still had a relatively low resistivity after a high temperature anneal at 1050 °C in the air. We attributed this effect to the Si substrate scavenging oxygen from SrTiO$_3$. This process expedited at higher temperature, becoming a determinant mechanism for the equilibrium oxygen vacancy concentration in the film, as discussed in detail below.

A subsequent low temperature annealing process in dry air was developed to drive out oxygen vacancies by ‘backfilling’ oxygen into the lattice to obtain an insulating film. The samples were annealed in dry air for 10 hours at various temperatures ranging from 200 °C to 700 °C. Even though p-type Si wafer ($\rho \sim 3 \, \Omega \, \text{cm}$) is the most common and economical substrate, the low sheet resistance ($R_s \sim 80 \, \Omega/\text{sq}$) could give rise to a pronounced parallel conduction. In order to elucidate the situation, we further grew 120-nm-thick SrTiO$_3$ films on semi-insulating (SI) Si and (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) substrates as control samples under the exact same conditions inside the stoichiometric growth window. The sheet resistance and estimated carrier concentration are plotted as a function of annealing temperature and shown in Fig. 7-6.

The sheet resistance of unannealed SrTiO$_3$ film on SI-Si was about 2 orders of magnitude higher compared to films grown on p-Si, indicating a pronounced parallel conduction through the substrate in the latter case. The amorphous SiO$_2$ interface layer was too leaky to electrically decouple SrTiO$_3$ completely from the substrate. Note that in the case of SrTiO$_3$ on SI-Si, the
measured sheet resistance was over one order lower than the sheet resistance of the SI-Si substrate. Therefore, the correct sheet resistance of unannealed SrTiO₃ was ~4 kΩ/sq. The difference in sheet resistance of unannealed SrTiO₃ films on SI-Si and LSAT substrates was attributed to the existence of the grain boundary, dislocation, and other defects in SrTiO₃ films on SI-Si substrate, which could act as sinks for electrically activated traps, increasing the unintentional carrier concentration and thus the overall electrical conductance of SrTiO₃ on Si.

For a second-step anneal at low temperatures (200 °C), the re-oxidation process was kinetically limited. The diffusion coefficient of oxygen vacancy is 3.9×10⁻⁸ cm²/s at 500 °C, about 8 orders higher than 4.4×10⁻¹⁶ cm²/s at 100 °C. Carrier concentrations for films on p-Si annealed at 500 °C were as low as 10¹⁵ cm⁻³ and in good agreement with the sheet resistance (~200 MΩ/sq) of 300 nm SrTiO₃ thin films, homoepitaxially grown by hybrid MBE in oxygen plasma. As shown in Fig. 7-6 (b), the oxygen vacancy concentration was suppressed below (10¹⁵ cm⁻³) after the annealing, assuming no comparable contributions from defects or interface traps.

The reduction in sheet resistance of SrTiO₃ films grown on both, p-Si and SI-Si, and annealed at higher temperature can be understood by taking the formation of SiOₓ into account.

Oxygen diffusion through SrTiO₃ to Si was significantly promoted at elevated temperature (>500–600 °C). The formation of silicon oxide at the interface has been previously observed, both in vacuum and oxygen-rich environment between 675 to 1075 K, indicating that the oxidation of Si is thermodynamically preferred over the reduction of oxygen vacancies in SrTiO₃. The higher temperature (>500 °C) enabled an efficient oxygen diffusion through the SrTiO₃ as well as through the SiOₓ already present at the Si/SrTiO₃ interface, therefore limiting the ‘backfilling’ of oxygen vacancies in the SrTiO₃ lattice.

This hypothesis is further supported by the sheet resistance of SrTiO₃ films on LSAT substrates using similar growth and annealing conditions (700 °C), which were found highly insulating (>2000 Ω cm, over the measurement limit). This comparison experiment suggests that
the direct contact of SrTiO$_3$ films with Si substrate is related to the pronounced oxygen deficiency in SrTiO$_3$/Si after high-temperature annealing in the air. Annealing temperatures have to be high enough to kinetically enable and expedite the oxidization process of SrTiO$_3$, but also low enough to limit the rate of silicon oxidation at the interface$^{243}$.

