THE INTERPLAY OF SURFACE ADSORBATES AND CATIONIC INTERMIXING IN THE 2D ELECTRON GAS PROPERTIES OF LAO-STO HETEROINTERFACES

by

RICHARD AKROBETU

Submitted in partial fulfillment of the requirements

For the degree of Master of Science

Thesis Adviser: Dr. Alp Sehirlioglu

Department of Materials Science and Engineering

CASE WESTERN RESERVE UNIVERSITY

May, 2017
The Interplay of Surface Adsorbates and Cationic Intermixing in the 2D Electron Gas Properties of LAO-STO Heterointerfaces

Case Western Reserve University
Case School of Graduate Studies

We hereby approve the thesis\(^1\) of

RICHARD AKROBETU

for the degree of

Master of Science

Dr. Alp Sehirlioglu

Committee Chair, Adviser 01-25-17
Department of Materials Science and Engineering

Dr. James McGuffin-Cawley

Committee Member 01-25-17
Department of Materials Science and Engineering

Dr. Peter Lagerlof

Committee Member 01-25-17
Department of Materials Science and Engineering

\(^1\)We certify that written approval has been obtained for any proprietary material contained therein.
Dedicated to my parents:
Your enduring sacrifices, love, and support were always worth it.
# Table of Contents

List of Tables vii

List of Figures viii

Acknowledgements x

Abstract xii

Chapter 1. Introduction 1

Introduction 2. Background 12

Surface Adsorbates and Conductivity 12

Cationic Intermixing 14

Conclusions 18

References 20

Background 3. Sample Fabrication 23

As-received Crystal 23

Etching Process 24

Thin Film Growth 27

Samples Prepared 37

Conclusions 37
## List of Tables

3.1 Relaxation Rates of Films 36  
5.1 Processing Conditions of Films in Surface Adsorbate Study 55  
5.2 Atomic Percentage Values for Regions of Interest for Samples at Room Temperature 60  
5.3 Atomic Percentage Values for Regions of Interest for Samples at 500°C 60  
5.4 Bond Energies for Different Bond Combinations Related to H₂O Dissociation 61  
5.5 Core Level Binding Energy Shifts of Different Species Related to H₂O Dissociation 62  
5.6 Initial and Final Percentage Amounts for Each Component Comprising the C1s Region 69  
5.7 Core Level Binding Energies Relative to Vacuum, and Core-Hole Binding Energy Shifts of O1s State (in eV) as Related to Carbonaceous Species 69  
6.1 Processing Conditions for Cationic Intermixing Study 79
# List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Perovskite Unit Cell</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Polar Discontinuity</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>LAO-STO Electrical Properties</td>
<td>7</td>
</tr>
<tr>
<td>2.1</td>
<td>Tunability of the 2-DEG</td>
<td>13</td>
</tr>
<tr>
<td>2.2</td>
<td>Conductivity vs. Plume Angle</td>
<td>16</td>
</tr>
<tr>
<td>2.3</td>
<td>La/Al Ratio vs. Plume Angle</td>
<td>17</td>
</tr>
<tr>
<td>3.1</td>
<td>Quality of As-Recieved Crystals</td>
<td>24</td>
</tr>
<tr>
<td>3.2</td>
<td>Etching Process</td>
<td>25</td>
</tr>
<tr>
<td>3.3</td>
<td>Quality of Ti-Terminated Substrate</td>
<td>27</td>
</tr>
<tr>
<td>3.4</td>
<td>Schematic of PLD Process</td>
<td>29</td>
</tr>
<tr>
<td>3.5</td>
<td>Different Deposition Plume Angles</td>
<td>30</td>
</tr>
<tr>
<td>3.6</td>
<td>Picture of PLD Equipment</td>
<td>30</td>
</tr>
<tr>
<td>3.7</td>
<td>Pictures of Sample and Target</td>
<td>31</td>
</tr>
<tr>
<td>3.8</td>
<td>RHEED Patterns Before and Post-Deposition</td>
<td>33</td>
</tr>
<tr>
<td>3.9</td>
<td>RHEED Intensity Fluctuations vs. Deposition Phase</td>
<td>33</td>
</tr>
<tr>
<td>3.10</td>
<td>Sample Growth RHEED Intensity Oscillations</td>
<td>34</td>
</tr>
<tr>
<td>3.11</td>
<td>Film-Substrate Orientation Relationship</td>
<td>35</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic of XPS Instrument</td>
<td>42</td>
</tr>
<tr>
<td>4.2</td>
<td>Regular vs. Angle-Resolved XPS</td>
<td>45</td>
</tr>
<tr>
<td>4.3</td>
<td>XPS Survey Spectrum</td>
<td>46</td>
</tr>
</tbody>
</table>
6.7 Plot of Mean Counts per Sputtering Layer of Cr$^+$ Ions for 10 u.c.
LAO-STO Film Grown at $1 \times 10^{-4}$ Torr 89

6.8 Comparison of the Locations of the Interface Marked by Cr$^+$ Ions 91

6.9 Estimation of the Magnitude of La$^+$ Indiffusion 92

6.10 Graph of the Distances of the LaSrO$_2$ Fragment from the Location of the Interface Marked by Cr$^+$ as a Function of Temperature 94
Acknowledgements

0.1 Acknowledgements

I would like to give special thanks to Dr. Alp Sehirlioglu, for making my conversion from Physics to Materials Science a wonderful experience. I would also like to acknowledge all the help and guidance from various collaborators who helped make this work a successful one, including Dr. Marie-Helene Berger, and Dr. Hicham Zaid, of Ecole des Mines des Paris, as well as Dr. Xuan Gao, Dr. Nicholas Goble, Dr. Walter Lambrecht, and Dr. Kevin Abassi, of Case Western Reserve University. Final thanks to Dr. Mike Jespersen, of the Air Force Research Laboratory (AFRL) on the Wright-Patterson Air Force base. This work was made possible by funding from the Air Force Office of Scientific Research (AFOSR).
0.2 Abbreviations

- 2DEG: 2-Dimensional Electron Gas
- AFM: Atomic Force Microscopy
- EELS: Electron Energy Loss Spectroscopy
- ESCA: Electron Spectroscopy for Chemical Analysis
- IMFP: Inelastic Mean Free Path
- LAO: Lanthanum Aluminate (LaAlO3)
- MEIS: Medium-Energy Ion Spectroscopy
- MBE: Molecular Beam Epitaxy
- PLD: Pulsed Laser Deposition
- RHEED: Reflection High Energy Electron Diffraction
- RSF: Relative Sensitivity Factor
- SIMS: Secondary Ion Mass Spectrometry
- STEM: Scanning Transmission Electron Microscopy
- STO: Strontium Titanate (SrTiO3)
- TEM: Transmission Electron Microscopy
- ToF SIMS: Time-of-Flight Secondary Ion Mass Spectrometry
- UHV: Ultra-High Vacuum
- XPS: X-ray Photoelectron Spectroscopy
- XRD: X-ray Diffraction
Abstract
The Interplay of Surface Adsorbates and Cationic Intermixing in the 2D Electron Gas Properties of LAO-STO Heterointerfaces

Abstract
by

RICHARD AKROBETU

0.3 Abstract

Ever since its discovery merely over a decade ago, the phenomenon of a tunable 2D electron gas at the heterointerface of SrTiO$_3$ (STO) and LaAlO$_3$ (LAO) has been a source of keen interest and scientific debate. Amongst the list of obstacles in understanding this phenomenon are the understanding of the role of surface adsorbates, the difficulty in elucidating the degree of intermixing at the LAO-STO interface, and marking the heterointerface itself. Films of varying thicknesses grown via Pulsed Laser Deposition (PLD) at varying O$_2$ partial pressures and temperatures were studied. The role of surface adsorbates was investigated via detailed in-situ X-ray Photoelectron Spectroscopy (XPS). O1s regions were split into three components with the main peak identifying main oxide oxygen, while the two shoulder peaks, at 1 and 2 eV from the main peak, respectively, were related to hydrous and carbonaceous species. Links between differences in their respective ratios, their energies of bond formation, and ambient atmosphere exposure
were established. Changes in the peak ratios vs. temperature were then related to binding energies of adsorbed species and the oxygen content from carbonaceous adsorbates through detailed analyses of C1s regions. Investigations into mechanisms of cationic intermixing were cognizant of conventional electron microscopy methods, which are limited by the respective masses of the atoms present and the small length of the interface examined. Films were subjected to surface and depth analyses via Secondary Ion Mass Spectrometry (SIMS). Intermixing was studied as a function of deposition temperature and film thickness by utilizing fragmented ions containing cations of both the film and the substrate through the use of proprietary Matlab software, and were modeled in 3D with Avizo modeling software. The position of the heterointerface was also marked by tracking a minor amount of Cr⁺ ions present on the surface of the substrate prior to deposition. Finally, evidence of a temperature-driven intermixing mechanism was established by studying the extent of La⁺ interdiffusion into the substrate at varying temperatures. All these investigations added to ongoing conversations on the effects of extrinsic mechanisms on the LAO-STO system and its efficacy in the fabrication of functional oxide electronics.
1 Introduction

"Oil and water don't mix," is a common adage stemmed from the age-old knowledge of a simple scientific concept - an interface. An interface, as described by the Merriam-Webster dictionary, is a surface forming the common boundary of two bodies, spaces, or phases [1]. Even though interfaces may be comprised of different phases, i.e. solid-liquid, solid-gas, or liquid-gas, they may also be comprised of two different materials of the same phase. This is referred to as a heterointerface. The above mentioned example of oil and water may also be classified as a heterointerface. In materials science, heterointerfaces are very important because they exhibit certain characteristics and properties, such as conductivity or magnetic scattering, that neither component possesses individually. Heterointerfaces are usually fabricated by a thin film deposition process, where epitaxial growth can occur. Epitaxy is the process of depositing a crystalline coat or overlayer onto a substrate, conforming it into the growth direction of the substrate. A perfect orientational relationship between the film and the substrate also indicates in-plane epitaxy, in addition to the epitaxy in growth direction [2,3]. Therefore, in this work, a heterointerface refers to the intersection within epitaxially-grown single crystal thin films where the film and the substrate show both types of epitaxy. Perhaps, the most popular heterointerface within materials science used in semiconductor applications is
GaAs/Al$_x$Ga$_{1-x}$As [4-6], but recently, there has been growing interest in the STO/LAO heterointerface, the focus of this work.

Interesting phenomena observed at the heterointerface of LaAlO$_3$ (LAO) and SrTiO$_3$ (STO) have been under increasing scrutiny over the past decade. The significance in observing metallic conductivity [7] and even magnetism [8], at this specific heterointerface of two insulating and nonmagnetic perovskites (Figure 1.1), has galvanized immense interest from the scientific community, as it holds possibilities of superconductivity [9] and a new realm of possibilities for oxide electronics applications [13]. Even more interesting is the appearance of a critical thickness of 4 unit cells (u.c.), above which, the observed conductivity is attained. It was also shown that when the film is just below the critical thickness (i.e., 3u.c.), the conductivity of the interface is tunable with the application of an external field like a gate through the use of a conductive Atomic Force Microscopy (AFM) tip [10]. However, the exact origins of the formation of this metallic region at the heterointerface, as well as its tunability, has been hotly debated, and many mechanisms have been proposed and contested, including: (1) electronic reconstructions in the LAO film to avoid a polar catastrophe, (2) formation of oxygen vacancies (VO) throughout the heterostructure [7,10,12], which results in an electron-donation mechanism, (3) cationic balance and intermixing [14,21-24,29], and (4) electronic reconstructions stemming from the presence of surface adsorbates [15-20,26].
Introduction

The polar catastrophe phenomenon states the need for an intrinsic reconstruction to occur within the film in order to avoid a divergence of electrostatic potential as more layers of LAO are grown onto the [001]-oriented, Ti-terminated STO substrate (Figure 1.2). The surface of the Ti-terminated STO substrate is charge-neutral, so a dipole is created as the first positively-charged (LaO)$^{1+}$ layer is deposited on to the charge neutral (TiO$_2$) layer creating a finite electric field increase in potential. The next layer of oppositely charged (AlO$_2$)$^{1-}$ brings the field back to zero and keeps the potential that formed due to the polarization discontinuity at the interface constant. The consecutive layer of (LaO)$^{1+}$ then increases the potential further. This electrostatic potential is substantially low when the films are below the critical thickness of 4 u.c., which can be screened by lattice polarization. However with increasing thickness this potential diverges to physically unsustainable levels resulting in a possible electronic reconstruction to avoid this polar catastrophe. Thus, at this critical thickness, the valence band maximum at the surface effectively overlaps with the conduction band minimum at the interface, resulting in a
charge transfer from the surface to the interface forming the observed metallic behavior, [7,10] termed a 2-dimensional electron gas (2DEG). The problem with this model is the assumption of a defect-free system which credits conductivity solely to intrinsic properties, yet does not explain discrepancies in experimental charge-densities which should be $3.5 \times 10^{14}$ cm$^{-2}$ theoretically. This density corresponds to having one extra electron per two unit cells of STO resulting in average valance of Ti$^{3.5+}$. The same hypothesis suggests that the lack of conduction at the SrO terminated surface is due to the lack of Ti ions forming the conduction band. Instead it is argued that the charge balance is achieved through formation of Oxygen vacancies ($V_O$) (Figure 1.2). The observation of defects like the formation of oxygen vacancies $V_O$, throughout the heterostructure during film processing refutes the defect-free model. $V_O$ are formed at the interface and in the substrate due to the highly energetic ionic bombardment of the deposited ions and the low Oxygen partial pressures used during deposition (e.g., $10^{-4}$ T.orr. $V_O$ can be charge-balanced by electronic disorder with two electrons donated that, can result in high conductivity [12]. Similar results were observed at the surface of the as-deposited films as films annealed in oxygen atmosphere after deposition experienced a significant decrease in conductivity. However, the presence of $V_O$ at the interface or surface alone is not enough to explain the origin of the 2-DEG, and neither is our own work with our collaborators [30]. Regardless, the deposition condition in general was kept to $10^{-4}$ Torr, at which the oxygen defects were negligible based on the Electron Energy Loss Spectroscopy (EELS) studies by our collaborators. In addition, at such partial pressures, the conductivity at the interface was two-dimensional. At lower partial pressures, the existence of $V_O$ increases the charge carriers orders of magnitude from $10^{13}$ cm$^{-2}$ to $>10^{16}$ cm$^{-2}$, and the resulting conduction is not confined anymore, showing three
dimensional characteristics. The as-processed films have also been found to exhibit a degree of cationic intermixing, especially at the interface, which is attributed to the non-equilibrium conditions of deposition and deposition parameters, such as the laser fluence, deposition angle, and the deposition temperature [14,21]. Hand-in-hand with this concept is the idea of cationic stoichiometry, which experimentally attributes conductivity to Aluminum-rich films. A Lanthanum-Aluminum stoichiometry of $\leq 0.97 \pm 0.03$ was therefore proposed for conductivity to occur [21]. Holding precise control over deposition conditions is key to all of the aforementioned extrinsic effects, and it is evident that each effect is supported by experimental data [10,12,14,21].
Figure 1.2. (Top Left) Polar Discontinuity for a Ti-terminated (n-type) STO substrate. A dipole is formed upon deposition of the first (LaO$_2$)$^{1+}$ layer on the neutral substrate. Upon deposition of the (AlO$_2$)$^{1-}$ layer, the electric field is passivated, yet the potential is compounded. This potential continues to increase as the LaAlO$_3$ film grows thicker. (Top Right) Electronic reconstruction for a Ti-terminated (n-type) STO substrate. $\frac{1}{2}$ an electron is transported from the surface (AlO$_2$)$^{1-}$ layer and is transferred per each alternating layer within the LaAlO$_3$ unit cell until it reaches the interface. (Bottom Left) Polar Discontinuity for a Sr-terminated (p-type) STO substrate. Similar to n-type, a potential increases upon compounding deposition of oppositely-charged (AlO$_2$)$^{1-}$ and (LaO$_2$)$^{1+}$ layers. (Bottom Right) Electronic reconstruction for a Sr-terminated (p-type) STO substrate, the opposite mechanism as the n-type reconstruction is required, as $\frac{1}{2}$ a hole needs to be transported from the charge-neutral SrO$_2$ layer to the surface. This mechanism has not yet been observed in experiments [27]

