Thesis

Emergent Physical Properties via Anomalous Atomic and Electronic States in Oxide Heterostructures

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February, 2009

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No problem is too small or too trivial if we can really do something about it.

- Richard P. Feynman

Preface

This thesis describes work carried out in the masters course of the Department of Advanced Materials Science, University of Tokyo. The main scope of this study is to observe the emergence of physical properties via creating novel atomic and electronic states in oxide artificial structures grown by pulsed laser deposition. Especially, it focuses on the broken inversion symmetry of the atomic stacking at polar surfaces and interfaces. Controls of the electronic states in atomic-scale heterostructures were achieved via various strategies: modulation doping from a polar surface, changing the stacking sequence of the two materials forming the interface, and inserting other materials at the interface. In addition, related chemical phenomena during the growth process are presented. These results provide a general approach to tunable electronic states in oxide heterostructures.

Parts of this thesis have been published, or prepared for publication as detailed below.

[1] T. Higuchi, Y. Hotta, T. Susaki, A. Fujimori, and H. Y. Hwang, "Modulation doping of a Mott quantum well by a proximate polar discontinuity," Phys. Rev. B **79**, 075415 (2009, selected as Editors' Suggestion).

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[4] N. Ogawa, K. Miyano, M. Hosoda, T. Higuchi, C. Bell, Y. Hikita, and H. Y. Hwang, "Nonlinear Optical Study of $SrTiO_3/LaAlO_3$ superlattices," submitted to Phys. Rev. Lett., cond-mat/0902.0070.

Takuya Higuchi
February, 2009

Acknowledgments

One way to open your eyes is to ask yourself, "What if I had never seen this before? What if I knew I would never see it again?"

- Rachel Carson

At the top of the list, I would like to show my deepest gratitude to my advisor, Prof. Harold Y. Hwang in the Department of Physics, University of Tokyo for his continuing support and education. Without his particular patience and courtesy, this thesis would not have taken shape. Through daily discussions as well as formal opportunities to have scientific debates, I learned from him a true attitude to pursue research. Also, let me express my appreciation to the members of our lab, Dr. Yasuyuki Hikita, Dr. Christopher Bell, Ms. Makiko Tanaka, Mr. Yusuke Kozuka, Mr. Takeaki Yajima, Mr. Yuichi Ota, Mr. Minu Kim, Mr. Motohide Kawamura, Mr. Yasuo Nakanishi, Mr. Hiroki Sato, Mr. Kotaro Takeyasu, Mr. Satoshi Harashima, Mr. Takeaki Hidaka, as well as some of the former members, Dr. Tomofumi Susaki, Dr. Yasushi Hotta, Dr. Kei S. Takahashi, Mr. Yasushige Mukunoki, Mr. Motoshi Nakayama, Mr. Mitsuru Nishikawa and Mr. Masayuki Hosoda, and also collaborating visitors, Prof. Bog Gi Kim, Mr. Daeyoung Kwon, Mr. Bongju Kim, Mr. Youngsu Wu in Pusan National Univeristy, and Prof. Jong-Hyun Song in Chungnum National University, Prof. Art Hebard and Ms. Guneeta Singh in University of Florida, and Mr. James M. Rondinelli in University of California at Santa Barbara for helpful discussions and kind support. I greatly enjoyed working with such talented and sincere people in a close relationship. Especially, I cannot express my gratitude by words to my colleague, Mr. Yajima, for not only the collaborations on the manganite films, which is described in Chapter 6, but also for his daily discussions. Also, let me express my special appreciations to Dr. Hikita and Dr. Bell for their critical readings and important suggestions, which extensively improved the quality of the writing.

Outside the lab, I really appreciate Prof. David A. Muller in Cornell University and his group members, especially Ms. Lena Fitting Kourkoutis and Mr. John L. Grazul. They were kind enough to host me during my stay there to work on microscopic studies, and provided me opportunities to grow both scientifically and personally in a foreign environment. Also, I am grateful to Prof. Atsushi Fujimori in the Department of Physics, University of Tokyo, Prof. George A. Sawatzky and Dr. Hiroki Wadati at the University of British Columbia for spectroscopic measurements and helpful discussions. Through collaborations of the optical characterizations of oxide superlattices, I would like to thank Prof. Kenjiro Miyano and Dr. Naoki Ogawa in RCAST, University of Tokyo. Also, let me express my deep gratitude to Prof. Hidefumi Akiyama in ISSP, University of Tokyo and his group members especially Dr. Yuhei Hayamizu and Mr. Shun Maruyama for their special courtesy to let me work on their photoluminescence measurement systems. I also appreciate Prof. Hidenori Takagi and his group members for the permission to

use their equipments for chemical synthesis. As a result of important discussions and suggestions, I would like to thank Prof. Takahisa Yamamoto and Dr. Kenji Itaka in the Department of Advanced Materials, University of Tokyo, Prof. Mikk Lipmaa and Dr. Tsuyoshi Ohnishi in ISSP, University of Tokyo, Prof. Toshiro Higuchi in the Department of Precision Machinery Engineering, University of Tokyo, and Dr. Akira Ohtomo at Tohoku University.

For financial supports, I am thankful to the International Academic Exchange Program of University of Tokyo, and the Endowed Graduate Student Financial Aid of Cornell University for supporting living costs and covering tuition during my stay in Cornell University.

Last, but not least, let me thank my family and friends for their continuing support and kindness. Especially, it would be impossible to imagine such a fruitful life in the graduate school without the encouragement of my parents.