7.4 Conclusion

In conclusion, high quality SrTiO$_3$ thin films on p-Si (001) substrate were successfully grown by hybrid MBE in a layer-by-layer growth fashion at high temperatures. High quality, stoichiometric SrTiO$_3$ films were obtained. A two-step post growth annealing process was developed to improve the crystal quality of SrTiO$_3$ thin films and to reduce the high oxygen vacancy concentration in the films. An optimal annealing temperature and duration of the two-step annealing process was identified. The two-step annealing method is a viable and cost effective way to improve the structural quality of SrTiO$_3$ buffer layers on Si, as well as its electrical resistivity.
Chapter 8

Future Work

8.1 Determination of work function for vanadates

In this dissertation work, vanadates have been demonstrated as promising candidates for transparent conductors. Moving forward, searching for a scalable process by taking advantage of the short electron mean free path of correlated metal is crucial. An important aspect is that whether the materials can be fabricated using low-temperature deposition method on less-reflective substrate. Another important task is to keep exploring material properties which are critical for practical applications, such as work function, etchability, thermal stability, etc.

Work function is an important characteristic for metals, which could be understood as the minimum energy required removing an electron from the conduction band to the vacuum level. Since the band alignment of two adjacent materials is determined by their individual work functions, controlling over work function is the key, for instance, in reducing the contact resistance between metal and semiconductor in optoelectronic devices such as a Si heterojunction solar cell. For Si heterojunction solar cell with amorphous Si layer, both sides of the devices need a transparent conductor with different requirements of work function to reduce the resistance barrier, as shown in Fig. 8-1 (a). The most accurate and reliable method to extract work function is the capacitance-voltage measurement on a metal-semiconductor interface, or a Schottky barrier device. Depends on the difference of work function between the metal and the semiconductor, there could be accumulation, neutral or depletion contacts, as shown in Fig. 8-1 (b).
Figure 8-1. (a) Band structure of a Si heterojunction solar cell with intrinsic amorphous Si layer. The work function of transparent conductor at both side play an important role in the contact resistance. (b) Schottky model of a metal-semiconductor interface. The upper and lower parts of the figure show the interface before and after contact, respectively. The left, middle and right parts of the figure show three conditions: accumulation, neutral and depletion. Schottky barrier forms in the condition of depletion.

By building a Schottky barrier device on SrVO₃ and CaVO₃ with a known perovskite oxide semiconductor and analyzing the current-voltage and capacitance-voltage measurement data of a Schottky barrier device, the work function information could be extracted. Ignoring series and shunt resistance, the thermionic current-voltage relationship can be given by:\[63\]:
Where $A$ is the diode area, $A' = 4\pi qk^2 m^* / h^3 = 120(m^*/m)$ is the Richardson’s constant, $n$ is the ideal factor of the diode, $\phi_B$ is the effective barrier height and $T$ is the temperature. If $V \gg kT / q$, the equation can be reduced to:

$$1n(1 / T^2) = 1n(AA') - q(\phi_B - \frac{V}{n}) / kT$$

A plot of $1n(1 / T^2)$ as a function of $1/T$ at a constant forward bias, $V_1$ is sometimes called a Richardson plot, which has a slope of $q(\phi_B - \frac{V}{n}) / k$ and an intercept $1n(AA')$ on the $1n(1 / T^2)$ axis, as shown in Fig. 8-2 (a).

Figure 8-2. Schematic of current-voltage-temperature and capacitance-voltage measurement that can be use to extract barrier height.