If the intrinsic polar catastrophe model’s weakness is the assumption of perfect crystals, the weakness of the above extrinsic models is the sole focus on just one aspect of the film at a time to describe the characteristics of each film grown with varying deposition conditions. It is thereby worthwhile to propose a unifying theme which takes into account both intrinsic and extrinsic contributions to the formation of the 2DEG at the
interface. In addition, most measurements have been conducted after removing the deposited film from the chamber. Once exposed to atmosphere, the surface is expected to include adsorbed species, both hydrous and carbonaceous. For these ultra-thin films (e.g., 1.2 nm), the changes in the electrostatic environment on the surface can influence the interfacial properties. It was suggested that the dissociation of water on the surface results in H$^+$ ions acting as donors, changing the interface from conducting to an insulating one, or vice versa, with the addition and removal of these surface-adsorbed species by the AFM tip [11]. This work is a part of a greater collaboration that tries to quantitatively identify the effects of all the aforementioned factors together on the observed conductivity and the presence of the critical thickness. The work presented here focuses on the quantification of film composition and surface adsorbates to contribute to the comprehensive understanding of the physics of these complicated heterointerfaces.

This thesis is organized into seven chapters. Chapter 2 introduces the background and the motivation for investigations into surface adsorbate and cationic intermixing
mechanisms. Chapter 3 outlines the processes of sample preparation, as well as deposition conditions, while Chapter 4 provides some understanding of the surface characterization methods used to analyze each film, namely X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS). Chapters 5 and 6 delve into the various investigations into the role of surface adsorbates and the mechanisms of cationic intermixing within the films, respectively. Finally, Chapter 7 provides a summary of conclusions and suggests future work to not only further the understanding of these complicated mechanisms, but to also grow the insight into their interplay.
References


2 Background

2.1 Surface Adsorbates and Conductivity

The link between surface conditions and interfacial properties was first formed by Thiel et al. in 2006, when the tunability of the interface conductivity was achieved locally on samples just below the critical thickness by introducing a conductive AFM tip to the surface [4]. It was observed that a positively biased tip resulted in localized conductivity while a negatively biased tip converted the area back to an insulating environment. The initial conclusion was that a positive or negative bias resulted in oxygen being removed or added to the surface of the films, respectively, resulting in changes in electronic contributions at the interface [5]. This fascinating behavior was then attributed to adsorbed water on the film’s surface in 2010 by Bi et al., who realized that the dissociation of H₂O into OH⁻ and H⁺ ions created the prior observed localized regions under the influence of a biased conductive AFM tip [9], resulting in near-infinite stability of these regions under vacuum for 3 u.c. films. In atmospheric conditions, the conductivity of these regions deteriorated rapidly, but could be sustained indefinitely under vacuum conditions.
Such observations further galvanized scientific interest, and through a series of independent work, it was concluded that: (1) Localized conductivity depended on the
presence of polar liquids [10], with the liquids dissociating into acceptors and donors, which could be picked up by a positive or negatively biased tip; (2) H$_2$O, being a polar molecule, was able to not only dissociate easily into these acceptors (OH$^-$) and donors (H$^+$), but was capable of aligning itself with the electrostatic potential on the surface in order to do so [11]; (3) rapid deterioration of conductivity in samples below the critical thickness could be attributed to instabilities wrought on by an excess of H$_+$ ions either diffusing into, or being desorbed out of the films, after a positively biased tip was introduced, since the extent of diffusion of H is proportional to the thickness of the films [12]; and (4) for the most stable cases, a full monolayer of H$_2$O needed to be present on the film, with $\frac{3}{4}$ of it dissociated and $\frac{1}{4}$ remaining on the surface as a screen to maintain stability [13].

Finally, encompassing the above-mentioned experimental results is the observation that the extent of hydroxylation on the surface of the films can be greatly reduced, either actively or passively, by heating [21], Ar-ion sputtering [28], or through storage in ultra-high vacuum (UHV) over time [22].

### 2.2 Cationic Intermixing

Fabrication of these LAO-STO films is usually accomplished through the process of Pulsed Laser Deposition (PLD), which, because of its highly-energetic occurrence in non-equilibrium conditions, can result in the creation of anion and cation vacancies on the surface of the substrate [6,19]. The creation of V$_{Sr}$ or V$_{Ti}$ at the interface can also affect intermixing throughout the film, as the film is deposited onto a non-equilibrated substrate [17,19]. As stated before, the ideal stoichiometric conditions in order to achieve the desired electron conductivity for films grown in medium O$_2$ partial pressure and above the critical
thickness of 4 u.c. was proposed to be a La/Al ratio of $\leq 0.97 \pm 0.03$ [15], calculated by Warusawithana et al in 2013. The result of this calculation is that Al-rich films are essential for achieving electron conductivity—a result negated both by our calculations and by literature [18,20]. However, this same work also reported the existence of film cation antisites and their effects on the conductivity of the films. It was suggested that Al-rich films contain $\text{Al}_{\text{La}}$ antisite defects. It was also suggested that La-rich films do not form any antisite defects and the Al-poor lattice results in enhancing the diffusion of Al from the interface to the surface to counteract the electrostatic potential building up with thickness and to avoid the polar catastrophe. Indeed, because of the relative atomic radii of La and Al, 240 pm and 184 pm, respectively, the formation of antisites within the film is only a physical reality for $\text{Al}_{\text{La}}$, but not $\text{La}_{\text{Al}}$. Consequently, a "La-rich" film is more of a misnomer, and rather, "La-rich" films should be considered "Al-poor" films.

In the same fashion, a strong correlation between the off-axis plume angle and the subsequent cationic ratios has been formed [18,19,20, 24], most likely explained by the differences in masses of the La and Al cations, which constitute differences in kinetic energies delivered into the growth of the film—exacerbated by this change in plume angle. The significance of Warusawithana et al.’s work proved that although the stoichiometric discrepancies with relation to the plume angle is evident in highly energetic deposition methods such as PLD [17,19], this same physical phenomenon is evident in lower energetic methods which do not exhibit effects from extreme ionic bombardment. By employing the use of Molecular Beam Epitaxy (MBE) and creating a mosaic of cationic ratios relative to the off-axis deposition angles (Figure 2.2), it was possible to prescribe
the ideal plume angle for obtaining stoichiometrically-balanced and consistently conductive films [15].

Figure 2.2. (Left) Mosaic arrangement of substrates for each growth studied by Warusawithana et al. [15] The La/Al ratio was found to decrease from left to right across each mosaic. White circles denote the location of stoichiometric LaAlO$_3$, determined by ex-situ RBS measurements for each mosaic growth. Conductive samples are denoted by green and were found to be located to the right of each white stoichiometric location. (Right) Temperature dependence of resistance is plotted for a representative set of conducting samples from the mosaic growths, named with the mosaic number and sample number.
In addition, studies from both Ohnishi et al. and Qiao et al. have observed that an increasing La/Al ratio in the films have resulted in increased lattice parameters and a subsequent decrease in tetragonality [17,24], introducing an additional complicating factor at the interface—the local strain. Whether the uneven stoichiometry within the films during deposition sparks additional intermixing from the substrate, or vice-versa, is not entirely clear, but intermixing throughout the structure happens readily despite achieving a stoichiometric balance within the films [19]. More specifically, La ions have been found to diffuse a few unit cells in depth across the interface from the film to the substrate, commonly observed as an A-site cation exchange with Sr ions [8,17,25]. In fact, recent research with collaborators has yielded results which suggest V_{Sr} may provide a mechanism for La interdiffusion from the film to the substrate [26]. It is generally

Figure 2.3. Change in La/Al atomic ratio as a function of changing plume angle [20]
deduced that this is a temperature-driven mechanism whose occurrence may consequently result in the out-diffusion of Sr ions into the film, yet an alternate thermodynamic explanation is being cultivated and studied, which attributes the observed in-diffusion of La into the substrate to $V_{Sr}$ formed within the substrate due to the high volatility of Sr at deposition temperatures [17]. This explanation hinges on the postulation that due to the similar atomic radii of La and Sr, 240 pm and 249 pm, respectively, the creation $V_{Sr}$ results in a thermodynamic drive for the in-diffusion of La into the substrate. The implication of this mechanism is that its implementation should result in increasingly Al-rich films.

It is evident that cationic intermixing within the LAO-STO system is a readily-occurring and ubiquitously observed phenomenon. What is important is designating its importance within the narrative of the origin of the 2D electronic gas and the presence of a critical thickness. If changing cationic ratios may result in donors at the interface, there may be implications in how the system responds through the intrinsic mechanism of the polar catastrophe scenario, or how a change in the local strain can change both the presence and confinement of electrical charge carriers, as well as induce additional intermixing to relieve mechanical energy stored in these epitaxial films. Such changes could be manifested in the observation of different critical thicknesses, for example.

### 2.3 Conclusions

It is with the above-mentioned observations in mind that this work was initiated. The link between surface conditions and electron conductivity at the interface is very strong, and this work seeks to expound on observed phenomena by taking into consideration the dissociation of H$_2$O and carbonaceous adventitious species on the film and their
contributions to electrostatic environments on the surface. In the same vein, this work also aims to attempt to understand the mechanisms controlling cationic intermixing within the films. Ultimately, a reconciliation of all these phenomena into a unified theme as highly important extrinsic mechanisms will aid in shedding light on their contributions to electronic conductivity at the interface.
References


3 Sample Fabrication

Fabrication of samples is broken down into two steps, namely, the preparation of the substrate from an as-received crystal and the growth of the film. Each of these steps further consists of two sub-steps. Preparation of the substrate comprises an etching process and an annealing process while epitaxial growth of films on the prepared substrate comprises Pulsed Laser Deposition (PLD) and in-situ Reflection High Energy Electron Diffraction (RHEED).

3.1 As-received Crystal

STO substrates were received from CRYSTAL GmbH and were initially of a mixed termination in their as-received state. These substrates were cut from bulk into 10 x 10 x 0.5 mm plates and subsequently epi-polished on one side. The successful fabrication of a final epitaxial film depends on the integrity of the substrate, and our studies have shown that not all manufacturers share the same quality in manufacturing a substrate suitable for epitaxial growth. The presence of domains hindered the integrity of the substrate, and Figure 3.1 shows the difference between the qualities of substrates from two different manufacturers.
Figure 3.1. (Left) Φ vs. ω scans of substrates from two manufacturers. Bottom crystal demonstrates poorer quality with observable domains. The curvature is due to the miscut angle. (Right) Intensity vs. ω graphs derived from initial Φ vs. ω scans where Φ is approximately 100°, clearly illustrating domains present in bottom crystal.

### 3.2 Etching Process

In order to be able to grow epitaxial films on these substrates, they needed to be changed from their original as-received mixed-termination to a Ti-terminated surface. This was achieved through an etching process using a hydrofluoric acid etchant buffered with ammonium-fluoride. There have been numerous studies on the specifications of this buffered hydrofluoric solution (BHF), prescribing a range of different pH levels [1-3], however, our studies have shown the best pH for our BHF solution was 6. Lower pH solutions and/or longer etching times can result in etch pits on the surface of the substrate, further damaging it. The detailed process for achieving Ti-terminated films is outlined below.
3.2.1 Mixing the Etchant

In order to prepare this BHF solution, stock solutions of 10 M HF and 10 M NH₄F were used. First, 10 ml of the NH₄F was poured into a plastic solution container. A measurement of the pH of this solution with pH strips should be between 8 or 7.5. Since the goal was to reach a final pH of 6, the HF was carefully introduced into the NH₄F solution with a plastic pipette at intervals of 10 drops, checking the pH level gradually. From experience, a pH of 6 was attained after approximately 40 drops of HF acid for 10 ml of ammonium fluoride.