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Symbols

a	Pseudocubic lattice constant
$C_{k,i}$	Linear fitting coefficient
C_i^{tot}	Total sum of linear fitting coefficient
d	Superlattice period
d_{A-B}	AB-difference
D, $\mathbf{D}$	Electric flux density
D	Beam diameter
e^{ex}	Extra electron number
e^*	Ionic charge
E, $\mathbf{E}$	Electric field
E_{A_n}	Activation energy of carrier density
E_{A_μ}	Activation energy of mobility
E_{cut}	Cutoff energy at mobility edge
E_{F}	Fermi energy
E_{sur}	Energy cost of surface reconstructions
E_{val}	Energy cost to change valence states
f	Lens focal length
H	Magnetic field
k	Boltzmann constant
m, n, t	Thickness of layers
N	Density of states
P, $\mathbf{P}$	Polarization density
$\mathbf{P}_{\mathrm{ind}}$	Induced polarization density
$\mathbf{P}_{\mathrm{unit}}$	Polarization density arising from dipoles
P_{O_2}	Oxygen partial pressure
$P_{R\mathrm{VO}_x}$	Oxygen partial pressure for $R\mathrm{VO}_x$ growth
q_0	Elementary charge
r	Residual function
R_i	Residue size
R_{H}	Hall coefficient
R_{xy}	Hall resistance
S	Seebeck coefficient
T	Temperature
T_{sub}	Substrate temperature
V	Electrostatic potential
V_{dip}	Potential difference arising from dipoles
V_{sur}	Potential difference arising from surface charge
V_{tot}	Total potential
X_{Ph}	Phillips electronegativity
Z	Atomic number
α	Ionicity parameter
β	Imaginary part of scattering factor
δ	Real part of scattering factor

$\delta(z)$	Dirac delta function in one dimension
Δ_z	Cumulative displacement
Δ_z	Sampling width of measurement
δ, Δ, $\Delta(n)$	Dipole shift in potential
ε	Dielectric constant
ε_0	Vacuum permittivity
θ	Surface coverage ratio
θ	Incident angle of lasers
$\theta(z)$	Step function in one dimension
2θ	Detector angle for x-rays
λ	Wavelength
μ	Dipole moment
μ	Carrier mobility
μ	Magnetic permeability
ρ	Charge density
ρ_{bound}	Bound charge density
ρ_{free}	Free charge density
ρ_{total}	Total charge density
σ	Conductivity
Φ_i	Principal component
Φ	Reference spectral function
Ψ_i	Recorded spectral function
ω	Incident angle of x-rays
$2\omega_0$	Gaussian beam waist diameter

Abbreviations

AFM	Atomic Force Microscopy
ADF	Annular Dark Field
CBED	Convergent Beam Electron Diffraction
CCD	Charge Coupled Device
COBRA	Coherent Bragg Rod Analysis
CTEM	Conventional Transmission Electron Microscopy
DFT	Density Functional Theory
2D	Two dimensional
3D	Three dimensional
EELS	Electron Energy Loss Spectroscopy
FWHM	Full Width at Half Maximum
GMR	Giant Magnetoresistance
LEED	Low-Energy Electron Diffraction
PES	Photoemission Spectroscopy
PCA	Principal Component Analysis
PL	Photoluminescence
PLD	Pulsed Laser Deposition
RHEED	Reflection High-Energy Electron Diffraction
RP	Rotary Pump
SHG	Second Harmonic Generation
STEM	Scanning Transmission Electron Microscopy
SXRS	Soft X-ray Resonant Scattering
TEM	Transmission Electron Microscopy
TMP	Turbo Molecular Pump
uc	unit cell(s)
XAS	X-ray Absorption Spectroscopy
XPS	X-ray Photoemission Spectroscopy

Chapter 1

Introduction

1.1 Atomic-scale oxide heterostructures

When the size of materials is comparable to the characteristic length scale of their physical properties, novel functionalities can emerge. The concept of "superlattice" proposed by Esaki and Tsu is a good example, where the width of the repeated stacking of semiconductor layers is comparable to the electron penetration depth[1], resulting in novel confined states with negative differential resistance perpendicular to the layers [1]. Not only the electronic superlattices in semiconductors, but also magnetic superlattices were investigated with magnetic and nonmagnetic metals. Here, the layered films of these metals are thinner than the spin scattering length and the giant magneto-resistive (GMR) effect appeared [2], which is currently used in the read heads of hard disc drives.

Besides the potential application of such unconventional functionalities, the discovery of novel states in heterostructures has expanded the horizon of condensed matter physics. For example, the observation of the integer quantum Hall effect in the two dimensional electron gas in semiconductor field effect transistors revealed the quantum nature of the electromagnetic interactions [3], and is used to determine the fine-structure constant, which is one of the fundamental physical constants. Therefore the exploration of novel properties in artificial structures, has been of particular interest for decades from both scientific and technological viewpoints.

In particular, heterostructures of transition metal oxides with the perovskite structure [Fig. 1.1] have been one of the leading candidates to seek such novel properties, due to the accessibility to a variety of exotic physical properties of the perovskite family [4], for instance high-T_{C} cuprates [5] or colossal magneto-resistive manganites [6]. Adding to that, epitaxy can be maintained due to their relatively small lattice mismatch, and owing to their ionicity and multi-valency, they can adapt to the change of the local composition without losing their lattice structure. Good examples are given by the discoveries of a metallic interface between two insulators, $LaTiO_3$ and $SrTiO_3$, with nanometer-scale distribution of itinerant electrons close to the interface [7], or enhanced magnetic properties

[1] It can be determined either by the mean free path of electrons or the length scale of the hydrogenic wave function.

Figure 1.1: Cubic perovskite structure of ABO_3.

of $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ interfaces by inserting 2 unit cells (uc) of $LaMnO_3$ at the interface [8]. A recent theoretical prediction of enhanced superconductivity in atomic-scale cuprate superlattices by the proximity effect with enhanced order parameters also shows the possibility of novel ground states in complex oxide heterostructures [9], which may have been experimentally realized [10].

As expected from these examples, atomic-scale properties can be essential in oxide heterostructures, and in such length scales, broken inversion symmetry of the stacking sequence of ionic charges can play a key role in achieving non-trivial reconstructed states [11]. An example is the observation of metallic conductivity at a polar interface between two insulators, $LaAlO_3$ on TiO_2-terminated $SrTiO_3$, which has motivated many studies to seek its origin [12]. One explanation is that the instability of polar discontinuities can be solved via electronic reconstructions in transition metal oxides due to their mixed valence states [13]. However, the mismatch between the ionic charge picture and the traditional semiconductor language has hindered the understanding of this phenomenon.

In this Thesis, we provide a general framework to treat the effect of the ionic stacking, and subsequently describe the characteristic examples following this concept. We first define the terms "polar" and "non-polar" for discontinuities between materials in analogy to the surface of polar crystals. Then, we refine the polar discontinuity model: taking dipole-free unit cells and discussing stability in terms of local charge neutrality. Subsequently, it is derived that the unit cells at polar interfaces and surfaces can be treated as δ-dopants. The equivalence of these models is understood using Maxwell's equations. In order to reveal the nature of the atomic-scale oxide heterostructures, a wide variety of complex structures were grown by pulsed laser deposition (PLD), and various methods were used to characterize their transport, structural, spectroscopic, and photoluminescent properties. Based on these studies, we describe our recent observations of reconstructions at polar interfaces and surfaces, as well as their nanoscale couplings, and related chemical phenomena during PLD growth.