Another method to extract the barrier height and thus the work function is to use capacitance-voltage measurement. The capacitance per unit area of a Schottky diode is given by:

$$\frac{C}{A} = \sqrt{\frac{\pm qK_{low} (N_A - N_p)}{2(\pm V_{bi} \pm V - kT / q)}}$$
Where the “+” sign is for p-type and the “−” sign is for n-type, \( A \) is the area, \( V \) is the reserves-bias voltage, \( N_A \) is the density of acceptors, \( N_D \) is the density of donors, \( k \) is the Boltzmann constant, \( T \) is the temperature, \( q \) is the elementary charge, \( K \) is the dielectric constant of material, \( \varepsilon_0 \) is the permittivity of vacuum, \( V_{bi} \) is the barrier height. Plotting \((A/C)^2\) as a function of voltage gives the intercept of \(-V_{bi} + kT/q\) on the \( V \)-axis, Fig. 8-2 (b). The barrier height then can be deduced from:

\[
\phi_B = -V_i + V_0 + kT/q
\]

Where \( V_0 = (kT/q)\ln(N_C/N_D) \), \( N_C \) is the effective density of states in the condition band, \( N_D \) is the doping density.
Figure 8-3. RHEED images at different azimuths and height of sample stage after growth at 200 °C for 10nm SrVO₃ thin films on Nb-SrTiO₃ substrates with (a) Nb doping of 0.5%, (b) Nb doping of 0.7%, (c) Nb doping of 0.1% and (d) Nb doping of 0.05%. (e) Schematic of influence of different surface termination of Nb-SrTiO₃ substrates on the interface of SrVO₃/Nb-SrTiO₃. Note that the final interface of SrVO₃/Nb-SrTiO₃ is independent of starting termination.
Since commercial semiconducting SrTiO$_3$ substrates with various doping can be easily acquired on the markets and the properties of SrTiO$_3$ are also well studied, SrTiO$_3$ substrates are chosen to build heterojunction with SrVO$_3$. SrTiO$_3$ substrates have been previously used to form Schottky barrier and study the properties of SrRuO$_3$ and La$_{0.7}$Sr$_{0.3}$MnO$_3$. 10 nm SrVO$_3$ thin films were grown on Nb-doped SrTiO$_3$ substrates with different doping (0.1% Nb, 0.05% Nb, 0.5% Nb and 0.7% Nb). The RHHED images after the growth are shown in Figs. 8-3 (a)–(d). Though it is reported that metal with perovskite might exhibit different working function, depends on the surface termination, SrVO$_3$/ SrTiO$_3$ heterojunction has an interface which is independent of SrTiO$_3$ termination, as shown in Fig. 8-3 (e).

The information of work function extracted from an electrical measurement approach will also be very helpful to precisely design strong correlated metals, such as SrVO$_3$ and CaVO$_3$-based heterostructure and superlattice structure, which would possibly lead us to new physics phenomenon.

8.2 Understanding of low-temperature transport properties of vanadates

SrVO$_3$ thin films synthesized in this dissertation work are of great quality, comparing with previous SrVO$_3$ bulk and thin film, as seen by the high RRR value reported$^{92,135,149}$. Though this is not necessarily needed for the application of transparent conductors used at room temperature, it provides an opportunity to study the intrinsic transport properties and electron state of SrVO$_3$ at low temperature.

A nonlinear Hall resistance at low temperature was observed under the measurement conditions of temperature down to ~2 K and the magnetic field up to ~8 T, which could be generally explained by a multiple band conduction model$^{250-254}$. The nonlinear Hall resistance has a very unique dependence on the magnetic field, as seen in Fig. 8-4. From 120K to 40K, a
decrease of the absolute value of derivative of hall resistance is observed as the magnetic field increase, which is very different from previous two electron channel report. Below 16K, a deep hump is observed at low field.

Nonlinear hall effects could originate from multiple band conduction. Next, we will discuss the possible origin of multiple band scenario for nonlinear hall resistance from a two band model by sorting it into three different conditions, which are (1) two types of holes; (2) two types of electrons; (3) One electron and one hole.