3.2.2 Ti-Termination

Application of the etchant was done with a plastic pipette using the newly mixed pH 6 BHF acid. First, an as-received substrate was placed at the bottom of a small beaker.
Carefully, the BHF acid was pipetted onto the surface of the substrate, forming a domed “bubble” on the top of the crystal. Usually under 5 drops was needed to cover enough of the surface of the crystal without overcoming the surface tension of the BHF and overflowing from the surface of the substrate. After 10 seconds, the acid was quickly flushed with deionized water. After initial flushing, the etched substrate was transferred to another bath of deionized water and then cleaned in an ultra-sonicator for 2 minutes. After cleaning, the substrate was dried with compressed nitrogen to rid it of any remnants.

### 3.2.3 Annealing

Annealing of the etched crystals was done with a Carbolite Eurotherm 2404 tube furnace with a clean ceramic tube (i.e., not used for any other purpose in order to avoid cross-contamination). Annealing was done under ambient oxygen atmosphere with a custom program consisting of a target temperature of 950°C at a ramp rate of 10°C per minute, a dwell time of 60 minutes, and a cooling rate of 5°C per minute to room temperature. Once samples were properly annealed, there is usually a visible color change as the crystals seem to gain a slight yellowish hue. The process of annealing serves as a means to thermally stabilize the newly Ti-terminated surface, and doing so in an oxygenated atmosphere ensures excess Vo within the surface of the substrate are filled. Chemically etched surfaces without annealing afterwards have been shown to degrade significantly in temperatures as low as 300°C [4] over time in a simulation of deposition conditions. This observation is critical, since film deposition for this research occurs at temperatures up to 750°C. This crucial step of annealing results in thermally stable Ti-terminated surfaces exhibiting terraces separated by steps that are approximately 4 Å high, corresponding to the size of the STO unit cell. The terraces were formed due to the miscut angle during manufacturing of the substrates, and this step ensured a clean and well-defined
interface for the resulting film, which is crucial for successful homoepitaxial growth at a temperature of 750°C.

![Figure 3.3. (Left) AFM image of pH 6 BHF acid etched STO substrate resulting in Ti-termination with no visible etch pits. (Middle) Higher magnification AFM image of the same etched and annealed sample. Well-defined terraces are visible across surface due to the miscut angle during manufacturing. (Right) Section analysis showing height of terraces are just under 4 Å](image)

### 3.3 Thin Film Growth

Epitaxial thin film growth was accomplished through a process of pulsed laser deposition. Prior to deposition, the etched and annealed substrates were cleaned in an acetone bath with an ultra-sonicator for two minutes. This was followed by cleaning in a methanol bath for the same amount of time. The clean substrate was then dried with compressed nitrogen in order to rid it of any remnants. Once the substrate was dry, it is mounted onto an inconel sample mount with silver paste. A drop of high temperature silver paste was preferred, but room temperature silver paste was also shown to work if the drop was not very viscous. After 5 minutes that allowed the silver paste to dry in air, the surface was dusted off by compressed nitrogen one last time. Then the sample mount was then loaded into the pulsed laser deposition chamber to undergo the PLD process.
3.3.1 Pulsed Laser Deposition Process

Deposition is then conducted in a pulsed laser deposition chamber (Kurt J. Lesker) in conjunction with a Lambda Physik KrF excimer laser operating at a wavelength of 248 nm. A schematic of the PLD process is displayed in Figure 3.4. The laser was focused onto a spot area of 0.158 cm$^2$, and had a pulse width of 20 ns. The energy of the laser was varied by changing the internal voltage depending on the position of deposition (Figure 3.5) to provide a uniform deposition rate, but its frequency was kept the same at 2 Hz during each deposition. The laser fluence, measured in J/cm$^2$, was calculated by dividing its energy with its spot area following the equation

$$\Phi = \frac{E}{A}$$

(3.1)

where $\Phi$ is the fluence, $E$ is the amount of energy in a pulse of the laser as it ablates the target, in Joules, and $A$ is the size of the spot, in cm$^2$.

For deposition, each substrate was loaded into the chamber on-axis with the ablation target. Because of the orbital shape of the ionic plume and its position, four locations on the inconel sample mount were mapped out where the off-axis plume angle varied. For the most uniform, conductive films, thin films are deposited at the second position on the sample holder, shown in Figure 3.5. This is because the ionic plume is the densest at this position. The most noticeable effect of changing the deposition position and its corresponding off-axis plume angle was the difference in La-Al ratio in the resulting films. Concurrently, during deposition, because the physical density of the ionic plume was less at position four on the sample mount as compared to position two, more pulses of the laser were needed to grow the same thickness of film at position four as at position two. This was corrected by modifying the fluence of the laser.
On average, the laser fluence for samples grown at position two averaged at approximately 1.2 J/cm\(^2\), whereas the average fluence for samples grown at position four was approximately 2 J/cm\(^2\). The standard temperature of deposition was 750\(^\circ\)C, however, for experiments studying temperature-driven intermixing, samples were also grown at 550\(^\circ\)C. At lower temperatures, after the initial epitaxial layers, amorphous films started to form. In all cases, the distance between the substrate and the target was constant at 6 inches. Figures 3.6 and 3.7 display the PLD system, as well as the target and substrate holder post-deposition.

Figure 3.4. Schematic of PLD process. A laser ablates a LAO (001) target which is located across a STO (001) substrate [6]
Figure 3.5. (Left) Picture of different positions on substrate mount marked out by a mask. Position two is directly on-axis with the target and ionic plume, whereas positions one, three, and four have different off-axis plume angles. Next to mask is the substrate mounted in position four. (Right) schematic of plume interaction with the sample position. Highest differences in La-Al stoichiometric ratios are observed at varying deposition positions between positions two and four, as the plume densities have the largest differences at these positions.

Figure 3.6. Picture of the PLD system used at the NASA Glenn Research Center
Figure 3.7. (Left) Picture of both the sample and target loaded inside the PLD chamber. (Middle) Picture of the PLD chamber during deposition. The ablation plume is visible. (Right) Picture of the target and sample holder post-deposition. A dark ring is visible on the target, owing to the traced path of the laser during deposition

3.3.2 Oxygen Partial Pressure

After substrates were mounted into the deposition chamber, the pressure was decreased to the base pressure of approximately $10^{-6}$ Torr achieved with a Leybold vacuum turbo-molecular pump. This base pressure was then varied to deposition pressure by flowing oxygen through a mass flow controller from MKS Instruments. A range of deposition pressures were studied varying from $10^{-6}$ Torr to $10^{-3}$ Torr. The focus of this thesis is on samples that were grown at either the base pressure with no oxygen introduced, or at an oxygen partial pressure of $1\times10^{-4}$ Torr. The presence of oxygen during the deposition process was important to control the formation of oxygen vacancies ($V_O$) throughout the film, at its surface, and in the substrate, which can subsequently affect both the magnitude and confinement of electrical conductivity near the interface [7].
3.3.3 RHEED Intensity Oscillations

During deposition, the thicknesses of the resulting films were monitored in-situ by Reflection High Energy Electron Diffraction (RHEED) intensity oscillations (Staib Instruments). After the aforementioned selective etching and annealing process, the substrates exhibited clearly-defined terraces of unit cell height ($\approx 4 \text{ Å}$). A RHEED pattern was attained by diffracting a high energy electron beam at an angle of low incidence relative to the surface of the substrate. Typical RHEED patterns of the Ti-terminated STO substrate consisted of a high-intensity main specular spot bordered by secondary spots on each side [3], shown left in Figure 3.8. The periodicity of the terraces on the surface resulted in a subsequent periodicity in the secondary spots bordering the main specular spot. Visible Kikuchi lines provided more evidence to the smoothness of the STO surface and the quality of etching in the Ti-termination process. The rate of growth was recorded and monitored using a KSA 400 camera and professional software package, manufactured by K-Space Industries. Sinusoidal oscillations during growth recorded the number of unit cells of LAO epitaxially grown on the Ti-terminated STO surface with each period corresponding to the growth of a monolayer [3]. In high resolution RHEED intensity plots, the roughness on the sinusoidal plots was attributed to each laser pulse, and consequently, the number of pulses for the growth of each layer was monitored and recorded in real time. At the moment of deposition, the RHEED intensity was visibly dampened as a result of the increased scattering from the bombardment of the heavy La atoms during processing (Figure 3.9). Figure 3.10 displays the RHEED intensity oscillations for a 10 unit cell deposition on the top, and on the bottom, a single period of the growth, showing approximately 20 pulses of the laser for the growth of one LAO
layer. After deposition, it is common to observe more blurred streaks than high intensity diffraction spots in the resulting RHEED patterns. This is evidence of the scattering of the RHEED pattern due to the presence of a newly Al-termination on the grown LAO surface relative to the Ti-terminated STO substrate, displayed on the right in Figure 3.8.

Figure 3.8. (Left) RHEED pattern for Ti-terminated STO substrate. High Intensity spots are present, as well as Kikuchi lines. (Right) RHEED pattern for the LAO-STO epitaxial film post 5 u.c. deposition. Pattern is visibly dimmed and spots are more blurred

Figure 3.9. Effects of ionic bombardment on the RHEED intensities of Ti-terminated STO substrates. (Right) The pristine surface does not yield any significant changes in the RHEED intensity (Middle) Once ions bombard the surface, the intensity is significantly decreased (Right) After the growth of a layer is completed, the RHEED intensity increases. This cycle is repeated for each layer grown
3.3.4 Epitaxial Films

The resulting films were confirmed to be epitaxial by X-ray Diffraction both in growth direction with a 2-theta scan and in the in-plane direction through a phi scan of the 002 peak. The strain in both directions were calculated from the lattice mismatch measured by Reciprocal Lattice Mapping. Films were found to demonstrate complete epitaxial growth with respect to the substrate, with the crystallographic relationship [001] STO//[001] Film and [100] STO//[100] Film (Figure 3.11) [11]. Due to the difference in
Sample Fabrication

Lattice parameters of unit cells for STO (3.905 Å) and LAO (3.787 Å) above 435°C, respectively, a strain developed in the [001] plane during heteroepitaxial growth. Any relaxation in the in-plane direction was found to be negligible, as the relaxation rates remained below 4% for films with thicknesses varying from approximately 5 nm to 84 nm (Table 3.1) [11]. Most of this relaxation was in the growth direction.

Figure 3.11. X-ray Diffraction measurements confirming crystallographic relationship between heteroepitaxial growth of LAO on STO in the [001] direction [11]
Table 3.1. Measurements of relaxation rates of LAO grown heteroepitaxially on STO from thicknesses of ≈5 nm to 84 nm. Relaxation was negligible at <4% despite large thicknesses of grown films.

<table>
<thead>
<tr>
<th>Laser Pulse</th>
<th>Thickness (nm)</th>
<th>( f_{pp} )</th>
<th>( f_{pl} )</th>
<th>( \varepsilon_{pp} )</th>
<th>( \varepsilon_{pl} )</th>
<th>( a_{pp} ) (nm)</th>
<th>( a_{pl} ) (nm)</th>
<th>Relaxation Rate</th>
<th>( a_{pp}/a_{pl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.9</td>
<td>-0.03958</td>
<td>-0.00913</td>
<td>0.375045</td>
<td></td>
<td></td>
<td></td>
<td>1.83%</td>
<td>0.965332</td>
</tr>
<tr>
<td>200</td>
<td>7.9</td>
<td>-0.03522</td>
<td>-0.00056</td>
<td>-0.00437</td>
<td>0.03139</td>
<td>0.376750</td>
<td>0.390280</td>
<td>2.48%</td>
<td>0.967165</td>
</tr>
<tr>
<td>500</td>
<td>18.3</td>
<td>0.03358</td>
<td>-0.00076</td>
<td>-0.00268</td>
<td>0.03119</td>
<td>0.377390</td>
<td>0.390202</td>
<td>3.26%</td>
<td>0.967711</td>
</tr>
<tr>
<td>1000</td>
<td>38.4</td>
<td>-0.03326</td>
<td>-0.00100</td>
<td>-0.00261</td>
<td>0.03067</td>
<td>0.377513</td>
<td>0.390109</td>
<td>3.83%</td>
<td>0.967293</td>
</tr>
<tr>
<td>1500</td>
<td>65.4</td>
<td>-0.02987</td>
<td>-0.00117</td>
<td>-0.00321</td>
<td>0.03050</td>
<td>0.377284</td>
<td>0.390041</td>
<td>1.68%</td>
<td>0.967283</td>
</tr>
<tr>
<td>2000</td>
<td>84</td>
<td>-0.03322</td>
<td>-0.00052</td>
<td>-0.00257</td>
<td>0.03117</td>
<td>0.377529</td>
<td>0.390298</td>
<td>1.68%</td>
<td>0.967283</td>
</tr>
</tbody>
</table>
3.4 Samples Prepared

There were 7 films processed at a variety of temperatures, deposition atmosphere and plume angles as defined earlier in this chapter. In addition to the films used as a part of this thesis, films were prepared for our collaborators in the Physics Department at Case Western Reserve University for electrical measurements, and in Ecole De Mines at Paris for Medium Energy Ion Spectroscopy (MEIS) and high-resolution Transmission Electron Microscopy (HRTEM). The films developed as a part of this M.S thesis led to finalization of two Ph.D. theses. In the early parts of the research, additional samples were prepared for some device development at the Electrical Engineering Department of the University of Michigan. In some cases, a full crystal was shared with other collaborators, but in most cases, the films were cut into 4 pieces to ensure that different characterization techniques were applied to the same films—not just to different films grown at the same conditions—in order to minimize error and to develop a better understanding of structure-compositionproperty relationships.

3.5 Conclusions

Ti-terminated STO substrates were prepared by a selective etching process using a BHF acid etchant followed by annealing for thermal stability. LAO films were then grown via Pulsed Laser Deposition at varying O₂ partial pressures and were monitored in-situ via RHEED, demonstrating precise control over growth rates and film thicknesses. Finally,
the integrity of the resulting epitaxial films were confirmed via XRD, proving a crystal-
lographic relationship of [001] STO//[001] Film and [100] STO//[100] Film. The het-
teroepitaxially grown films followed a perfect cube-on-cube symmetry with a negligible
relaxation rate of <4%.
References


4 Surface Characterization Methods

Deposited films were analyzed using two main surface characterization methods, namely X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS). For studying the surface adsorbates, an XPS instrument (Kratos Axis Ultra) equipped with an in-situ heating stage was used. This was performed in the Air Force Office of Scientific Research (AFOSR), located on the Wright-Patterson Air Force Base in Dayton, OH. Studies on cationic intermixing were conducted with a SIMS instrument (PHI TRIFT V nanoTOF Spectrometer) situated in the Swagelok Center for the Surface Analysis of Materials (SCSAM), located on the campus of Case Western Reserve University in Cleveland, OH.