1.2 Outline

The outline of this Thesis is as follows. In Chapter 2, the fabrication and characterization techniques for oxide heterostructures are described. In Chapter 3, the role of broken inversion symmetry at polar interfaces and surfaces is described, and an equivalent but different perspective to treat the charge structure is presented based on local charge neutrality in dipole free unit cells. In the subsequent three Chapters, examples of controlling the local electronic states based on these considerations are presented. In Chapter 4, modulation doping of holes in $LaVO_3$ wells by proximate polar discontinuities is presented. In Chapter 5, the asymmetric nature of the atomic and electronic structures in $LaAlO_3/SrTiO_3$ superlattices is presented, indicating possible control of interface compositions by stacking sequences. Chapter 6 describes the change of Mn valence states at $LaMnO_3/SrTiO_3$ interfaces by varying the interface compositions. The rest of this thesis presents some characteristic phenomena during kinetic growth by PLD to understand its chemistry. The latter half of Chapter 6 presents the precise microscopic observations of precipitates formed on $LaMnO_3$ films. In Chapter 7, optical evidence of the enhanced solid solubility limit of Eu in $LaVO_4$ thin films is presented, providing a possible synthesis process of meta-stable materials. In Chapter 8, we summarize the results presented, to provide a comprehensive view for potential control of atomic and electronic states in oxide heterostructures.

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Chapter 2

Fabrication and characterization methods

2.1 Pulsed laser deposition (PLD)

2.1.1 Apparatus of PLD

Pulsed laser deposition (PLD) is a widely used technique particularly suitable for growing multi-component oxide structures, because of its simplicity and versatility [1, 2]. In this study, the films were fabricated by the PLD system [Fig. 2.1(a)] with a pulsed KrF excimer laser with wavelength of 248 nm and a pulse duration time of $\sim$ 25 ns. As schematically shown in Fig. 2.1(b), the excimer laser is introduced into the chamber through a 4 lens afocal zoom stage, which will be discussed later, and focused on to the target to ablate the target surface. Single crystals or polycrystalline pellets are used as target materials and they are ablated by the focused laser and deposited on substrates to form thin films. To control the oxygen stoichiometry of films and kinetic and thermodynamic conditions during growth, oxygen partial pressure was tuned by introducing high purity oxygen gas into the chamber through a variable leak valve, where the background pressure in the chamber was kept below 3×10^{-8} Torr achieved by turbo molecular pumps (TMP) backed by rotary pumps (RP).

We used commercial $LaAlO_3$ (001) and $SrTiO_3$ (001) single crystal substrates (Shinkosha Co. Ltd.) with atomically-flat step-and-terrace structures at the surface. Substrates are attached to a sample holder with clamps as well as platinum paste to realize a uniform heat contact to the holder. The backside of the sample holder is heated by a lamp heater and the temperature of the substrate is monitored by a pyrometer.

2.1.2 Reflection high-energy electron diffraction (RHEED)

During deposition, the growth process was monitored by reflection high-energy electron diffraction (RHEED). The sample was irradiated by an electron beam which was accelerated in the electron gun and the RHEED patterns at the phosphor screen were measured with a high sensitive CCD camera as shown in Fig. 2.1(b). The coherent reflections of elec-

Figure 2.1: (a) Overview picture and (b) schematic illustration of the PLD apparatus. (c) Schematic surface structures during layer-by-layer growth and RHEED intensity oscillations as a function of the deposition time.

trons are possible when the condition that the wave vectors of the incident and diffracted electrons differ by a reciprocal lattice vector. The RHEED pattern shows streaks and spots, which correspond to the two dimensional and three dimensional periodic structures in real space, respectively [3].

Due to the shallow incident angle ($0.5° \sim 3°$) and strong interaction between the electrons and the atoms, the RHEED patterns are very sensitive to the topmost surface of the material. During layer-by-layer deposition, oscillations of the RHEED intensity are observed since the RHEED intensity strongly depends on the surface roughness, proportional to $|2\theta - 1|^2$ assuming only the kinetic scattering from the surface. Here θ gives the ratio of surface area covered by incrustations to the total area [Fig. 2.1(c)]. In reality, the RHEED intensity can be strongly affected by other features; for example, the incident angle of the electron beam changing the phase of the RHEED oscillations dramatically [4]. However, the number of oscillations can still provide useful information on the thickness of the films, and once confirming that one cycle of the oscillations corresponds to the growth of one monolayer by directly measuring the thickness of a standard sample e. g. by thickness profilometry, x-ray diffraction, or atomic force microscopy, it can be used to determine the thickness of the films deposited.

2.1.3 Laser conditions

It has been pointed out that the precise control of the laser conditions is necessary to achieve stoichiometric transfer of the target materials to the films [5, 6]. To control the fluence and the spot size of the excimer laser at the target surface, we introduced an optical zoom stage [Fig. 2.2]. The zoom stage consists of four lenses with focal lengths of $f_1 = 360$ mm, $f_2 = -26$ mm, $f_3 = 206$ mm, and $f_4 = 360$ mm. By changing the

Figure 2.2: Schematic illustration of the zoom stage. Orange lines indicate the path of the KrF excimer laser beam which is imaged on the target through four lenses.

distance between the lenses, we can control the magnification of the laser image after the aperture on the target surface without changing the total distance between the KrF laser and the chamber. At the target surface, the spot size of the laser can be varied from 0.24 mm^2 to 2.8 mm^2, and the fluency of the laser is available up to 9 J/cm^2. Another way to control the laser condition was by attenuators and a variable aperture. Together with these instruments, we controlled the laser conditions precisely in a wide range.

One severe problem here was the contamination of the laser entrance viewport due to the deposited materials which lowered the effective laser intensity reaching the target surface, sometimes even by 40 % [7]. We therefore measured the laser transmittance through the viewport before depositions so as to accurately determine the laser condition.