![Figure 8-4. Derivative of hall resistance as a function of magnetic field at different temperatures (Photo courtesy of Matthew Brahlek).](image)

Since the electrical conductivity can only be positive, it is expressed as:

\[
\sigma = ne\mu, n > 0
\]

\[
\sigma = -ne\mu, n < 0
\]
Where \( n \) is carrier concentration, \( e \) is the elementary charge, \( \mu \) is the carrier mobility. \( n \) can be either a positive or negative value. If \( n > 0 \), the conducting carriers are holes; if \( n < 0 \), the conducting carriers are electrons. The Hall coefficient and Hall resistance are shown below:

\[
\rho_{xy} = B \times \frac{R_1 \sigma_1^2 + R_2 \sigma_2^2 + \sigma_1^2 \sigma_2 R_1 R_2 (R_1 + R_2) B^2}{(\sigma_1 + \sigma_2)^2 + \sigma_1^2 \sigma_2^2 (R_1 + R_2)^2 B^2}
\]

\[
\rho_{xx} = \frac{\sigma_1 + \sigma_2 + \sigma_1 \sigma_2 (\sigma_1 R_1 + \sigma_2 R_2) B^2}{(\sigma_1 + \sigma_2)^2 + \sigma_1^2 \sigma_2^2 (R_1 + R_2)^2 B^2}
\]

\[
\rho_{xy} = \frac{B}{e} \times \frac{n_1 \mu_1^2 + n_2 \mu_2^2 + B^2 \mu_1^2 \mu_2^2 (n_1 + n_2)}{(n_1 \mu_1 + n_2 \mu_2)^2 + B^2 \mu_1^2 \mu_2^2 (n_1 + n_2)^2}, \text{if } n_1 \times n_2 > 0
\]

\[
\rho_{xy} = \frac{B}{e} \times \frac{n_1 \mu_1^2 + n_2 \mu_2^2 + B^2 \mu_1^2 \mu_2^2 (n_1 + n_2)}{(n_1 \mu_1 - n_2 \mu_2)^2 + B^2 \mu_1^2 \mu_2^2 (n_1 + n_2)^2}, \text{if } n_1 \times n_2 < 0
\]

\[
\rho_{xx} = \frac{1}{e} \times \frac{n_1 \mu_1 + n_2 \mu_2 + B^2 \mu_1 \mu_2 (n_1 \mu_1 + n_1 \mu_2)}{(n_1 \mu_1 + n_2 \mu_2)^2 + B^2 \mu_1 \mu_2 (n_1 + n_2)^2}, \text{if } n_1 \times n_2 > 0
\]

\[
\rho_{xx} = \frac{1}{e} \times \frac{n_1 \mu_1 + n_2 \mu_2 + B^2 \mu_1 \mu_2 (n_1 \mu_1 + n_1 \mu_2)}{(n_1 \mu_1 - n_2 \mu_2)^2 + B^2 \mu_1 \mu_2 (n_1 + n_2)^2}, \text{if } n_1 \times n_2 < 0
\]

Since mobilities, \( \mu_1 > 0, \mu_2 > 0 \), there’re four possibilities of the sign of \( n_1 \) and \( n_2 \):

1. If \( n_1 > 0, n_2 > 0 \), both carriers are holes. In the low field limit (\( \mu B \ll 1 \)):

\[
\rho_{xy}(LF) = \frac{B}{e} \times \frac{n_1 \mu_1^2 + n_2 \mu_2^2}{(n_1 \mu_1 + n_2 \mu_2)^2} > 0
\]

In the high field limit (\( \mu B \gg 1 \)):

\[
\rho_{xy}(HF) = \frac{B}{e} \times \frac{1}{(n_1 + n_2)} > 0
\]

\[
\frac{\rho_{xy}(HF)}{\rho_{xy}(LF)} = \frac{(n_1 \mu_1 + n_2 \mu_2)^2}{(n_1 + n_2)(n_1 \mu_1^2 + n_2 \mu_2^2)} = \frac{n_1 \mu_1^2 + n_2 \mu_2^2 + 2n_1 n_2 \mu_1 \mu_2}{n_1 \mu_1^2 + n_2 \mu_2^2 + n_1 n_2 \mu_1^2 + n_2 \mu_2^2} < 1
\]