4.1 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) relies on the photoelectric effect, a characteristic of materials which describes the ejection of electrically charged particles from or within a material when it absorbs electromagnetic radiation [1], discovered in 1887 by Heinrich Rudolf Hertz. This phenomenon was crucial to the gradual understanding of the dual nature of light as both a particle and a wave, and proved integral to the development of Modern Physics. XPS relies on the excitation of a material with a focused...
beam of X-rays, and creates a spectral map of the secondary electrons emitted from the material as a function of its binding energy. Figure 4.1 illustrates a schematic for the X-ray Photoelectron Spectroscopy process.

Figure 4.1. Schematic of XPS instrument [4]. 1. Sample is irradiated with a focused beam of X-rays 2. Emitted photoelectrons are focused by a lens and then accelerated through an analyzer 3. A detector records the counts of electrons 4. Information is compounded into a spectrum of Intensity (c/s) vs. Binding Energy (eV)

The energy of the focused X-ray beam is usually greater than or equal to 100 eV, so as to be able to cause emission from not only the valence band, but also from the core levels. An electron spectrometer measures a spectrum of the counts of photo-emitted electrons vs. their respective kinetic energies, $E_K$. In a typical spectrum, each peak corresponds to emissions in either a specific core level within an atom or to secondary Auger electrons arising from the subsequent filling of core-holes. These peaks for each atomic
species are separated by a background, created by the inelastic scattering of photoelectrons. Due to the different symmetries of orbitals, peaks corresponding to emissions from core levels other than the spherical s orbital have different spin-orbit interaction numbers, inversely proportional to the n quantum number, i.e. \( p_{\frac{1}{2}} \) and \( p_{\frac{3}{2}} \) for the p level orbital.

### 4.1.1 XPS Details

As mentioned above, XPS relies on the resulting kinetic energy of an electron after photonic interaction. The amount of kinetic energy an electron possesses is further related to its binding energy, \( E_B \), i.e. the relative strength of its bonds in whatever compound or element it comprises, measured in electronvolts (eV). Core level electrons give a signature of the specific atomic species, and valence electrons, due to their unique degree of ionicity or covalency, affect the position of the initial core level peaks. XPS’s ability to distinguish between each electron and its initial state is what makes it a formidable means of chemical identification and analysis. In fact, it is because of this that XPS is also known as ESCA, Electron Spectroscopy for Chemical Analysis. Due to the conservation of energy principle, the kinetic energy of an electron, \( E_K \), can be expressed as:

\[
E_K = h\nu - E_B - \Phi \tag{4.1}
\]

Conversely, because the final spectrum in XPS is composed of electron counts vs. the binding energies, Equation 4.1 may be expressed as:

\[
E_B = h\nu - E_K - \Phi \tag{4.2}
\]
where $\Phi$ is the work function, the amount of energy needed to transport the photoemitted electron from the sample to the vacuum, and $h\nu$ is the energy of the x-ray beam. XPS is conducted in Ultra-High vacuum (UHV), $\leq 10^{-9}$ Torr, and the work function is required in order for the photoemitted electron to break free into this vacuum. The work function is unique to each sample analyzed, and $h\nu \geq 100$ eV. In short, the binding energy of each electron is found by subtracting its kinetic energy from the initial input beam energy, and then calibrating that result with respect to the individual sample by subtracting its work function. Electrons resulting from the Auger process are not included in this conservation of energy because they rely on internal atomic relaxation and are independent of the photon energy.

In solids, the limit to the depth of probing results from the inelastic mean free path (IMFP) of the electrons within the solid. The IMFP, $\lambda$, is the distance an electron can travel within a material after absorbing a substantial amount of kinetic energy. This means once a sample is irradiated with X-rays, its electrons drift through the material before finally breaking out into vacuum. At energies encountered in XPS, the length of the IMFP is generally 1-2 nm. Due to this, the XPS process is sometimes described by a "three-step" model consisting of:

- Photoemission from the atom
- Electron drift within the solid (IMFP)
- Escape of the electron from the solid into vacuum (Work-function)

The limit to the depth of probing can be understood in detail by looking at the Beer-Lambert Law. The Beer-Lambert Law, expressed by

$$I_d = I_0 e^{\frac{-d}{\lambda \cos(\theta)}}$$  (4.3)
states that the intensity of the signal received from a layer of atoms at a certain depth, \( d \), is less than the signal received from a layer of atoms from the surface by a factor of \( e^{-\frac{d}{\lambda \cos(\Theta)}} \). At 1000 ev, \( \lambda \approx 1.6 \text{ nm} \), hence, at \( 3\lambda \), \( \frac{I_d}{I_0} = 0.05 \). This means, on average, approximately 95% of the signal in XPS comes from a depth of 5 nm or less within the sample, with the limit to its sensitivity being at approximately 10 nm deep. Thus, XPS is classified as a fairly surface-sensitive analysis technique. Furthermore, even greater surface sensitivity may be achieved by changing the angle of the sample relative to the detector. This practice is termed Angle-Resolved XPS.

Figure 4.2. (Left) Regular XPS. Sample is at a 45° angle relative to the x-ray source. (Right) Angle-resolved XPS. By manipulating the angle variable in the Beer-Lambert law (Equation 4.3), greater surface sensitivity (segment in green) may be achieved for the sample. Angle-resolved XPS may be useful in the depth-profiling of certain samples [5]
4.2 Secondary Ion Mass Spectrometry (SIMS)

Secondary Ion Mass Spectrometry (SIMS), is a surface analysis method which relies on the process of "sputtering," the bombardment of a solid sample with an energized particle beam which yields the subsequent ejection of particles from within the sample. As this sputtering occurs, a cascade of collisions takes place, and various particles are ejected (Figure 4.5). Among these "secondary" particles are molecular fragments, whole atoms, and atomic clusters, all of which may be charged. This process essentially relies on the identification of the secondary ions, which make up only about 1% of the ejected...
species [8], through mass analysis. As these secondary ions are accelerated toward the
detector, it is possible to record the "time-of-flight" for each, on the order of nanoseconds from the instant of bombardment to the instant they reach the mass spectrometer. Hence, the method of SIMS used for the purposes of this research is the ToF-SIMS analysis method.

4.2.1 ToF-SIMS Details

Different particle beams yield different degrees of secondary ion emissions. Usually, these are Ga or Cs ionic beams, with particles measuring $\geq 0.1$ keV atom$^{-1}$, resulting in secondary particles emitted at $\approx 1$ nm from the initial point of bombardment [7], due to the cascading nature of the collisions outlined in Figure 4.5. A mass-to-charge ratio is recorded by a time-of-flight mass spectrometer, and this is compiled into a spectrum of Intensity (counts) vs. Mass (amu), which provides very detailed information about the surface of the sample. This is expressed by Equation 4.4, where $s$ denotes the flight path length:

$$\frac{m}{q} = \frac{2eU}{s^2} t^2$$

(4.4)
ToF SIMS is differentiated into three different modes. The above mentioned mode, focusing on surface characterization of very shallow depths (< 1nm), may also be called the Static ToF SIMS mode. This refers to the beam being effectively discharged at such a low energy that only the incident ions from the very top monolayers of the sample are emitted. When the energy is drastically increased, the particles in the beam are strong enough to form a crater in the sample. As the crater is formed, secondary ions from not only the surface, but from the inner bulk of the sample, are also emitted. A rudimentary "depth profile" may be studied once the sputtering time is effectively related to the depth through a calibration of the rate of erosion of the sample. This is referred to as the Dynamic ToF SIMS mode. Finally, the positions of selected secondary ions may be tracked along the surface of the sample in the third mode, the Imaging mode.
The Static mode's downside is that it yields fewer secondary ions, and thus, exhibits a lower accuracy. In contrast, whereas the Dynamic mode increases its accuracy through a significant increase in secondary ions, this method can be extremely destructive to the sample, and the energy of the primary beam spurs localized intermixing, further complicating the integrity of the depth profile. Both modes share a weakness in a lack of quantitative analysis capability, and may be described as semi-quantitative, at best. Finally, the cascading internal collisions from the sputtering process also spur disparities in the proximity of the site of emission to the point of initial bombardment, adding to the challenge of precise spatial mapping. As this research deals with thin films below 5 nm in thickness, great care was taken in using the depth-profiling capabilities of ToF SIMS so as to limit the extent of damage done to each film in the process.
Overall, the strengths of ToF SIMS include its ability to detect the masses of all secondary ions, molecular fragments, and even isotopes, from 1 to 10,000 atomic mass units (amu), with a mass resolution of 0.00x amu, allowing for the easy distinction between particles of the same nominal mass due to the slight shift in mass that occurs when atoms form bonds. Further, its extreme sensitivity to even trace amounts of ions on the order of a few parts per million (ppm) makes it a formidable tool in investigating the chemical integrity of samples such as those used in this research. Finally, SIMS possesses a capability of "retrospective analysis," where, due to its ability to record counts for every secondary particle it encounters in a full mass spectrum, an analyst is able to
retrospectively produce analysis maps for any mass of interest or even study the chemical composition of entire regions of interest well after data acquisition has occurred.

4.3 Conclusions

In conclusion, the two surface analysis techniques used for this research were X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS). XPS was conducted on PLD-grown LAO-STO thin films in the regular mode. Each sample was studied through a survey scan (Figure 4.3), and also in-depth through focusing on the ions of interest. SIMS was conducted on similarly-processed films in both the Static and Dynamic ToF analyses modes. Great care was taken in depth-profiling methods so as to minimize the destruction to the sample as well as localized intermixing spurred by the primary beam bombardment.
References


5 Surface Adsorbates

Due to the highly hydrophilic surface of the LAO-STO films and immediate breaking of vacuum, post-deposition exposure results in the subsequent adsorption of atmospheric moisture and other adsorbates onto the surface of the films. Chapter 2 introduces the link between surface adsorbates and the underlying interfacial properties of the system and credits Thiel et al. for observing the local tunability of the conductivity at the interface by applying a conductive AFM tip to the film [1]. Further investigations into this phenomenon by Bi et al. reported that the dissociation of H$_2$O into H$^+$ and OH$^-$ ions on the surface of these films was responsible for this behavior [2]. The theory suggests that upon the introduction of a biased AFM tip, these H$^+$ and OH$^-$ ions act as electron donors or acceptors, respectively, resulting in a population or depletion of the electron concentration at the interface. Further, the H$^+$ and OH$^-$ ions occupy specific sites on the film surface, forming bonds with surface cations, surface oxygen, or even filling vacancy sites. Evidently, the dissociation of water on the film surface is important to understanding the mechanisms behind changing electrostatic environments on and within the film, but equally as important is the presence of carbonaceous species, which are also spontaneously adsorbed unto the surface.
This chapter reports on investigations into the water dissociation process on the film surface, as well as the presence of carbonaceous species, and implements XPS as a viable means of chemical analysis on the film surface. As outlined in Chapter 4, XPS proves to be an extremely sensitive and minimally-destructive surface analysis method which also harbors excellent chemical analyses capabilities. These traits were employed to distinguish between the different chemical components that make up oxygen and carbon spectra, further understanding the mechanisms related to the presence of surface adsorbates.

### 5.1 Experimental Methods

#### 5.1.1 Sample Processing Conditions

Four LAO-STO samples were fabricated via PLD for these investigations. These films were grown at two different thicknesses (2 u.c. and 5 u.c.), and at two different oxygen partial pressures ($1 \times 10^{-4}$ Torr and $1 \times 10^{-6}$ Torr). Table 5.1 displays the sample processing conditions for the films used in this study.

<table>
<thead>
<tr>
<th>Thickness (u.c.)</th>
<th>Temperature ($^\circ$C)</th>
<th>$O_2$ Partial Pressure (Torr)</th>
<th>Plume Angle (Pos. #)</th>
<th>Deposition Rate (ppl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>750</td>
<td>$1 \times 10^{-4}$</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>$1 \times 10^{-6}$</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>750</td>
<td>$1 \times 10^{-4}$</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>750</td>
<td>$1 \times 10^{-6}$</td>
<td>2</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 5.1. Summary of the processing conditions of four films studied in this experiment. Position number, as refers to the plume angle is the position as marked on the sample holder to give access to densest part of plume (See Chapter 3 for details). PPL, as recorded for deposition rate stands for Pulses per Layer.
5.1.2 XPS

X-ray Photoelectron Spectroscopy was conducted at the Air Force Office of Scientific Research (AFOSR) at the Wright-Patterson Air Force Base in Dayton, OH. Thin films grown via PLD were subjected to XPS with a Kratos Axis Ultra spectrometer outfitted with an in-situ heated stage. Samples were irradiated with a monochromatic AlK$_{\alpha}$ beam with $hv = 1486$ eV in UHV at close to $10^{-10}$ Torr. Survey scans for each sample were conducted at a pass energy of 160 eV, while high resolution scans for La4d, Al2p, Sr3d, Ti2p, O1s, and C1s were conducted at a pass energy of 20 eV. The samples were also subject to charge compensation to neutralize the positive charge buildup on the irradiated surface. For heat treatment experiments, the samples were heated in-situ to $500^\circ$C for up to 10 hours, and the resulting O1s and C1s spectra were propagated and analyzed. Results from these experiments are presented in section 5.2.

5.1.3 XPS Analyses

The resulting spectra from XPS measurements were analyzed via the software, Casa XPS. Some preliminary analyses were conducted on-site at the AFOSR by collaborator, Mike Jespersen, through the software license provided at the Wright Patterson Air Force Base. Further analyses were conducted with the demo version of the software, which allows for the execution of most processes in the software without the need for purchasing a license. All analyses relied on Relative Sensitivity Factor (RSF) values which were calculated for the film cations, La (2.341) and Al (0.193), by calibration with a LAO single crystal and a sapphire (Al$_2$O$_3$) sample, respectively. Likewise, the RSF values for the substrate cations, Sr (3.76) and Ti (3.21), were calculated by calibration with a STO single crystal sample. The RSF values suggested through the Casa XPS library for O (0.78)
and C (0.278) were also used. In conjunction with Casa XPS, an adventitious carbon calculator was employed for quantifying carbonaceous species on the surface of the films. More information about this calculator, created by B.P. Payne et al. [14], may be found in section 5.2.2.