2.2 Basic characterization of thin film crystallinity

The crystallinity of the thin film samples were characterized by atomic force microscopy (AFM) and x-ray diffraction (XRD). AFM is widely used for studying the surface morphologies of materials on an atomic scale [8]. In this study, surface topography was investigated using an AFM (Digital Instruments Dimension^{TM} : Veeco) with a sharp tip as a probe (the tip radius of curvature of less than 5 nm). The tip is located at the end of the cantilever which is oscillated by a piezoelectric device. A change in the oscillation of the cantilever due to a change in the atomic force between the tip and the surface of the material is used to obtain a topographic image of the surface.

XRD measurement is one of the most important techniques to study crystal structures. In this Thesis, we employed a high resolution XRD system (D8 Discover : Bruker AXS Inc.) for thin film characterization, where the specimen was irradiated by the Cu $K\alpha_1$ line ($\lambda = 1.54056$ Å) which was isolated by a Ge (220) monochromator. The diffraction intensity is enhanced when the x-ray incident angle ω and the detector angle 2θ from the source satisfy the Bragg's condition of the measured crystals [9]. In thin films epitaxially grown on substrates, the out-of-plane lattice constant is available from the measured diffraction intensity by scanning angles keeping the relation $\omega = \theta$. For superlattices or thin films on substrates, fringes in the XRD peak patterns are observed according to the superlattice periodicity or the thickness of the film [10].

2.3 Transport measurements

2.3.1 Resistance and Hall measurement

The resistance and the Hall voltage of the samples were measured by the commonly-used five-probe measurement technique. Aluminum wire bonding or indium ultrasonic soldering was used to make ohmic contacts to the samples. Only when the sample resistance is very high (> 10 MΩ), the resistance was measured in two probe configurations, in order to reduce the distance between the two current electrodes, and by a high-voltage sourcemeter (model 2410 : Keithley Instruments Inc.), which can apply a voltage of up to 1100 V. When measuring by the two probe method, the linear current-voltage relation was always checked to confirm that the contact resistance was negligible compared to the sample resistance.

We measured the resistance and Hall voltage of the samples under variable temperature and magnetic field. To control these conditions, the a superconducting magnet dewar (Physical Property Measurement System, PPMS : Quantum Design Inc.) was used. The available range of temperature and magnetic field is 2 K - 400 K and 0 T - ±14 T, respectively.

2.3.2 Thermoelectric power measurement

Thermoelectric power was measured by an apparatus built for this thesis, "Thermy", specialized for measurement of thin films. As shown in Figs. 2.3(a) and (b), Thermy consisted of two copper blocks which were electronically and thermally isolated by glass and epoxy insulation. Two indium electrodes were soldered on top of the samples, and they were attached to the blocks by silver paste. The temperature of the two blocks was separately measured by two platinum resistor thermometers (M-FX 416 : Okazaki Manufacturing Company) attached close to the sample position, and their resistance was measured by the PPMS resistance bridge. A heater (121 Ω resistor) was attached to the smaller copper block, and a temperature gradient was applied to the sample bridging the two copper blocks. Typically, a current of 50 mA was applied to achieve temperature gradient of 5 K between the two sides. The thermoelectric voltage generated by the sample was measured between the copper blocks by an electrometer (model 6517A : Keithley Instruments Inc.), and measurement was carried out in an electromagnetically shielded environment at room temperature, which enabled measurement of highly resistive samples (up to 10 MΩ).

To measure the temperature dependence of the thermoelectric power, Thermy was installed in the PPMS dewar, attached on a probing stick with shielded cables connecting the sample stage and the head of the stick. Figure 2.3(c) shows the measured Seebeck coefficient of Nb:$SrTiO_3$ (0.5 wt%) as a standard sample, which showed similar values to the known reference [11] within the measured temperature range.

Figure 2.3: (a) Schematic illustration and (b) photograph of the thermoelectric power measurement system. (c) Seebeck coefficient of Nb:$SrTiO_3$ (0.5 wt%) measured by this apparatus. Inset shows the thermoelectric voltage at 300 K as a function of the temperature difference.

2.4 Scanning transmission electron microscopy (STEM)

2.4.1 Apparatus of STEM

The microscopic structure of the thin film samples was studied by annular dark field (ADF) scanning transmission electron microscopy (STEM), in a 200 kV FEI Tecnai F20 equipped with a Gatan imaging filter 865-ER for electron energy loss spectroscopy (EELS) analysis [Fig. 2.4]. A ZrO_2/W Schottky field emitter gun was used as the electron source, providing brightness of $> 10^8$ $Acm^{-2}Sr^{-1}$, sufficient for STEM imaging and small energy dispersion of ~ 0.5 eV at FWHM. By using focusing and scanning coils, a thin (< 100 nm) specimen was scanned two-dimensionally by an electron beam with minimum probe size of ~ 1.6 Å, which was limited by the spherical aberration and the diffraction limit. In order to avoid magnetic, mechanical, acoustical, and thermal disturbances, the environment of STEM was carefully designed [12]. The specimen was held by a cold double tilting stage which enables rotation of the sample around two axes.

When electrons penetrate through the specimen, they are scattered elastically or inelastically. For high collection angles, elastic scattering dominates, and is used to achieve ADF imaging. On the other hand, analysis on the inelastically scattered electrons for low collection angles enables spectroscopic studies in STEM. Based on these combined

Figure 2.4: (a) Schematic illustration and (b) photograph of the STEM apparatus.

observations of the elastic and inelastic scatterings, atomic-scale observations of atomic and electronic structure are available.

2.4.2 Annular dark field (ADF) imaging

The elastic component of the scattered electrons in STEM is collected by the ADF detector for the ADF imaging. To first approximation, the ADF intensity for high collection detector angles scales as $\sim Z^{1.7}$, where Z is the atomic number of the element, and with the small probe size in the STEM, atomic-scale Z contrast imaging is available, even with single atom sensitivity [13]. One advantage of STEM-ADF imaging is that it is free from phase contrast and diffraction contrast, which are observed in CTEM coherent imaging, and thus the information of the Z-contrast appears enhanced [14].