Therefore, it can be seen that:

\[
\rho_{xy}(HF) > 0, \quad \rho_{xy}(LF) > 0
\]
If we plot $\rho_{xx}$ as a function of magnetic field by assuming the following conditions:

\[ 0 < \frac{\rho_{xy}(HF)}{\rho_{xy}(LF)} < 1 \]

(2) If $n_1 < 0$, $n_2 < 0$, both carriers are electrons. In the low field limit ($\mu B \ll 1$), nonlinear Hall resistance can be expressed as the following:
\[ \rho_{xy}(LF) = \frac{B}{e} \times \frac{n_1 \mu_1^2 + n_2 \mu_2^2}{(n_1 \mu_1 + n_2 \mu_2)^2} \leq 0 \quad (XX) \]

In the high field limit \( (\mu B \gg 1) \):

\[ \rho_{xy}(HF) = \frac{B}{e} \times \frac{1}{(n_1 + n_2)} < 0 \]

\[ \frac{\rho_{xy}(HF)}{\rho_{xy}(LF)} = \frac{(n_1 \mu_1 + n_2 \mu_2)^2}{(n_1 + n_2)(n_1 \mu_1^2 + n_2 \mu_2^2)} = \frac{n_1^2 \mu_1^2 + n_2^2 \mu_2^2 + 2n_1 n_2 \mu_1 \mu_2}{n_1^2 \mu_1^2 + n_2^2 \mu_2^2 + n_1 n_2 (\mu_1^2 + \mu_2^2)} \]

\[ \rho_{xy}(HF) < 0, \rho_{xy}(LF) < 0 \]

\[ 0 < \frac{\rho_{xy}(HF)}{\rho_{xy}(LF)} \leq 1 \]

If we plot \( \rho_{xx} \) as a function of magnetic field by assuming the following conditions:

Figure 8-6. Simulated Hall resistance as a function of magnetic field if both carriers are electrons.

Table 8-2. Carrier density and mobility used in Fig. 8-6.

<table>
<thead>
<tr>
<th>Electron mobility 1</th>
<th>Electron mobility 1</th>
<th>Electron density 1</th>
<th>Electron density 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm(^2) V(^-1) s(^-1)</td>
<td>cm(^2) V(^-1) s(^-1)</td>
<td>×10(^{22}) cm(^{-3})</td>
<td>×10(^{21}) cm(^{-3})</td>
</tr>
<tr>
<td>10000</td>
<td>2000</td>
<td>4</td>
<td>8</td>
</tr>
</tbody>
</table>
The curves under the condition that both carriers are electrons is in the second and fourth (skipped here) quadrants, as shown in Fig. 8-6. The absolute value of the derivative of Hall resistance \(d\rho_{xx}/dB\) versus magnetic field \(B(T)\) decreases with the increase of magnetic field.

(3) If \(n_1 \times n_2 < 0\), one is electron, and the other is hole. For instance, \(n_1 < 0, n_2 > 0\), \(n_1\) is electron and \(n_2\) one is hole, Hall resistance is expressed as the following:

\[
\rho_{xy} = \frac{B}{e} \times \frac{n_1 \mu_1^2 + n_2 \mu_2^2 + B^2 \mu_1^2 \mu_2^2 (n_1 + n_2)}{(n_1 \mu_1 - n_2 \mu_2)^2 + B^2 \mu_1^2 \mu_2^2 (n_1 + n_2)^2}, \text{ if } n_1 \times n_2 < 0
\]

In the low field limit (\(\mu B \ll 1\)):

\[
\rho_{xy}(LF) = \frac{B}{e} \times \frac{n_1 \mu_1^2 + n_2 \mu_2^2}{(n_1 \mu_1 - n_2 \mu_2)^2}
\]