5.2 Data

5.2.1 Surface Adsorbates: O1s Spectra

The nature of surface adsorbates was studied by conducting heat treatments on the films grown. Preliminary XPS measurements were conducted for each sample in vacuum close to $10^{-10}$ Torr. All four films were then heated to $500^\circ$C in-situ, and secondary measurements were conducted. For both sets of measurements, the high resolution O1s spectra were analyzed in Casa XPS, and changes to these regions were attributed to changes in the adsorbed species. Figures 5.1 and 5.2 display the O1s regions for the 2 u.c. and 5 u.c. LAO-STO films, respectively, before and after heating. Tables 5.2 and 5.3 summarize the atomic percentage amounts of all regions of interest for all four films at both room temperature and at $500^\circ$C.
Figure 5.1. O1s Regions for 2 u.c. films at $1 \times 10^{-6}$ Torr and $1 \times 10^{-4}$ Torr. Shoulder peaks located at $\approx 2$ eV away on the left shoulder of O1s regions were noticeably reduced after heating after 2 hours. No further reduction was observed after heating for up to 10 hours.
Figure 5.2. O1s Regions for 5 u.c. films at $1 \times 10^{-6}$ Torr and $1 \times 10^{-4}$ Torr. Shoulder peaks located at $\approx 2$ eV away on the left shoulder of O1s regions were noticeably reduced after heating after 3 hours. No further reduction was observed after heating for up to 10 hours.
Table 5.2. Atomic percentage values for regions of interest for samples at room temperature. O1s region is split into three components: Oxide-Oxygen, defining the main oxygen forming the oxide, and two shoulder peaks at +1 and +2 eV away.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ox-O</th>
<th>+1 eV</th>
<th>+2 eV</th>
<th>La4d</th>
<th>Al2p</th>
<th>C1s</th>
<th>Ti2p</th>
<th>Sr3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 u.c. 10(^{-5}) Torr</td>
<td>27.74</td>
<td>7.40</td>
<td>4.21</td>
<td>6.26</td>
<td>5.71</td>
<td>41.40</td>
<td>3.49</td>
<td>3.78</td>
</tr>
<tr>
<td>2 u.c. 10(^{-4}) Torr</td>
<td>30.97</td>
<td>9.47</td>
<td>3.55</td>
<td>5.07</td>
<td>4.31</td>
<td>37.06</td>
<td>5.13</td>
<td>4.44</td>
</tr>
<tr>
<td>5 u.c. 10(^{-6}) Torr</td>
<td>30.90</td>
<td>8.22</td>
<td>9.82</td>
<td>10.41</td>
<td>9.38</td>
<td>26.60</td>
<td>2.14</td>
<td>2.53</td>
</tr>
<tr>
<td>5 u.c. 10(^{-4}) Torr</td>
<td>27.84</td>
<td>8.35</td>
<td>5.92</td>
<td>8.43</td>
<td>7.56</td>
<td>36.98</td>
<td>2.28</td>
<td>2.64</td>
</tr>
</tbody>
</table>

Table 5.3. Atomic percentage values for regions of interest for samples at 500°C. O1s region is split into two components: Oxide-Oxygen and +1 eV shoulder.

<table>
<thead>
<tr>
<th>Sample (Heated)</th>
<th>Ox-O</th>
<th>+1 eV</th>
<th>La4d</th>
<th>Al2p</th>
<th>C1s</th>
<th>Ti2p</th>
<th>Sr3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 u.c. 10(^{-6}) Torr</td>
<td>34.19</td>
<td>9.13</td>
<td>5.57</td>
<td>5.33</td>
<td>37.31</td>
<td>4.43</td>
<td>4.04</td>
</tr>
<tr>
<td>2 u.c. 10(^{-4}) Torr</td>
<td>33.63</td>
<td>10.28</td>
<td>4.42</td>
<td>4.00</td>
<td>37.24</td>
<td>5.63</td>
<td>4.82</td>
</tr>
<tr>
<td>5 u.c. 10(^{-6}) Torr</td>
<td>36.27</td>
<td>9.64</td>
<td>10.02</td>
<td>8.90</td>
<td>30.09</td>
<td>2.40</td>
<td>2.67</td>
</tr>
<tr>
<td>5 u.c. 10(^{-4}) Torr</td>
<td>37.96</td>
<td>11.38</td>
<td>12.30</td>
<td>10.37</td>
<td>22.91</td>
<td>2.36</td>
<td>2.73</td>
</tr>
</tbody>
</table>
Figure 5.3. Some of the possible dissociation combinations on the surface. Blue indicates event happens specifically after exposing the films to the atmosphere. (Left) H attaches to a surface O, and OH fills a V$_{O}(S)$ site that can form during processing as O$_2$ leaves the system. These two would yield identical results for XPS. (Middle) H is attached to Surface O, but quantitatively, it is not required to fill all the vacant sites. (Right) OH attaches to a cation, and in this case, acts as an acceptor while the OH in the lattice could act as a donor.

Table 5.4. Calculations of binding energies (in eV) per adsorbed molecule(s) in the dissociation of H$_2$O on the AlO$_2$-terminated surface of LAO-STO films [17]. Binding energy here refers to the energy bond formation, and not the electron binding energy in XPS.

<table>
<thead>
<tr>
<th>Model</th>
<th>Description</th>
<th>$E_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>H$_2$O on Al</td>
<td>-2.19</td>
</tr>
<tr>
<td>B</td>
<td>Al$_{\ell}$-OH and O$_x$H next to each other</td>
<td>-3.08</td>
</tr>
<tr>
<td>C</td>
<td>Al$_{\ell}$-O and 2 O$_x$-H</td>
<td>-1.55</td>
</tr>
<tr>
<td>D</td>
<td>Al$_{\ell}$-OH</td>
<td>-0.76</td>
</tr>
<tr>
<td>E</td>
<td>O$_x$-H</td>
<td>-2.25</td>
</tr>
<tr>
<td>F1</td>
<td>Al$_{\ell}$-O and O$_x$-H (close)</td>
<td>-0.78</td>
</tr>
<tr>
<td>F2</td>
<td>Al$_{\ell}$-O and O$_x$-H (far)</td>
<td>0.57</td>
</tr>
<tr>
<td>G</td>
<td>Surface V$_O$</td>
<td>-0.21</td>
</tr>
</tbody>
</table>
Table 5.5. Core-hole binding energy shifts of O-1s state (in eV) relative to center (bulk O) in the LAO slab or center of the STO slab in the LAO/STO/LAO cases. Positive values mean higher binding energy [17]

<table>
<thead>
<tr>
<th>Slab</th>
<th>Slab Termination</th>
<th>Core-Hole Site</th>
<th>CL-B.E. Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAO</td>
<td>Al-OH+O-H</td>
<td>O-H</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>OH-Al</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>Al-OH</td>
<td>O-H</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>-0.68</td>
</tr>
<tr>
<td></td>
<td>Al-OH(^{-1})</td>
<td>OH-Al</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>O-H</td>
<td>O-H</td>
<td>2.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>-0.14</td>
</tr>
<tr>
<td></td>
<td>VO</td>
<td>O</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>V(_0)+Al-OH</td>
<td>OH-Al</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>-0.45</td>
</tr>
<tr>
<td></td>
<td>V(_0)+O-H</td>
<td>O-H</td>
<td>3.17</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>COH</td>
<td>O on COH</td>
<td>6.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O beneath COH</td>
<td>5.08</td>
</tr>
<tr>
<td></td>
<td>COH with</td>
<td>O on COH</td>
<td>5.07</td>
</tr>
<tr>
<td></td>
<td>Al-OH+O-H</td>
<td>O beneath COH</td>
<td>3.57</td>
</tr>
<tr>
<td>LAO/STO</td>
<td>Al-OH+O-H</td>
<td>O-H</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>OH-Al</td>
<td>-0.19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>-1.08</td>
</tr>
</tbody>
</table>

**Discussion.** The presence of shoulder peaks on the higher binding energy side of the O1s peak was observed for both thicknesses of films. These shoulder peaks were located at +1 and +2 eV away from the main oxide peak. Historically, these shoulders on the O1s regions have been related to hydroxylation of the Al-terminated LAO surface due to H\(_2\)O dissociation (Figure 5.3). More specifically, the +2 eV peak has been linked to adventitious OH bonded to surface cations. Literature supports these observations in different metal oxides, including Al [3], Zn [4], Ni [5], and La [6], with a 1.3 eV binding energy shoulder for Al, and the last three resulting in approximately 2 eV binding energy shoulders, in their O1s spectra. In this case, the +2 eV peak, was shown to be desorbed easier from the surface. As the samples were heated, a noticeable reduction in the +2 eV shoulder peaks was observed (Figures 5.1 and 5.2). The reduction in this third peak was
calculated by first fitting two peaks to the heated O1s region. Attaining a perfect fit with two peaks confirmed that the heating process had rid the sample of whatever weaker bound adventitious species there were, and that more tightly bound +1 eV species in the lattice remained. This fit resulted in no change in the +1 eV : Oxide O ratio calculated for both the 2 u.c. and 5 u.c. films grown at varying partial pressures before and after heating. For the 2 u.c. film grown at 1×10^{-6} Torr, this ratio was 0.267, whereas that for the 5 u.c. film grown at the same pressure was 0.266. Likewise, for the 2 u.c. film grown at 1×10^{-4} Torr, the ratio was 0.306, whereas that for the 5 u.c. film grown at the same pressure was 0.300. Once these ratios were established, the second satellite peak +2 eV away was calculated by keeping the ratio of the +1 eV peak constant in the room temperature measurements and then finding the difference remaining through fitting a third peak (Figures 5.1 and 5.2, top). For the 2 u.c. film grown at 1×10^{-6} Torr, the +2 eV : Oxide O ratio was 0.152, whereas that for the 5 u.c. film grown at the same pressure was 0.318. Comparatively, for the 2 u.c. film grown at 1×10^{-4} Torr, the +2 eV : Oxide O ratio was 0.115, whereas that for the 5 u.c. film grown at the same pressure was 0.213.

The significance of these calculations is that the samples grown at a lower O2 partial pressure (1×10^{-6} Torr), and thus, containing more V_{O} on the STO surface, both exhibited lower +1 eV : Oxide O ratios (Figures 5.1 and 5.2). Recent work [17] with collaborators from the Department of Physics at CWRU, Fongkaew et al., yielded calculations into the filling of a V_{O} by an OH molecule yielded a reaction energy of -2.05 eV, in comparison with a -2.25 eV energy of a surface O + H bond. In the same collaborative work, computational models were executed which calculated formation energies for the different bonds of interest associated with the H2O dissociation mechanism, namely Al + OH, VO + OH, or O + H bonds. Table 5.4 summarizes these "binding energies," which refer to the
energies of the bonds, and not the electron binding energy in XPS. These calculations are extremely insightful to the understanding of the XPS data in Figures 5.1 and 5.2.

From this data, it can be concluded that not only is it energetically favorable to have H$_2$O dissociate into Al-OH and O-H on the surface, but indeed, OH is much easier desorbed from Al than H is from O. This would generally be in agreement with the observed loss of the +2eV peak with heating if that peak were defined as the adventitious OH peak. However, further calculations by collaborators [17], concerning the shifts in the core binding energies in oxygen ions occurring with the presence of adventitious OH showed that for Al-OH and O-H bonds, the positions for their peaks are not more than 1eV away from the main oxide peak for this system (Table 5.5). With this knowledge, it would be incorrect to attribute the +2 eV shoulder peak to the hydroxylated Al-OH or even surface O-H species. In addition to this observation, both OH and H are found to be too strongly bonded to Al and O on the surface to be desorbed thermally when $k_B T$ is calculated at 500$^0$C.

So far, adventitious species in the O1s regions have been observed, and the tendency of H$_2$O dissociation on the surface is confirmed through modeling and calculations. Yet, the question still remains as to the origin of the +2 eV peak, and why it is easily desorbed after heat treatments. This research thus sought to answer this question by studying the C1s regions in tandem with the prior observed O1s calculations.

5.2.2 Surface Adsorbates: C1s Spectra

In addition to studying H$_2$O dissociation in the form of surface adsorbates, it was important to understand the contribution of adventitious carbon in this equation. B.P. Payne et al., established this contribution by studying the C1s peak in detail [14]. As samples are introduced to ambient atmosphere post-deposition, this adventitious carbon acts as
one of the greatest contaminants on the film surface and physically bonds on the surface as different carbonaceous species. Due to this, it was imperative to find a link between the amount of oxygen on the surface and these carbonaceous species. The C1s may be split into four components, displayed in Figures 5.4 - 5.7. For the four samples studied in Section 5.2.1, C1s regions were studied both before and after heat treatments at 500°C. Just as a reduction of the +2 eV shoulder peaks were observed before, a similar reduction of shoulder components of the C1s region was observed.