In the ADF imaging, one of the important effects is channeling of the electron beam. When the sample is aligned, so that a zone axis is parallel to the incident electron beam direction, channeling of the electron probe along the column of atoms occurs, resulting in enhancement of the ADF intensity [15]. *Per contra*, when the sample is aligned off-axis to the probe, the channeling effect is lost, and the ADF intensity becomes darker compared to the on-axis region. In order to obtain lattice images of crystals, the sample should be aligned perfectly on-axis to the beam, and thus the enhancement by the channeling is maximized. Practically, to find the crystallographic axis, the most useful information is obtained by the convergent electron beam diffraction (CBED) patterns, and the sample

Figure 2.5: Schematics of the STEM sample preparation procedures.

is aligned on-axis by rotating the sample using the tilting stage.

2.4.3 Electron energy loss spectroscopy (EELS)

By spectroscopically studying the energy loss of the inelastically scattered electrons, important electronic and chemical informations are obtained. The scattered electrons are sorted by energy using a magnetic prism inside the spectrometer, and their numbers are counted to obtain the energy loss spectra. at a spectrometer dispersion of 0.2 eV per channel The energy resolution was determined by the FWHM of the zero-loss peak, and was as narrow as 0.6 eV in this study.

Core-loss EELS contains useful information on electronic states of elements. In core-loss processes, the transition energies of the core electrons to the unoccupied state are unique to the elements, and thus the edge structure corresponding to these processes can be used as fingerprints of the elements. Also, the near edge structure of the core-loss spectra strongly depends on the local density of states of the atoms, reflecting their chemical and valence states. Therefore, analyzing the near edge structure provides precise electronic structure within the probe size.

2.4.4 STEM sample preparation

For STEM study, the thickness of the specimen should be thinner than the penetration depth of the probing electron beam, and to obtain clear ADF images and reliable EELS spectra, extremely thin specimens are necessary, usually much thinner than 100 nm. To meet this requirement, the samples were thinned by a combination of mechanical polishing and ion milling [16].

Figure 2.5 shows the procedures of the sample preparation. First, the sample was cut into two pieces, and they are glued with the regions of interest facing to each other. The glued sandwich was then cut into a few slides with thickness of 1 mm, and polished from both sides, with a wedge angle of 4°, so as to obtain a very thin part at the end of the wedge. When the sample was thin enough, clear optical fringes reflecting the thickness variation of the sample were observed under an optical microscope, and then the sample was further thinned by Ar ion milling with an incident angle of 10° for the first stage and 8° for the final stage. To avoid carbon contamination, the sample was plasma cleaned just before introducing it into the microscope.

Figure 2.6: Schematic illustration of the PL measurement system.

2.5 Photoluminescence (PL)

The photoluminescent properties were measured using two TEM_{00}-mode lasers with different wavelength, $\lambda = 266$ nm and $\lambda = 351$ nm with maximum power on the sample of 60 mW and 10 mW, respectively [Fig. 2.6]. To obtain $\lambda = 266$ nm light, $\lambda = 532$ nm green laser (Verdi-5W : Coherent Inc.) was introduced into a second harmonic generator (MBD 266/003 : Coherent Inc.), and only the $\lambda = 266$ nm line was chosen using reflection by CaF_2/BK7 dielectric multilayer mirrors. On the other hand, $\lambda = 351$ nm light was generated by an Ar-ion laser (Innova 300 : Coherent Inc.) and the bright lines from the pumping lamp were eliminated from 400 nm to 680 nm by using a black-glass band pass filter, transparent for the $\lambda = 351$ nm light. These lasers are focused on the samples, attached on a sample holder in a cryostat where the temperature range of 10 K to 300 K is available by a closed He-gas cycle refrigerator and a heater controlled by a feedback circuit.

The Gaussian beam diameter D and focal length f of the laser focusing lens are $D = 4$ mm and $f = 500$ mm for $\lambda = 266$ nm light, and $D = 3$ mm and $f = 150$ mm for $\lambda = 351$ nm light. The beam spot size $2\omega_0$ at the focal position is derived by $2\omega_0 = 4\lambda f/\pi D$ [17], and is 4×10 μm and 2×10 μm for $\lambda = 266$ nm and $\lambda = 351$ nm, respectively. Since the light incident angle θ was $\sim 40°$, the spot shape was an ellipsoid, and its major axis was stretched by $1/\sin\theta$.

The emitted light from the sample was focused by a $f = 70$ mm lens and introduced to a grating spectrograph (Spectra Pro 300i : Acton Research Corp.) with a CCD spectrometer (Model 7496 : Princeton Instruments Inc.). The grating system has about 500 nm of spectral range, with a wavelength dispersion of 0.4 nm per channel. In order to avoid the incorporation of the scattered excitation lasers, UV cut filters were inserted in front of the detector, namely a BK7 glass plate (cutoff at $\lambda = 325$ nm) for the $\lambda = 266$ nm laser, and a color-glass filter with cutoff wavelength of $\lambda = 380$ for the $\lambda = 351$ nm laser.

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Chapter 3

Local charge neutrality at polar surfaces and interfaces

Broken inversion symmetry and associated reconstructions are at the heart of the rich characteristics of surfaces and interfaces. It has been pointed out that the discontinuity of the stacking sequence of ionic charges can play an important role to determine the charge structure. However, various ways of judging the stability and different models for the reconstructions have caused confusion of the understanding of these phenomena. In this Chapter, we first define the character "polar" and "non-polar" for the discontinuities of materials in analogy to the surface of polar crystals. Then, we refine the model of the *polar discontinuity* taking dipole-free unit cells and explain the experimental results of reconstructions from a viewpoint of *local charge neutrality*. The equivalence of the different models is understood based on Maxwell's equations.

3.1 The *polar discontinuity* picture

3.1.1 Stability of ionic crystal surfaces

The surface of crystals determines many of the physical, mechanical or chemical properties of materials. Due to the lack of inversion symmetry at the surface, the stable charge distribution at the surface can be completely different from that of the bulk, and the surface may reconstruct in a manner different from the bulk states. Imagine an ideal ionic crystal which consists of charged ions bound together by their attractive interactions, and all the ions are taken as fixed point charges. Since the charges are locally preassigned to the ions in this model, the ideal ionic surface apparently requires no reassignment of the charges from that of the bulk. However, the electrostatic potential in an ionic crystal diverges when there is a dipole moment in the unit cell perpendicular to the surface. The potential $-V$ should be constant in vacuum in the absence of external fields, and the potential can be obtained by integrating the electric field caused by the charged sheets, as shown in Fig. 3.1. A finite shift in the potential emerges due to the dipole moment of the unit cell and as the unit cells are stacked, so the potential shifts, and diverges in the crystal. This surface instability has been indeed observed

Figure 3.1: Schematic illustration of the charge density ρ, the dipole μ in the unit cell starting from the topmost layer, the electric field E induced by the dipoles, and the electrostatic potential $-V$ at the surface of ionic crystals with dipole moment in the unit cell.

by means of low-energy electron diffraction (LEED) and ion scattering. The associated reconstructions through absorption of foreign atoms or surface roughening were reported [1–3]. Due to the effectively infinite surface energy, such surfaces cannot exist without reconstructions, and the stability of an ionic surface randomly cut from a bulk is not trivial without knowing the stacking sequence of the charged sheets precisely.