In the high field limit (\(\mu B \gg 1\)):

\[
\rho_{xy}(HF) = \frac{B}{e} \times \frac{1}{(n_1 + n_2)}
\]

\[
\frac{\rho_{xy}(HF)}{\rho_{xy}(LF)} = \frac{(n_1 \mu_1 - n_2 \mu_2)^2}{(n_1 + n_2)(n_1 \mu_1^2 + n_2 \mu_2^2)} = \frac{n_1^2 \mu_1^2 + n_2^2 \mu_2^2 - 2n_1 n_2 \mu_1 \mu_2}{n_1^2 \mu_1^2 + n_2^2 \mu_2^2 + n_1 n_2 (\mu_1^2 + \mu_2^2)}
\]

Since \(-2n_1 n_2 \mu_1 \mu_2 > 0, n_1 n_2 (\mu_1^2 + \mu_2^2) < 0\). If \(n_1^2 \mu_1^2 + n_2^2 \mu_2^2 + n_1 n_2 (\mu_1^2 + \mu_2^2) > 0\), we have:

\[
\frac{\rho_{xy}(HF)}{\rho_{xy}(LF)} > 1
\]

If \(n_1^2 \mu_1^2 + n_2^2 \mu_2^2 + n_1 n_2 (\mu_1^2 + \mu_2^2) < 0\), we have:

\[
\frac{\rho_{xy}(HF)}{\rho_{xy}(LF)} < 0
\]
The sign of $\rho_{xy}$ could change as magnetic field increases. $\rho_{xx}$ as a function of magnetic field is plotted in Fig. 8-7.

![Graph showing Hall resistivity as a function of magnetic field.](image)

Figure 8-7. Simulated Hall resistance as a function of magnetic field if both one type of carriers is electron and the other is hole.

<table>
<thead>
<tr>
<th>Electron mobility</th>
<th>Hole mobility</th>
<th>Electron density</th>
<th>Hole density</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm$^2$V$^{-1}$s$^{-1}$</td>
<td>cm$^2$V$^{-1}$s$^{-1}$</td>
<td>$10^{22}$ cm$^{-3}$</td>
<td>$10^{21}$ cm$^{-3}$</td>
</tr>
<tr>
<td>10000</td>
<td>2000</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>10000</td>
<td>2000</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>10000</td>
<td>2000</td>
<td>1.2</td>
<td>8</td>
</tr>
<tr>
<td>10000</td>
<td>2000</td>
<td>0.7</td>
<td>8</td>
</tr>
<tr>
<td>10000</td>
<td>2000</td>
<td>0.4</td>
<td>8</td>
</tr>
<tr>
<td>10000</td>
<td>2000</td>
<td>0.1</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 8-3. Carrier density and mobility used in Fig. 8-7

By qualitatively comparing the data with three different conditions shown in Figs. 8-5 to 8-7, it could be concluded that only the scenario of one electron-channel and one hole-channel
could explain the field dependence of hall resistance of SrVO₃ films above 40K. One of the interesting questions yet not fully understood is that what causes such a hole-conduction channel in well-studied SrVO₃ system which was largely ignored previously due to the poor film quality or nonstoichiometric defects. What else could contribute to the nonlinear hall resistance below 40K, could it be another conduction channel? Is there any structural-related transformation that occurs at low temperature for SrVO₃? A careful quantitative fitting should be applied for obtain the information of carrier density and mobility for multiple channels. DFT calculation and the temperature-dependent structure characterization, for instance, high-resolution x-ray diffraction could be performed to help understand and unveil the origin of low-temperature transport data.

8.3 Exfoliation of functional oxide from Si: a pathway to flexible application

Recently, Lu et al. in Hwang group reported a new method of obtaining freestanding single-crystal perovskite films and heterostructure by etching of sacrificial wafer-soluble layer (Sr₃Al₂O₆, a cubic structure with lattice parameter of 15.844Å, which is very close to four unit cells of SrTiO₃)²⁵⁵. Similar to the sacrificial layer of AlAs in III-V materials and devices²⁵⁶, it opens a new gate of utilizing functional epitaxial oxide in the flexible electronic application, which is currently dominant by Si and organic materials, by a simple method²⁵⁷,²⁵⁸.
Figure 8-8. Schematic of processing steps for heterostructure growth, oxide membrane release and transfer. (Adapted from ref\textsuperscript{255})