Figure 5.4. C1s Regions for 2 u.c. film grown at 1x10^-6 Torr. Carbon is split into four components: 1. The main peak containing no oxygen (Peak A) 2. Methyl-alcohol, dimethyl ether, and ester (Peak B) 3. Ketones (Peak C) and 4. Carboxylic Acid (Peak D). After heating, a total reduction in the ketone peak (Peak C) is observed.
Figure 5.5. C1s Regions for 2 u.c. film grown at $1 \times 10^{-4}$ Torr. Carbon is split into four components: 1. The main peak containing no oxygen (Peak A) 2. Methyl-alcohol, dimethyl ether, and ester (Peak B) 3. Ketones (Peak C) and 4. Carboxylic Acid (Peak D). After heating, a total reduction in the ketone peak (Peak C) is observed.
Surface Adsorbates

Figure 5.6. C1s Regions for 5 u.c. film grown at $1 \times 10^{-6}$ Torr. Carbon is split into four components: 1. The main peak containing no oxygen (Peak A) 2. Methyl-alcohol, dimethyl ether, and ester (Peak B) 3. Ketones (Peak C) and 4. Carboxylic Acid (Peak D). After heating, a total reduction in the ketone peak (Peak C) is observed.
Figure 5.7. C1s Regions for 5 u.c. film grown at 1x10^{-4} Torr. Carbon is split into four components: 1. The main peak containing no oxygen (Peak A) 2. Methyl-alcohol, dimethyl ether, and ester (Peak B) 3. Ketones (Peak C) and 4. Carboxylic Acid (Peak D). After heating, a total reduction in the ketone peak (Peak C) is observed.
Table 5.6. Initial and final percentage amounts for each component comprising the C1s Region for all four samples. After heat treatments at 500°C, significant reductions in Peaks B and D were observed, while Peak C was completely reduced. This corresponds to a loss of the Ketone component of the adventitious carbon species.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Initial</th>
<th>Final</th>
<th>Initial</th>
<th>Final</th>
<th>Initial</th>
<th>Final</th>
<th>Initial</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak A</td>
<td>60.85</td>
<td>79.84</td>
<td>47.31</td>
<td>64.36</td>
<td>55.15</td>
<td>77.79</td>
<td>52.63</td>
<td>75.23</td>
</tr>
<tr>
<td>Peak B (CH₃-OH)</td>
<td>24.32</td>
<td>17.89</td>
<td>25.98</td>
<td>30.54</td>
<td>24.70</td>
<td>18.77</td>
<td>32.51</td>
<td>21.89</td>
</tr>
<tr>
<td>Peak C (CH₃-(C=0)-CH₃)</td>
<td>8.86</td>
<td>0</td>
<td>18.24</td>
<td>0</td>
<td>9.71</td>
<td>0</td>
<td>6.35</td>
<td>0</td>
</tr>
<tr>
<td>Peak D (CH₃-(C=O)-O-H)</td>
<td>5.97</td>
<td>2.27</td>
<td>8.47</td>
<td>5.11</td>
<td>10.45</td>
<td>3.44</td>
<td>8.51</td>
<td>2.28</td>
</tr>
</tbody>
</table>

Table 5.7. Core level binding energies relative to vacuum, and core-hole binding energy shifts of O1s state (in eV) in the different molecules relative to center of a LAO slab (already covered with OH and H) after aligning them with the vacuum level (539.05 eV). Ester and Carboxylic Acid components exhibit a ≈ 2 eV shift, corresponding to the observed ≈ 2 eV reduction in O1s regions [17].

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Chemical Formula</th>
<th>O-Site</th>
<th>Screened</th>
<th>Shift</th>
<th>Initial</th>
<th>Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hline Bare Ref.</td>
<td></td>
<td></td>
<td>539.05</td>
<td>0.00</td>
<td>505.34</td>
<td>0.00</td>
</tr>
<tr>
<td>Water</td>
<td>H₂O</td>
<td>540.39</td>
<td>1.34</td>
<td>506.45</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃-OH</td>
<td>539.97</td>
<td>0.95</td>
<td>505.39</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>CH₃-CH₂-OH</td>
<td>540.13</td>
<td>1.19</td>
<td>506.40</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>Dimethyl Ether</td>
<td>CH₃-O-CH₃</td>
<td>540.72</td>
<td>1.68</td>
<td>506.66</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>CH₂-CH₂-O-CH₂-CH₃</td>
<td>540.71</td>
<td>1.66</td>
<td>506.38</td>
<td>1.04</td>
<td></td>
</tr>
<tr>
<td>Ketone</td>
<td>CH₃-(C=O)-CH₃</td>
<td>538.53</td>
<td>-0.50</td>
<td>506.08</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td>Ester</td>
<td>CH₂-(C=O)-O-CH₃</td>
<td>C=O</td>
<td>538.67</td>
<td>-0.38</td>
<td>505.96</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-O-C</td>
<td>540.99</td>
<td>1.94</td>
<td>507.86</td>
<td>2.2</td>
</tr>
<tr>
<td>Carboxylic Acid</td>
<td>CH₂-(C=O)-O-H</td>
<td>C=O</td>
<td>538.95</td>
<td>-0.10</td>
<td>506.31</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-O-H</td>
<td>540.85</td>
<td>1.80</td>
<td>507.70</td>
<td>2.1</td>
</tr>
<tr>
<td>Carbonate</td>
<td>CO₃</td>
<td>C=O</td>
<td>541.37</td>
<td>2.32</td>
<td>509.97</td>
<td>4.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-O</td>
<td>541.47</td>
<td>2.42</td>
<td>509.80</td>
<td>4.53</td>
</tr>
</tbody>
</table>
Discussion. From Payne et al. [14], a random adventitious carbon sample exhibits five main components: 1. the main carbon peak (C-C and C-H), expected to contain no oxygen, 2. a peak containing methy-alcohol (CH\textsubscript{3}-OH), dimethyl ether (\textsubscript{2}H\textsubscript{5})\textsubscript{2}O, and ester (CH\textsubscript{3}-(C=O)-O-CH\textsubscript{3}), 3. a peak containing ketones (CH\textsubscript{3}-(C=O)-CH\textsubscript{3}), 4. a peak containing carboxylic acid (CH\textsubscript{3}-(C=O)-O-H) and ester (CH\textsubscript{3}-(C=O)-O-CH\textsubscript{2}), and 5. a peak containing carbonates (CO\textsubscript{3}). For the LAO-STO samples used in these investigations, there are no observed carbonate components. Because of this, the four former components are used for analyzing the C1s region (Figures 5.4-5.7). In comparing the results before and after heating, there is a significant reduction in Peaks B and D, with Peak C, the Ketone component, being entirely eliminated after heat treatments (Table 5.6). These results make sense, considering the fact that the heat treatments at 500\textdegree C do rid the sample of some adventitious species. The reductions in Peaks B and D, in particular, are of particular importance because the Ester component in Peak D is directly proportional to that of Peak B. This assumption is one that is critical to the proper splitting of the carbonaceous species, and a proper observation of their reductions and oxygen contents. Due to this, one would expect similar behavior for these two peaks in terms of binding energy shifts. In addition, the total elimination of the Ketone in Peak C begs the question as to its effect on the electrostatic environment. It is easy to ascribe the origin of the +2 eV peak in O1s regions to the Ketone in Peak C, since they are both eliminated after subsequent heat treatments. Yet, there is a more nuanced explanation for this.

Once more, current work with collaborators from the Department of Physics at CWRU, Fongkaew et al. [17], sought to show links between the observed O1s reduction of the +2 eV peak and these observed C1s reductions, and suggests that the elimination of the +2
eV peak is not due to OH being thermally desorbed from the surface, but rather, due to the loss in these carbonaceous species, mainly the Ester and Carboxylic acid components of Peaks B and D. This hinges on a comparison of similar core binding energy shifts detected in the both the C1s regions after heat treatments at 500°C and the O1s spectra, and the fact that both OH and H are too strongly bonded to Al and O on the surface (Table 5.3) to be desorbed thermally in $k_B T$ at 500°C. In studying the core binding energy shifts of the components comprising carbonaceous species (Table 5.7), the Ester and Carboxylic acid components (Peaks B and D) yield $\approx 2$ eV shifts, whereas that of the Ketone component (Peak C) is only $\approx 0.74$. Hence, despite a total reduction of the Ketone in the C1s region, it can be concluded that the observed +2 eV peak reduction in O1s may be related more to O in physisorbed Ester and Carboxylic acid species on the surface of the films.

The ascribing of the +2 eV peak reduction to these physisorbed carbonaceous species rather than the previously thought chemisorbed hydrous species means that this reduction does not provide any net changes in the 2DEG properties of these films, nor its tunability. Rather, these adventitious carbon species adsorb spontaneously with ambient exposure, and can be easily removed via heat treatments.

### 5.2.3 Re-Adsorption: O1s Spectra

To demonstrate the spontaneity of the mechanism of surface adsorbates, a re-adsorption study was conducted on the 5 u.c. film grown at $1 \times 10^{-6}$ Torr previously studied in Section 5.2.1. After heat treatments were conducted in situ (10-10 Torr) at 500°C (Figure 5.2), the 5 u.c. sample was left exposed in ambient atmosphere for 24 hours, and then subsequent XPS studies were conducted on the O1s region. A re-introduction of the +2...
eV shoulder peak was observed, despite being reduced during the heat treatment. Figure 5.3 displays the evolution of the presence of the +2 eV peak for this film.

![Graph showing O1s regions of a 5 u.c. film grown at 1x10^{-6} Torr.](image)

**Figure 5.8.** O1s Regions of a 5 u.c. film grown at 1x10^{-6} Torr. (Left) Sample at room temperature, 2 eV peak is present, as expected. (Middle) Sample after heating in-situ at 500°C at 3 hours. Only +1 eV peak remains at the shoulder. (Left) Sample after exposure to ambient atmosphere for 24 hours. +2 eV peak is again present, confirming a spontaneous adsorption mechanism due to atmospheric moisture

**Discussion.** As expected, the presence of the +2 eV peak was evident in the initial room temperature measurement of the sample (Figure 5.3, Left). Quite similarly to the process explained in Section 5.2.1.1, ratios for the two shoulder peak components in the O1s spectra were calculated by first finding a perfect fit for the +1 eV component after heat treatment at 500°C, keeping that ratio constant for the room temperature measurements, and ascribing the remaining component to the +2 eV species. Interestingly, the +2 eV ratio was significantly lower now than previously reported in Figure 5.2. Even more interesting is the fact that upon re-introduction to atmosphere for 24 hours after heat treatment, the +2 eV shoulder peak seems to be 9% larger than before (Figure 5.3, Right). This is very important in understanding the nature of hydroxylation. This
data demonstrates the spontaneity of adventitious species interacting with the film, and also gives rise to the notion of the instability of the +2 eV species once exposed into atmosphere. It is safe to deduce that the amount of +2 eV detected on the films is very atmosphere-dependent, with different amounts of the +2 eV species observed, perhaps, on different days or locations exhibiting different humidity readings with different organic carbonaceous species in the air. Such a deduction is also further supported by Liu et al., observed increased hydroxylation on the single crystal corundum ($\alpha-Al_2O_3$) surface only when certain threshold pressures were met [16], i.e. near-ambient atmosphere pressures.

5.3 Conclusions

In conclusion, this chapter sought to comprehend the nature of adsorbed species on the surface of LAO-STO films. By depositing four films of varying thicknesses at varying pressures and applying heat treatments, a detailed study of the O1s regions was conducted where these regions were split into three components, namely, Oxide-O, a +1 eV shoulder, and a +2 eV shoulder. Regardless of thickness, samples grown at lower O$_2$ partial pressures reported lower ratios for +1 eV, and vice versa for +2 eV species (Figures 5.1 and 5.2). The origin of the +2 eV peak was established by noting the contribution of adventitious carbon to this mechanism, and a relationship between the reduction in the +2 eV peak from O1s spectra and subsequent reductions in the Ester and Carboxylic acid components from C1s regions was proposed (Figures 5.4 - 5.7, Tables 5.5 and 5.6) through studies of corresponding core binding energy shifts for all species of interest. Finally, all of these investigations were concluded by noting spontaneity in the nature of
adsorption on the surface in Section 5.2.3, as a sample was recorded through its desorption and re-adsorption of the +2 eV species after heat treatment and subsequent exposure to ambient atmosphere for 24 hours. The added complexity in this mechanism was evident, as the +2 eV component seemed to differ, not only before and after heat treatments, but also with initial reports in Section 5.2.1. A connection between observed adsorbate population and the ambient pressures was then established as a cause of these observations (Figure 5.3), giving rise to the belief that not only humidity, but other ambient species play a role in the behavior of these surfaces and heterointerfaces, and all may work hand-in-hand to define this extremely complex system's behavior.
References


[16] P. Liu et al., Reaction of Water Vapor with $\alpha$-Al$_2$O$_3$(0001) and $\alpha$-Fe$_2$O$_3$(0001) Surfaces: Synchrotron X-ray Photoemission Studies and Thermodynamic Calculations, Surface Science 417:1, 53-65 (1998)


[18] Q. Fu et al., Hydroxylated a-Al$_2$O$_3$ (0001) Surfaces and Metal/a-Al$_2$O$_3$ (0001) Interfaces, Surface Science 600, 4870-4877 (2006)


6 Cationic Intermixing

As stated in Chapter 2 and further expounded in Chapter 3, fabrication of the LAO-STO thin films used for this research is accomplished through the process of Pulsed Laser Deposition (PLD). Owing to the highly-energetic occurrence of the PLD process in non-equilibrium conditions, there is a creation of anion and cation vacancies on the surface of the substrate [1,2]. Subsequently, investigations have reported that when $V_{Sr}$ are created at the interface on the non-equilibrated STO substrate, there are noticeable changes in intermixing throughout the film [2,6]. In addition, intermixing is also a mechanism that can decrease the electrostatic potential that builds up as the films get thicker due to the initial polarization continuity at the interface (as introduced in Chapter 1). Since the point defects and intermixing detected at both the interface and throughout the film can be caused by the changing electrostatic environments, it is important to device effective means for in-depth observation of the film and the interface. Generally, cationic intermixing at the interface and throughout the film is studied by microscopy methods such as Scanning Transmission Electron Microscopy (STEM) [11,13-15], Electron Energy Loss Spectroscopy (EELS) [10,11,13,15], and Medium-Energy Ion Spectroscopy (MEIS) [11,12,14]. As effective as these microscopy methods are, there are
a few drawbacks to using them expansively, which include extensive sample preparation, limited scope of view of the interface, destruction of the sample, time-intensiveness, costs, and instrument availability. Furthermore, as this research is part of a larger body of collaborative work, it was important to choose a means of studying intermixing at the interface which was different from these microscopy methods, so as to build confidence in independently observed results.

The surface characterization technique of ToF SIMS was used in this study because of its capability for depth-profiling and its extreme sensitivity of emitted secondary ions for characterization methods, as outlined in Chapter 4. The depth-profiling capability of ToF SIMS was paired with a proprietary analysis method developed by Dr. Kevin Abassi of Case Western Reserve University, which allowed for the statistic representation of secondary ions and molecular fragments of interest retrospectively from the acquired SIMS data.