In order to survey the stability of such surfaces, Tasker introduced a classification of the surfaces from the viewpoint of the charge of the atomic sheets and the dipole in an unit cell which *starts from the topmost layer* [4]. Note he discussed the stability of *bulk frozen* surfaces[1], where the top most layer is one of the constituent atomic sheets of the bulk crystal and has no reconstruction. Tasker described three types of the surfaces, as shown in Fig. 3.2:

- Type 1 has equal number of anions and cations on each plane, and therefore the unit cell has no dipole moment. For example, the (100) and (110) surfaces of the rocksalt structure MX (e. g. NaCl, MgO, NiO) are classified to this type.
- Type 2 has charged planes, but no net dipole moment perpendicular to the surface. The anion X terminated (100) surface of the fluorite structure MX_2 (e. g. UO_2, ThO_2) is an example.
- Type 3 has charged planes and dipole moment normal to the surface. For example, the (111) surface of the rocksalt structure and (100) or (111) surface of the zincblende structure MX (e. g. GaAs, ZnS).

In Tasker's classification, type 1 and type 2 surfaces are stable while type 3 is not, since the instability of the surface comes from the stacking of the dipole in each unit cell. Macroscopically, the instability of the type 3 surfaces arises from the difference of the potential slope at the surfaces. Let us define the term "polar surface" following this manner, namely we call a surface is "non-polar" when it is type 1 or type 2, and "polar" when it is type 3.

[1]This definition of "*bulk frozen*" follows the manner by Goniakowski *et al.* [5]

Figure 3.2: Distribution of charges ρ on planes for three stacking sequences parallel to the surface. (a) Type 1, (b) type 2, and (c) type 3 (Tasker [4]).

These definitions are analogous to the definition of polar crystals, although polar surfaces and surfaces of polar crystals are not equivalent. Dielectric polarization is observed when electric field is applied to a material, but even in the absence of the field, some crystals keep the polarization, which is called spontaneous polarization [6, 7]. Only 10 out of 32 point groups show this behavior, and their members are called polar crystals, and others are called non-polar crystals. Twenty-one out of 32 point groups do not have inversion centers, and the polar crystals are included among them. When a material shows macroscopic spontaneous polarization, the electrostatic potential of its one end and the other end is distinctively different as a result of the stacking of the dipole in each unit cell, and the surface usually has the so called compensating charge to reconcile this potential difference. Since Tasker took unit cells from the topmost layer, even crystals with inversion symmetry can show dipoles in the unit cells in his model. For example, although NaCl belongs to cubic systems and has inversion center, its (111) surface is classified into type 3. Therefore, we have to be very careful when we use the word "polar", since it has different meanings in different contexts.

3.1.2 Stability of covalent surfaces

At a covalent surface, lacking full coordination, the topmost atoms of a covalent crystal have valence electrons which are not used for bond formation. These non-bonding electrons are called dangling bonds, and have higher energy than the bonding electrons, which causes the movement of the atom positions to decrease the number of such dangling bonds [8].

In a covalent crystal, since the bonds are formed as a hybridization of the valence electrons of charge-neutral atoms, one can describe the charge distribution staring from a bulk unit cell which is charge neutral and dipole-free. However, when the electronegativity of the atoms are different e.g., Ga and As in GaAs, charge transfer between anions and cations occurs, similar to the ionic case. This charge transfer is realized by the difference of the contribution of each bond, namely $1+\alpha$ electrons to the anions and $1-\alpha$ electrons to the cations. Here α is a parameter to describe the ionicity of the bond, determined by the electronegativity of the two atoms bonded. As a consequence, the unit cell can

have a dipole moment normal to the surface, which causes the same instability as that in the ionic crystal case. Therefore, even in a covalent crystal, a surface instability emerges from the dipole in the unit cell, independent of the surface instability naturally arising from the dangling bond formation. Even though Tasker's classification was introduced to describe the stability of ionic surfaces, it is also available for covalent surfaces in the presence of finite ionicity in the covalent bonds.

Both dangling bond formation and the instability of polar surfaces are relevant, and they are reconciled simultaneously at the surface of covalent crystals. Therefore, direct observation of the instability of polar surfaces in covalent systems has been difficult. When we consider an epitaxial interface which has similar charge structure as the polar surface, the instability from the dangling bonds disappears, and we can solely discuss the stability in the same manner as that for the ideal ionic surfaces, as discussed in the next section.

3.1.3 Polar semiconductor interfaces

Similar to the instability of the polar surfaces, dipoles in the unit cells stacking from the interface can cause potential divergence and instability, and require reconstruction. This point was first proposed at the heteroepitaxial interface of GaAs and Ge in the [001] direction by three groups from different starting points to treat ionicity. Based on their considerations, we define polar and non-polar interfaces, in analogy to polar and non-polar surfaces.

Charge transfer based on electronegativity

Frensley and Kroemer calculated the energy band diagram at abrupt semiconductor heterojunctions [9]. Their starting point was to describe the alignment of atoms around the interface without considering the ionicity, and then calculate the charge transfer based on the ionicity using the electronegativity of the atoms, under assumption that the charge transfer only occurs between the nearest neighbors. The Phillips electronegativity values X_{Ph} were used ($X_{\mathrm{Ph}}(\mathrm{Ga}) = 1.13$, $X_{\mathrm{Ph}}(\mathrm{Ge}) = 1.35$, and $X_{\mathrm{Ph}}(\mathrm{As}) = 1.57$ [10]). In a bulk zincblende structure AB, the A site is tetrahedrally coordinated by four B atoms and *vice versa*, and based on their calculation [11], the ionic charges e^* of the atoms are given by

$$e^*(A) = -e^*(B) = 0.76q_0 \times [X_{\mathrm{Ph}}(B) - X_{\mathrm{Ph}}(A)], \tag{3.1}$$

where q_0 is the elementary charge. This is equivalent to assuming a charge transfer of $0.76q_0 \times \frac{1}{4}[X_{\mathrm{Ph}}(B) - X_{\mathrm{Ph}}(A)]$ between any pair of the nearest neighbors.