Even though it is certainly an advance toward flexible functional oxide, an expensive and small size of single-crystalline oxide substrate is still used. Since a high quality epitaxial oxide could be fabricated on a 3 inch Si wafer, exfoliating functional oxide from large scale Si wafer is of course interesting in term of practical application. Large scale Si wafer is compatible with standard semiconductor equipment, and Si is also much cheaper than single crystalline oxides. The price of 2 inch LSAT (standard substrate for epitaxial oxide) is ~$400, while a 3 inch wafer is only ~$10. Most importantly, large size of Si wafers up to 12 inch could be easily grown by Czochralski process, which further facilitates the further development of functional oxide on Si device.

Figure 8-9. Schematic for epitaxial lift-off of single-crystal Au foil. (A) Miscut n-type Si(111) wafer without the native oxide layer. (B) Epitaxial electrodeposition of Au on Si(111) from a 0.1 mM HAuCl\textsubscript{4} solution at −1.9 V versus Ag/AgCl with prepolarized electrode. (C) Photoelectrochemical oxidation of Si under irradiation of light in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution at 0.75 V versus Ag/AgCl. (D) A polymer adhesive (tape/hot glue) is applied to the surface of Au to aid the foil separation. (E) A sacrificial SiO\textsubscript{x} interlayer is etched using dilute (5%) hydrofluoric acid to separate the foil from the Si substrate. (F) Single-crystal Au foil completely detached from the Si surface. (Adapted from ref\textsuperscript{259})

More recently, Mahenderkar \textit{et al.} reported that electrodeposited Au (111) foil on Si (111) could be released by oxidizing Si at Au/Si interface and lift-offing in dilute HF solution (5\%)\textsuperscript{259}. It will be very interesting to ask the question that whether epitaxial oxide be exfoliated
from Si wafer substrate? We have observed ~5 nm SiO$_x$ layer already with as-grown SrTiO$_3$ thin film on Si, as shown in Chapter 6. By annealing SrTiO$_3$/Si in the air at high-temperature, SiO$_x$ layer as thick as ~100 nm could be grow, as shown in Fig. 8-10. Therefore, an experiment of dilute HF etch could be systematically investigated.

![Figure 8-10](image)

Figure 8-10. Thickness of SiO$_x$ layer at the interface of SrTiO$_3$ thin film on Si wafer as a function of annealing temperature for 5 hours. The color of SrTiO$_3$/Si shown in the figure is an indication of various thickness of SiO$_x$ as an antireflection coating layer on Si wafer. (Photo courtesy of Yuanxia Zheng.)
Reference


43. Ihlefeld, J. F. *et al.* Optical band gap of Bi Fe O 3 grown by molecular-beam epitaxy.


ellipsometry: Applications for real time Stokes vector spectroscopy of thin film growth.  


66. Technical Product Note for PRS™-3000. (2017). Available at:

Chemical and Thin-Film Strategies for New Transparent Conducting Oxides. *MRS Bull.*  


111. Takatsu, H. *et al.* Roles of high-frequency optical phonons in the physical properties of the


128. Fuchs, K. The conductivity of thin metallic films according to the electron theory of metals. in Mathematical Proceedings of the Cambridge Philosophical Society 34, 100–108 (1938).


137. Fukuda, K., Lim, S. H. N. & Anders, A. Coalescence of magnetron-sputtered silver


147. Sayer, M., Chen, P., Fletcher, R. & Mansingh, A. The metal-insulator transition in


158. Schumann, T., Raghavan, S., Ahadi, K., Kim, H. & Stemmer, S. Structure and optical


170. Choi, M. *et al.* Strain relaxation in single crystal SrTiO3 grown on Si (001) by molecular


226. Gsell, S. *et al.* Reduction of mosaic spread using iridium interlayers: A route to improved


247. Zhong, Z. & Hansmann, P. Tuning the work function in transition metal oxides and their


259. Mahenderkar, N. K. *et al.* Epitaxial lift-off of electrodeposited single-crystal gold foils for
Appendix

Procedure of ultrafast reciprocal space mapping (RSM) with PIXcel3D

The configuration of the equipment and the definition of $2\theta$, $\omega$, phi and chi can be referred to Section 3.1.1 and 3.1.2.