6.1 Experimental Methods

6.1.1 Sample Processing Conditions

Varying thicknesses of LAO-STO films were grown via PLD at different deposition temperatures and at a constant oxygen partial pressure. Table 6.1 displays the parameters for three different kinds of films grown. Each processing condition was repeated at least three times to ensure reliability of samples and repeatability of data.
Table 6.1. Summary of the processing conditions of three films studied in this experiment. Positon number, as refers to the plume angle is the positon as marked on the sample holder to give access to densest part of plume (See Chapter 3 for details). PPL, as recorded for deposition rate stands for Pulses per Layer

<table>
<thead>
<tr>
<th>Thickness (u.c.)</th>
<th>Temperature (°C)</th>
<th>O₂ Partial Pressure (Torr)</th>
<th>Plume Angle (Pos. #)</th>
<th>Deposition Rate (ppl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>750</td>
<td>1 x 10⁻⁴</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>750</td>
<td>1 x 10⁻⁴</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>550</td>
<td>1 x 10⁻⁴</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>

6.1.2 ToF SIMS

ToF SIMS experiments were conducted in the Swagelok Center for the Surface Analysis of Materials (SCSAM), with a PHI TRIFT V nanoTOF Spectrometer. The ToF SIMS instrument was ran in both Static and Dynamic modes. Static mode experiments were conducted to study surface conditions of STO substrates in order to find trace contaminants. For these measurements, a Ga⁺ beam was used in positive ion mode at a beam current of 30 kV. A mass range of 0 - 500 amu was then analyzed by the ToF Spectrometer. Dynamic mode experiments were conducted in order to study depth-profiles of films. Depth-profile experiments were tailored to these samples, with care taken to ensure very limited localized intermixing spurred by the primary beam. With this in mind, each film was subject to sputtering with an Ar⁺ beam at 3 kV in positive ion mode. A mass range of 0 - 500 amu was then analyzed by the ToF Spectrometer. Positive ion mode was found to be best for these samples because of the higher yield of the cations of interest.
in both the film and the substrate. The interaction volume of each depth-profile experiment was a crater of size $\approx 250\mu m \times 250\mu m$ stretched to a depth of 80 sputtering layers. The results of these experiments are reported in section 6.2.

### 6.1.3 ToF SIMS Analysis

Analysis for ToF SIMS was conducted with proprietary codes created in Matlab by collaborator, Dr. Kevin Abassi of Case Western Reserve University. The analysis codes made use of the SIMS’s capability of "retrospective analysis" by transferring every count of data analyzed in the depth profile crater into a statistical grid. An extremely detailed representation of the mean counts of the ionic and molecular species throughout the film, interface, and substrate was gleaned from this analysis. By selecting secondary ions and molecular fragments of interest, this massive information was made useful in a statistically relevant manner. This statistical representation was projected visually via 3D rendering in Avizo software, and also graphically in histograms generated in Matlab. Data from this analysis is further reported in section 6.2. The proprietary codes used in this analysis were generated in collaboration with Physical Electronics (PHI), and are not subject to detailed discussion in this thesis.

### 6.2 Data

#### 6.2.1 Depth-Profiles and Analyses

ToF SIMS was employed to study the depth profiles of 10 u.c. and 5 u.c. films grown at $750^\circ C$. Upon calibration for erosion rate of the films, 80 sputtering layers were used for depth-profiles of a sampled area of $\approx 250\mu m \times 250\mu m$. ToF SIMS data were analyzed
through Matlab, and statistical representations of the mean ionic and molecular fragment counts were generated for the sputtered volume for each film. Results of mean ionic and molecular fragment counts were then represented graphically by histograms in Matlab, as well as visually by 3D rendering in Avizo. Figures 6.1 and 6.2 display such representations of the statistical distribution of ions and fragments in the sputtered volume for a 10 u.c. film grown at 750°C and 1×10⁻⁴ Torr in both histogram and 3D forms.

Figure 6.1. Histogram of mean counts for secondary ions and molecular fragments encountered during depth profile sputtering. A crater size of ≈ 250μm x 250μm was studied with a sputtering depth of 80 layers. Four inflection points of interest were marked, which reflect the changes in sputtering rates from the film to the substrate.
**Discussion.** Histograms generated in Matlab were observed to exhibit inflection points, owing to the changing sputtering rates as the primary beam interacts with different secondary ions and molecular fragments from the film through the substrate. If intermixing was present through the film, these inflection points should be a visual guide to the statistical limits for cationic intermixing. Four main inflection points of interest were marked for the histogram in Figure 6.1, and through these, four main areas of interest in studying cationic intermixing were determined:

1. Upper limit of substrate cation diffusion into the film
2. Position of the original interface
3. Lower limit of film cation diffusion into the substrate
(4) Pristine substrate

The upper and lower limits of intermixing were based on statistically significant data. It does not imply that there is no intermixing further than those layers. The position of the interface was determined to be inflection point #2, located at \( \approx 25 \) sputtering layers deep, due to it being the largest inflection point (Figure 6.1). This was determined deductively, as hypothetically, the interface should exhibit the greatest change in sputtering rate when the primary beam interacts with changing ionic and molecular species from the film going into the substrate. However, such a clear inflection cannot be observed in every film and does not form a good basis for standard procedure. As will be discussed later, an alternative method of marking the original interface will be introduced. All four inflection points of interest were then transposed onto the 3D projection in Avizo (Figure 6.2) as planes bisecting the sampled volume. These served as a guide to the eye and as a visual confirmation of the deduced conclusions in marking the interface and separating the film from the substrate.

### 6.2.2 Limits of Intermixing

As stated before, the first and third inflection points were determined to be the statistical upper limit of the substrate cation diffusion into the film, and the statistical lower limit of the film cation diffusion into the substrate, respectively. These deductions were confirmed by calibrating the known thickness of the film to the determined location of the substrate (\( \approx 25 \) sputtering layers). For the 10 u.c. film shown in Figures 6.1 and 6.2, this calibration means a single sputtering layer is equivalent to \( \approx 0.4 \) unit cells. Four ions and two molecular fragments from the film and substrate were studied (La, Sr, Al, Ti, Ti+O and La+O), and the ranges of statistically relevant interdiffusion were estimated. These
ranges were then projected in the 3D rendering images, and served as a visual confirmation of the upper and lower limits of diffusion from the substrate to the film, and vice versa.

Figure 6.3. 3D rendering of the estimated statistically significant upper bound of substrate cation interdiffusion into the film. Intensities of secondary emissions for Sr, Ti, and Ti+O were projected within the sampled volume. Upper limit of interdiffusion (inflection point #1) was determined to be ≈ 5 u.c. into the film, with the densest population at ≈ 3 u.c. Beyond inflection point #1, there is still some interdiffusion, although, not as statistically significant
Figure 6.4. 3D rendering of the estimated statistically significant lower bound of film cation interdiffusion into the substrate. Intensities of secondary emissions for La, Al, and La+O were projected within the sampled volume. Lower limit of interdiffusion (inflection point #3) was determined to be $\approx 7$ u.c. into the substrate, with the densest population at $\approx 4$ u.c. Beyond inflection point #3, there is still some interdiffusion, although, not as statistically significant. Beyond inflection point #4, there are no visible secondary emissions, and the pristine substrate is expected to exist.
Discussion. Since inflection points #1 and #3 were determined from the histogram to be the upper and lower limits of cation interdiffusion, it was important to translate the range and limits of intermixing into a tangible unit cell thickness. Calibrating these bounds with the known film thickness (10 u.c.) and known erosion rate of the film ($\approx 0.4$ u.c./sputtering layer) yields a statistically significant upper bound of substrate cation interdiffusion into the film at $\approx 5$ u.c., with the highest density at $\approx 3$ u.c., determined from intensity analyses (Figure 6.3). Likewise, assuming a near-similar erosion rate for the substrate, the statistically significant lower bound of film cation interdiffusion into the substrate was estimated at $\approx 7$ u.c., with the highest density at $\approx 4$ u.c. (Figure 6.4). It is important to note that visually, beyond these inflection point limits, there were still visible counts of secondary ion and molecular fragment emissions. However, neither of these proved to be as statistically significant when studied with intensity analyses.
Moreover, it is important to note that beyond inflection point #4, there is no evidence of any secondary emissions, further supporting this point as a boundary of the pristine substrate.

### 6.2.3 Location of the Interface

According to the histogram in Figure 6.1, the location of the interface was approximated by a deduction which related the largest inflection point to the most significant rate of change in sputtering, and subsequently, the change from the film into the substrate. This location was determined to be at approximately 25 sputtering layers into the sample. In order to further solidify the accuracy of this statistical analysis, a means of confirming this approximate location was devised through making use of residual amounts of Cr\(^+\) ion contamination found on the surface of the substrates after surface analyses in static mode. Utilizing SIMS’s capability of elemental analysis on the ppm scale, a profile of this trace amount of Cr\(^+\) was found on the very surface of the Ti-terminated STO substrate, displayed in Figure 6.6. This trace amount of Cr\(^+\) was employed as a marker for the location of the interface once the LAO-STO films were grown. A plot of the mean counts for the Cr\(^+\) found in the 10 u.c. sample during the 80 sputtering layers is then displayed in Figure 6.7. The location of the peak of the Cr\(^+\) ions (25 sputtering layers) signifies the location of the interface, and was found to confirm the approximated location from the histogram analysis in Figure 6.1.
Figure 6.6. (Top) Surface analysis of mixed-terminated STO substrate. No significant counts of Cr$^+$ ions were present. (Bottom) Surface analysis of Ti-terminated STO substrate. Etching and annealing process reports the presence of trace amounts of $^{52}\text{Cr}^+$ ions peaking at 51.9360 amu. Residual contamination may be introduced from the furnace used for annealing substrates.
Figure 6.7. Plot of mean counts per sputtering layer of Cr$^+$ ions for 10 u.c. LAO-STO film grown at $1 \times 10^{-4}$ Torr. Peak of Cr$^+$ signified exact location of the interface, and was present at 25 sputtering layers deep. This was in agreement with initial estimation from the histogram analysis in Figure 6.1

**Discussion.** Surface analysis of both mixed-terminated and Ti-terminated STO substrates yielded evidence of Cr$^+$ contamination on the surface of the Ti-terminated substrates. The amount of Cr$^+$ found was determined to be a trace amount since the highest counts were approximately 900 ions (Figure 6.6). The implication of this amount is that it was residual enough to not affect the system, yet significant enough to serve as an effective marker for the location of the interface. As observed in Figure 6.7, some diffusion occurs once processing of the thin films takes place. However, there were still no noticeable effects of this diffusion of Cr$^+$ ions on the system, with the highest observed mean counts at the interface being < 630 ions, and on the film surface < 25 ions. Films still behaved as expected, electrically and chemically. Despite diffusion, the majority of Cr$^+$ still remained at the original point of initial concentration (surface of the Ti-terminated
Cationic Intermixing

STO substrate), and this peak marked the exact location of the interface of the LAO-STO film at 25 sputtering layers deep.

6.2.4 A-Site Mixed Ion Diffusion

The mechanism of intermixing within the films was investigated by focusing on the behavior of A-site cations through studying the LaSrO$_2$ molecular fragment. The significance of this fragment lies in the fact that it contains A-site cations from both the film and the substrate sides and the fragment was emitted in a statistically significant amount. Beforehand, a Cr$^+$ profile was plotted for a 5 u.c. film grown at $1 \times 10^{-4}$ Torr in addition to the one studied in section 6.2.3, displayed in Figure 6.8. Similarly, a depth-profile analysis was conducted for the LaSrO$_2$ fragment, and a plot of the mean counts per sputtering layer was extracted. The diffusion of La$^+$ was then tracked by comparing the relative position of the peak of the LaSrO$_2$ molecular fragment with the position of the interface as marked by the Cr$^+$ ion peak. The position of the LaSrO$_2$ peak, relative to the position of the interface, provided evidence of a statistically significant amount of La diffusing into the substrate, an amount larger than the Sr counter diffusion. Such a study for the 5 u.c. film grown at $1 \times 10^{-4}$ Torr and 750°C is displayed in Figure 6.9. The peak of the LaSrO$_2$ fragment was located at 27 sputtering layers deep, compared to the location of the interface marked by Cr$^+$ at 13 sputtering layers deep, resulting in a 14 sputtering layer difference between the two. This distance reflected the magnitude of La$^+$ diffusion into the film. Likewise, for the 10 u.c. film grown under the same processing conditions, the peak of the LaSrO$_2$ fragment was located at 40 sputtering layers deep, compared to the interface located at 25 sputtering layers, resulting in a 15 sputtering layer difference between the two. These relative distances from the location of the interface served as
Cationic Intermixing

a semi-quantitative measure for the "magnitude" of relative La$^+$ ion diffusion into the substrate.

Figure 6.8. Comparison of the Cr$^+$ profiles for a 10 and a 5 u.c. film, both grown at $1 \times 10^{-4}$ Torr and 750$^\circ$C. The interface for the 5 u.c. film was located at 13 sputtering layers deep. Likewise, as determined in section 6.2.3, the interface for the 10 u.c. film was located at 25 sputtering layers deep.
Figure 6.9. Comparison of the peaks of Cr$^+$ ion and the LaSrO$_2$ molecular fragment. The location of the LaSrO$_2$ peak past the interface marked by the Cr$^+$ peak signifies a diffusion of La$^+$ into the substrate. The distance between the two peaks reflects the magnitude of La$^+$ diffusion into the substrate.