Consider the case of Ge/GaAs interfaces as shown in Fig. 3.3(a) the charge $e^*(\mathrm{Ga_{int}})$ on the Ga ions adjacent to the interface is

$$e^*(\mathrm{Ga_{int}}) = 0.76q_0 \times \left[\frac{1}{2}X_{\mathrm{Ph}}(\mathrm{Ge}) + \frac{1}{2}X_{\mathrm{Ph}}(\mathrm{As}) - X_{\mathrm{Ph}}(\mathrm{Ga})\right] = 0.25q_0. \tag{3.2}$$

Figure 3.3: (a) Model for a (100) Ge/GaAs heterojunction considering the ionic character of the bonds. The atomic positions and effective ionic charges are shown above. Below is a diagram of the plane-averaged potential (Frensley and Kroemer [9]). (b) Schematic diagram of the charge transfer from the neutral atoms with respect to the electronegativity.

Similarly, the charges $e^*(\mathrm{Ge_{int}})$ on the Ge ions at the interface and $e^*(\mathrm{As})$ at the As sites are $e^*(\mathrm{Ge_{int}}) = -0.08q_0$ and $e^*(\mathrm{As}) = -0.33q_0$, respectively.

Without ionicity, the electrostatic potential is constant, and even with ionicity, the potential does not diverge. This can be understood easily by tracking the virtual charge transfer processes from the starting alignment of the charge neutral atoms. The charge transfer is equivalent to the situation that each neutral atom loses $0.76q_0 \times X_{\mathrm{Ph}}$ charges and the half of them are transferred to the left atoms and the other half to the other side, as shown in Fig. 3.3(b). Therefore, charges are always transferred symmetrically, and each modulation creates no dipole, resulting in no potential shift in each charge transfer. Note in this case, they admitted the change of the number of electrons in the ions compared to the bulk state, which is equivalent to mixed valence assignments.

Self-consistent calculation and counting electrons of bonds

Baraff *et al.* performed a self-consistent calculation of the potential, charge density, and interface states for the abrupt interface between Ge and GaAs, terminated on a (100) Ga plane [12]. As shown in Fig. 3.4(a), their calculation showed the fractional occupancy of electronic states only at the interface, which cannot exist in bulk.

These interface states can be discussed from a local-bond counting point of view as well. The number of the valence electrons is 4 for Ge, 3 for Ga, and 5 for As. When we assume all the valence electrons of an atom are equally distributed to the four covalent bonds around it, Ge, Ga, and As atoms supply 1, 0.75, and 1.25 electrons to each bond, respectively. As shown in Fig. 3.4(b), the Ge-Ga bonds at the interface have 1.75 electrons per bond, while other bonds have 2 electrons in each. These partially occupied bonds are considered to form the interface states.

When the number of electrons are smaller than that in the bulk, attractive interaction

Figure 3.4: (a) Calculated contour plot of charge density for the partially occupied interface band around Ga-Ge bonds (Baraff *et al.* [12]). (b) Schematic model for counting electrons from the local-bond point of view.

between the bonded atoms should be weaker. According to their calculation, the energy is minimized when the Ge-Ga bond length is 4 % larger than that of the bulk. Without the change of the bonding length, the system requires long-range disturbance of the lattice, which is unlikely to be realized.

Solving potential divergence from the ionic picture

Both the charge transfer model by Frensley and Kroemer and the electron counting model by Baraff *et al.* predicted that there are interface states at a Ge/GaAs (100) interface even if it is perfectly abrupt. However, experimentally no considerable interface states were observed [13], and a model to treat this interface without changing the number of charges at the interface was required.

Harrison *et al.* constructed the model for the Ge/GaAs (001) heterojunctions by stacking the fully ionized atoms, and calculated the electrostatic potential based on the fixed assignment of the charges [14]. As shown in Fig. 3.5(a), the potential is very similar to the case of the polar surfaces since the unit cells which *start from the interface* have dipoles in GaAs, while the unit cells in Ge are always charge neutral. Therefore, the stacking of the dipoles causes potential divergence in this case as well.

Since they fixed the charges of each ion, in order to solve the instability of this interface it should be compensated by changing the stoichiometry at the interface. They proposed a simple model where 1/4 Ge atoms are replaced by As atoms at the interface while 1/4 Ga atoms adjacent to the interface are replaced by Ge. In this reconstructed model with two transition layers, the electrostatic potential does not diverge, as shown in Fig. 3.5(b).

It might be surprising that from two completely different starting points, namely one from purely covalent (Frensley and Kroemer) and the other from ionic pictures (Harrison *et al.*), exactly the same potential diagrams were obtained[2]. However, rearranging the number of charges at the perfectly abrupt interface or changing the interface composition

[2]See Figures 3.3(a) and 3.5(b). Note both pictures have finite potential shift, which can be considered as the existence of interface dipoles. To consider the interface dipoles, the concept of *quadrupolar discontinuity* and taking quadrupole free unit cells are useful, and they are discussed in Appendix B.

Figure 3.5: Schematic crystal structure and electrostatic potential ϕ in the heterojunctions of Ge and GaAs in the [001] direction. (a) An atomically abrupt interface. (b) A Ge/GaAs heterojunction with two transition layers (Harrison *et al.* [14]).

maintaining the ionic charges of the atoms can give the same charge distribution. On the contrary, the experimental absence of localized states demands the atomic reconstruction based on the ionic picture. Also it is remarkable that there is a possibility that the charge transfer picture (Frensley and Kroemer) and the electron counting picture (Baraff *et al.*), which require change of electron numbers from the bulk values, can be available to transition metal oxides with multi-valency, as described in Section 3.1.4.

Definition of the polar interface

Following the model by Harrison *et al.*, we can define the polar nature of a *bulk frozen* interface between two materials, where the interface consists of two *bulk frozen* surfaces connected together[3]. First let us classify the interfaces by the polar nature of the two consisting surfaces, as shown in Fig. 3.6.