1) Direct beam height alignment.
   a. Perform a manual scan of $2\theta$ with a scan range of $1^\circ$ and a step size of 0.01°.
   b. Perform manual scans of $z$ with a scan range of $2.5^\circ$ and a step size of 0.01°, $\omega$ with a scan range of $0.3^\circ$ and a step size of 0.001°, then $z$, $\omega$, etc. until neither $z$ nor $\omega$ needs to be further aligned.
   c. Record current offset by clicking “System Settings”→ “Sample Offsets”→ “Set New=0”.

2) Build reciprocal space by setting the primary and secondary axis of substrate and film that are relevant for the measurement.
Figure A-1. The structure information of substrate and thin film can be added in “User Setting” → “Unit Cell”.

a. Add the structure information of substrate and film under “User Setting” → “Unit Cells”.

b. Open “Tool” → ”Reciprocal Space Map”.

c. Click “Map”, insert the information of substrate and film in Lattice 1 and 2, and 3 if multilayers structures are used.

Figure A-2. The information of lattice and choice of primary and secondary axis can be added to build “Reciprocal Space Map”

d. Right-click and choose “Catch HKL mode”, and different diffraction plane can then be selected. The value of $\omega$, $2\theta$, phi, and chi at top right can been seen in top right of the figure.
Figure A-3. The goniometer can be moved to desired substrate peak by clicking the diffraction peak in “Reciprocal space map” in “Catch HKL mode”.

3) Alignment of out-of-plane (00L) substrate peak.
   a. Choose open “detector (OD) mode” in “Diffracted Beam Optics” → ”Diffracted beam path 1” → ”Usage”
   b. Move to out-of-plane peak (00L) by clicking on the desired diffraction peak in the “Reciprocal space map” and click “Move”.
   c. Perform manual scans of $\omega$, chi, $\omega$, chi, etc. until neither $\omega$ nor chi needs to be furthered aligned
   d. Add sample offsets so that current $2\theta$ angles equal expected angles on top right of the “Reciprocal space map” figure. Input offset of chi by setting chi=0.

4) Alignment of asymmetric peak e.g. (103) substrate peak.
   a. Move to asymmetric peak e.g. (103) of substrate peak.
   b. Perform manual scans of $\omega$, phi, $\omega$, phi, etc. until neither $\omega$ nor phi needs to be furthered aligned. For most of pseudo-cubic structures, an initial scan range of $90^\circ$ for phi will be used in the phi scan for asymmetric peaks.
c. Add sample offsets so that current 2θ angles equal expected angles on top right of the “reciprocal space map” figure. Input offset of phi by setting phi=0, otherwise the information of phi will be lost after moving to out-of-plane substrate peak.

5) Move between symmetric (00L) and asymmetric peaks e.g. (103) to repeat Steps 3 and 4, until neither phi nor chi needs to be furthered aligned.

6) Change the detector to “frame based” mode. Perform manual scan of ω-2θ, and the scan can be collected in about 40 second. However, the range of 2θ is limited to 2.5° due to the finite width of the detector in the ultrafast RSM mode.

Figure A-4. Change the detector to “frame based” mode and couples scans can be performed.
VITA

Lei Zhang

Education

2017  PhD in Materials Science, The Pennsylvania State University, University Park, PA
2010  M.Sc. in Materials Science, Arizona State University, Tempe, AZ
2007  B.Sc. in Applied Physics, Wuhan University, China

Honors & Awards

2017  Chinese Government Award for Outstanding Self-Financed Students Abroad
2016  MRS Graduate Student Gold Award, MRS Spring Meeting, Phoenix

Selected Publications