**Discussion.** The successful investigation of La$^+$ diffusion into the substrate hinged on the choice of the LaSrO$_2$ molecular fragment. As stated before, the importance of this fragment was in the fact that it contains A-site cations (La$^+$ and Sr$^+$) from both the film and the substrate, respectively. Further, the residence of these two cations within this molecular fragment means that the location of the LaSrO$_2$ peak was, in essence, the location within the system where the probability of finding both cations was 50%. What this means in practicality is that, if a peak of LaSrO$_2$ is found past the marked location of the interface (Cr$^+$ peak), there is, effectively, more La$^+$ diffusing into the substrate than there is Sr$^+$ diffusing out of it. The opposite would be true for Sr$^+$, were the peak of LaSrO$_2$ found before the location of the interface. For both the 5 and 10 u.c. films grown at 1x10$^{-4}$ Torr and 750°C, the LaSrO$_2$ peaks were located past the interface, within the
substrate. Further, the distances of the LaSrO$_2$ peaks from the interfacial Cr$^+$ peak for both samples were only 1 sputtering layer off. The implication of this is that, there is no evidence of a thickness-driven mechanism for diffusion of the La$^+$ ion as both films, despite being different thicknesses, still reported similar magnitudes for La diffusion when processed in similar deposition conditions. This suggests that intermixing was not necessarily driven by the electrostatic field build across the film. This conclusion was further supported by the MEIS work of our collaborators [11].

6.2.5 Temperature-Dependence

The final study of the nature of cationic intermixing within the LAO-STO films was an investigation into the temperature-dependence of the noticed La$^+$ ionic diffusion. To accomplish this, a final 10 u.c. LAO-STO film was deposited at $1 \times 10^{-4}$ Torr, but at a lower temperature of 550$^\circ$C. This temperature was chosen because it still met a threshold for crystallinity for the LAO deposition, but supplied a markedly lower thermal energy to the system. A similar study of La$^+$ diffusion as outlined in section 6.2.4 was thus conducted for this film, and the results were compared to those obtained for the previous 5 and 10 u.c. samples grown at 750$^\circ$C. The distances of the peaks of the LaSrO$_2$ fragments from the location of the Cr$^+$-marked interfaces were compared. The results, plotted in Figure 6.10, showed that whereas these distances for the samples grown at 750$^\circ$C were within 1 sputtering layer of each other, the 10 u.c. sample grown at 550$^\circ$C was up to 10 sputtering layers lower.
Cationic Intermixing

Figure 6.10. Graph of the distances of the LaSrO$_2$ fragment from the location of the interface marked by Cr$^+$ for the three films in this study: 10 u.c. (550°C), 10 u.c. (750°C), and 5 u.c. (750°C). Evidence of a temperature-driven mechanism for intermixing is observed as LaSrO$_2$ peak for sample grown at 550°C is much closer to the interface than those grown at 750°C.

**Discussion.** By changing the temperature of deposition from 750°C to 550°C, a significantly lower amount of thermal energy was supplied to the system. The implication of this is visible in Figure 6.10, which shows that there was a much shorter distance between the interface and the peak of the LaSrO$_2$ molecular fragment, indicating a temperature-driven mechanism for interdiffusion of La$^+$. The laser fluence was kept constant between the two samples, thus the kinetic energy of the ions emitted from the target was expected to be similar. In comparing the results of the samples grown at 750°C, there was just a sputtering layer difference in this distance from the interface. Hence, it is reasonable to accept this discrepancy as within the margin of error. Conversely, the sample grown at 550°C was up to 10 sputtering layers closer to the interface. From section 6.2.2, a sputtering layer of the primary beam in SIMS was estimated to erode approximately 0.4 u.c. of the sample, accounting for negligible differences in the
substrate and film. This means the lower-temperature sample was roughly 10 u.c. closer to the interface than those grown at higher temperatures. This determination was statistically significant, and cannot be a result of the margin of error, giving reasonable rise to a notion of a temperature-driven mechanism. It is important, however, to note that all three samples studied extensively still had La\(^+\) diffusing into the substrate, and consequently, had peaks of the LaSrO\(_2\) fragment located past the interface. Subsequently, it is important to accept that despite there being an obvious temperature dependence on the magnitude of intermixing in the film, temperature may not be the only factor that affects intermixing. Independent studies have reported the observation of a population of A-sites in the STO substrate occupied by La\(^+\) ions [11-13], as a result of V\(_{Sr}\). It is postulated that these vacancies cause a thermodynamic imbalance, which is relieved by the diffusion of La\(^+\) into the substrate. Sr\(^+\), itself, has been shown to exhibit high volatility at temperatures of 600\(\degree\)C in O\(_2\) atmosphere [6]. This volatility of Sr\(^+\) could be another contributing factor in explaining the observed difference in the magnitude of La\(^+\) diffusion into the substrate. It is thus reasonable to deduce that the amount of V\(_{Sr}\) created prior to deposition at 550\(\degree\)C could be lower, as compared to 750\(\degree\)C. Further adding to this mechanism could be the fact that ionic bombardment of the highly-energized particles from the ablation plume could also affect changes on the surface of the Ti-terminated substrate. These changes may not only include added formation of VSr, but also cationic displacements of Ti\(^+\) or Sr\(^+\), all adding to the promotion of intermixing. In fact, research has shown that for similar samples grown in high quality MBE environments, there was less observed La diffusion [16]. In effect, it is evident that a host of reactions, intrinsic to this highly complex system, work hand-in-hand, to cause the phenomenon of cationic intermixing observed within the films. However, this study has successfully observed
and (semi-quantitatively) recorded the magnitude of a temperature-driven mechanism for intermixing.

**6.2.6 Conclusions**

In conclusion, five investigations were conducted into the study of intermixing within the LAO-STO system:

1. The successful depth-profiling of the films and a successful statistical representation of the ionic population within a sampled area of $\approx 250\mu m \times 250\mu m$ stretched to a depth of 80 sputtering layers (Figures 6.1 and 6.2).

2. The successful limits of the extent of intermixing, where a range for the upper bound of substrate cation diffusion into the film and the lower bound of the film cation diffusion into the substrate were determined (Figures 6.3 and 6.4).

3. The determination of the exact location of the interface through a strategic employment of $\text{Cr}^+$ ions on the surface of the Ti-terminated substrate to serve as a marker within the grown films (Figure 6.7).

4. The tracking of the $\text{La}^+$ ion diffusion into the substrate through the selection of an important molecular fragment, $\text{LaSrO}_2$, and the semi-quantitative measure of the magnitude of this interdiffusion through observing the distance of the $\text{LaSrO}_2$ peak from the interface marked by $\text{Cr}^+$ (Figure 6.9).

5. The successfully observed evidence of a temperature contribution to the mechanism of intermixing within the film, through tracking the difference in the semi-quantitative measure of the magnitude of interdiffusion and its dependence on the thermal energy put into the system (Figure 6.10).
The successful conduction of these five investigations proved a novel demonstration of the capabilities of SIMS, and its efficacy in studying the LAO-STO thin film system in a very easy and visual manner. Through all the conclusions of each investigation, it is evident that intermixing is caused and driven by several factors, including the thermal energy input, the creation of $V_{Sr}$, and the kinetic bombardment of highly energetic particles within the plume and their effective displacement of resident substrate cations. Regardless of varying temperatures during processing, interdiffusion of La$^+$ into the substrate was observed, yet no statistically significant evidence of an effect on intermixing from the varying thicknesses of the samples was observed. In addition to this study, detailed investigations on the effect of the O$_2$ partial pressure of the sample may be conducted to add to study of the scope of factors contributing to this phenomenon.
References


7 Conclusions and Future Work

This work aimed to study in-depth two critical factors in the growth of LAO-STO perovskite thin films, namely, the role of surface adsorbates and a study of intermixing, studied in Chapters 5 and 6, respectively.

Through detailed studies of films of varying thicknesses both below and above the critical thickness of 4 u.c. grown at both low and medium O\textsubscript{2} partial pressures, a few conclusions were reached on the subject of surface adsorbates. Regardless of thickness, samples grown at higher O\textsubscript{2} partial pressures reported higher ratios for +1 eV, and yielded the opposite for +2 eV shoulder peaks in the O1s regions. The observed reduction of the +2 eV component in O1s regions after heat treatments was confirmed to be neither from the thermal desorption of the OH nor the H dissociated species, but rather, a relationship was established with physisorbed Ester and Carboxylic Acid components in C1s spectra. The corresponding reductions of both components in the O1s and C1s regions confirmed the important contribution of adventitious carbon on the film surface upon ambient exposure. Finally, the spontaneity of the formation of surface adsorbates on the surface of the films was demonstrated by observing different +2 eV ratios after different periods of ambient atmosphere exposure, which not only further proved
the adventitious nature of the observed hydroxylolation or physisorption on the film surface, but also demonstrated a spontaneous change with changing humidity.

Likewise, detailed studies of films of varying thicknesses both below and above the critical thickness yielded interesting investigations on the study of cationic intermixing. Films were successfully studied both visually and statistically by a novel 3D projection of their statistical ionic populations. The limits of the extents of intermixing, both from film cations and substrate cations, were established and visually observed. The exact location of the interface was also determined though the strategic employment of $\text{Cr}^+ \text{ ions}$ on the substrate surface, and were also confirmed visually in their 3D projections. Finally, the mechanism of interdiffusion of film cations was studied by tracking La+ diffusion into the substrate through the study of a molecular fragment, LaSrO$_2$. A link between intermixing and deposition temperature suggests this mechanism may be, in part, temperature-driven. In addition to this, concurrent studies of the LAO-STO system provided evidence between the formation of $\text{V}_{\text{Sr}}$ and observed La interdiffusion into the substrate due to the observed volatility of Sr+ at deposition temperatures.

Both of these studies sought to employ the use of useful surface characterization techniques, namely, XPS and SIMS. Both techniques proved to be highly useful in characterization due to their extreme sensitivities. Despite the successes of both investigations, further work may be conducted in understanding their interplay. The common link between both of these studies is the observation of differences in film stoichiometry. A link between the film stoichiometry and the effects of surface adsorbates or cationic intermixing may add more insights into intrinsic origins of these observed phenomena. These studies may be also extended to investigations in the role of antisites on the films, and how antisites also affect observed surface adsorbates or cationic intermixing.
Finally, the studies of these observed phenomena beg the question as to their effects on the observed conductivity. Subsequent conductivity studies need to be executed for these investigations in order to understand their full effects on the efficacy of these films as oxide data storage devices. In all, useful insights were gleaned from these investigations, and the successful employments of XPS and SIMS lays groundwork for more conclusive studies in the future.
Index

2DEG, 4, 71
annealing, 26
binding energy shifts, 62, 69, 71
carbonaceous species, 65–68, 70, 71
cationic intermixing, 18, 41, 77, 83, 90, 94, 101
depth profile, 48
dissociation, 12, 61, 63
domains, 24
epitaxial growth, 27, 35
epitaxy, 1
etching, 24, 25
heterointerface, 1, 87, 91
inelastic mean free path, 44
interdiffusion, 17
laser fluence, 28, 29
mixed-termination, 23, 24, 88
molecular beam epitaxy, 15
partial pressure, 31
perovskite, 3
plume angle, 15, 17, 28, 30
polar catastrophe, 3
pulsed laser deposition, 28
RHEED intensity, 33, 34
RHEED pattern, 32, 33
secondary ions, 46, 50, 80
stoichiometry, 17
substrates, 23
surface adsorbates, 12, 54, 57, 71, 100
Ti-termination, 24, 25, 27, 88
ToF SIMS, 41, 46, 48, 78, 83, 101
tunability, 12
unit cell, 3
XPS, 41, 42, 45, 56, 101
Complete References


[64] P. Liu et al., Reaction of Water Vapor with α-Al2O3(0001) and α-Fe2O3(0001) Surfaces: Synchrotron X-ray Photoemission Studies and Thermodynamic Calculations, Surface Science 417:1, 53-65 (1998)

[66] Q. Fu et al., Hydroxylated $\alpha$-Al$_2$O$_3$ (0001) Surfaces and Metal/$\alpha$-Al$_2$O$_3$ (0001) Interfaces, Surface Science 600, 4870-4877 (2006)


[73] S. Das et al., Static and reversible elastic strain effects on magnetic order of La$_{0.7}$Ca$_{0.3}$MnO$_3$/SrTiO$_3$ Superlattices, Journal of Applied Physics 115, 143902 (2014)

[74] C. Cen et al., Oxide Nanoelectronics on Demand, Science 323, 1026 (2009)


tion State at the (001) LaAlO$_3$/SrTiO$_3$ Interface as a Function of LaAlO$_3$ Growth Con-

[81] B. Jalan and S. Stemmer, Two-Dimensional Electron Gas in $\delta$-doped SrTiO$_3$, Physical
Review B 82, 081103(R) (2010)

[82] G. Drera et al., Spectroscopic Evidence of in-Gap States at the SrTiO$_3$/LaAlO$_3$ Ultra-
thin Interfaces, Applied Physics Letters 98, 052907 (2011)

[83] A. Savoia et al., Polar Catastrophe and Electronic Reconstructions at the
Review B 80, 075110 (2009)

[84] N.Y. Chan et al., Palladium Nanoparticle Enhanced Giant Photoresponse at
LaAlO$_3$/SrTiO$_3$ Two-Dimensional Electron Gas Heterostructures, American Chemical
Society NANO 7:10, 8673-8679 (2013)

[85] G. Drera et al., Intrinsic Origin of Interface States and Band-Offset Profiling of
Nanostructured LaAlO$_3$/SrTiO$_3$ Heterojunctions Probed by Element-Specific Reso-
nant Spectroscopies, Physical Review B 90, 035124 (2014)

[86] M. Basletic et al., Mapping the Spatial Distribution of Charge Carriers in

[87] A. Janotti et al., Controlling the Density of the 2DEG at the SrTiO$_3$/LaAlO$_3$ Interface,
Physical Review B 86, 241108(R) (2012)

[88] J. A. Bert et al., Direct Imaging of the Coexistence of Ferromagnetism and Super-

[89] G. Drera et al., Band Offsets and Density of Ti$^{3+}$ States Probed by X-ray Photoemis-
sion on LaAlO$_3$/SrTiO$_3$ Heterointerfaces and their LaAlO$_3$ and SrTiO$_3$ Bulk Precur-
sors, Physical Review B 87, 075435 (2013)

[90] P. Brinks et al., Anisotropic Electrical Transport Properties of a Two-Dimensional


[92] G. Herranz et al., High Mobility in LaAlO$_3$=SrTiO$_3$ Heterostructures: Origin, Dimen-