- Type I is formed between two non-polar surfaces, and the electrostatic potential V is flat.
- Type II is formed between polar and non-polar surfaces, and the electrostatic potential diverges from the interface in the material with the polar surface.
- Type III is formed between two polar surfaces, and the direction and the size of the dipoles in the unit cells which starts from the interface is same. Although V looks diverging from the interface in both materials by only considering the stacking of the dipoles, there is no macroscopic difference in the potential slopes at the interface.

[3]Here, we consider only interfaces between two semi-infinite materials – we ignore the coupling to other interfaces or surfaces. Coupling of two or more surfaces and interfaces is discussed in Sections 3.2.3 and 3.2.4.

Figure 3.6: Schematic distribution of charges ρ on planes, the dipole moment μ in unit cells starting from the interface, and the electrostatic potential for the four stacking sequences parallel to the interface. (a) Type I, (b) type II, (c) type III, and (d) type IV. In order to treat a *bulk frozen* interface as a set of two *bulk frozen* surfaces, vacuum is inserted between them (dashed lines). The electrostatic potential $-V$ was calculated taking the vacuum as the potential reference except for the right plot in (c), where the constant electric field was added so as to show the absence of macroscopic band bending at the interface.

We can cancel the potential slopes in both sides by adding constant electric field which does not change the Maxwell's equation, as shown in Fig. 3.6(c). Therefore, this interface is stable as constructed.

- Type IV is formed between two non-polar surfaces, where the dipoles in the two different unit cells are not identical, which results in a macroscopic difference of the potential slope at the interface. It is impossible to find any constant electric field to cancel out the potential divergence in the both media, due to the different potential slopes[4].

Type I and type III are stable due to the absence of macroscopic difference of the potential slopes, while type II and type IV are not stable. This difference arises from the continuity/discontinuity of the dipoles in the unit cells which starts from the interface. Following these discussions, let us define the polar nature of interfaces. A *bulk frozen* interface is non-polar, when the dipoles in the unit cells starting from the interface are identical across the interface, and thus no change of the macroscopic potential slope exists. On the other hand, it is polar if a *bulk frozen* interface has discontinuity of the dipole moment in each unit cell. For example, from a purely ionic view point (Harrison *et. al*) the abrupt Ge/GaAs (001) interface is classified into type II, and thus polar.

This definition of polar nature of interfaces is consistent with that of surfaces. When the vacuum is treated as a charge neutral material, the non-polar surface is type I,

[4]Note type IV is the most common and general case in reality, since electronegativity can never perfectly match.

and polar surface is type II in the classification of the interfaces, and the polar nature is maintained following the definitions for the interface. We can treat surfaces and interfaces in one framework, which is the polar nature of discontinuities of materials. In summary, polar discontinuities, which consist of polar surfaces and interfaces, are unstable due to the macroscopic potential folding arising from the discontinuity of the stacking of dipoles in the unit cells, and require reconstructions to stabilize them. Non-polar discontinuities, on the other hand, are stable without any reconstructions.

3.1.4 Metallic conductivity between two insulators

The high-mobility electron gas observed at the interface of two perovskite insulators, $LaAlO_3$ and $SrTiO_3$, is one of the striking examples of the novel properties of oxide interfaces [15]. $LaAlO_3$ and $SrTiO_3$ are well studied dielectric materials with bandgap of 5.6 eV [16] and 3.2 eV [17, 18], respectively. Many studies have been motivated to find the origin of the metallic interface between insulators. One of the proposed scenarios is based on electronic reconstructions driven by the polar discontinuity at the interface [19–21], another remarked on the importance of oxygen vacancies induced by kinetic growth [22–25], another focused on the charge accumulation at the interface due to the internal electric field in the structure [26], and yet another study found the interdiffusion of the elements at the interface which can change the charge structure [27]. Discriminating between these mechanisms has been controversial, since the change of Ti valence shows similar transport, spectroscopic, and optical properties, independent of its origin. Related to the origin, the amount of interface charge and its spatial extent have been current issues as well.

Explanation based on the *polar discontinuity* picture

The perovskite structure ABO_3 consists of alternating stacking of AO and BO_2 planes in the [001] direction. Assuming pure ionicity, the stacking order of the charges in the planes are different in these two materials, namely the planes of $LaAlO_3$ are $(La^{3+}O^{2-})^+$ and $(Al^{3+}O_2^{2-})^-$, while those of $SrTiO_3$ are $(Sr^{2+}O^{2-})^0$ and $(Ti^{4+}O_2^{2-})^0$. Therefore, the abrupt interface between $LaAlO_3$ and $SrTiO_3$ is polar (type II)[5] and requires reconstruction, in analogy to the GaAs/Ge (001) interface.

Unlike polar semiconductor interfaces where only atomic reconstructions are available due to the fixed ionic charge of each element, we have another possibility to reconcile the instability of polar interfaces, for example, through electronic reconstructions of transition metal oxides where various valence states are available for a single element. In the example of the $LaAlO_3/SrTiO_3$ interface, when the interface termination is LaO/TiO_2 (n-type), it requires a net half negative charge per 2D unit cell to reconcile the potential divergence.

[5] Allowing for covalency, SrO and TiO_2 planes in $SrTiO_3$ are no longer charge neutral, and thus the (001) surface is weakly polar, but still the dipole size of the unit cells which start from the interface is different from that of of $LaAlO_3$. Therefore, this interface should be classified as type IV, but still it is polar.

Figure 3.7: Possible reconstructions at the $LaAlO_3/SrTiO_3$ interfaces. The unreconstructed (a) LaO/TiO_2 terminated interface and (b) AlO_2-SrO terminated interface, and (c) and (d) the corresponding reconstructed interfaces, respectively. (Nakagawa *et al.* [19]).

Accessibility of Ti^{3+} can realize this negative charge by accommodating electrons at the Ti $3d$ level, which makes this interface metallic. On the other hand, when the interface is terminated by AlO_2/SrO (p-type), the sign of the required charges is opposite, and due to the difficulty of accommodating holes in this structure, the positive charges are realized by the formation of oxygen vacancies close to the interface. Oxygen vacancies are known as electron donors, but in this case they are formed to provide positive charges, and thus no electrons are supplied from these vacancies compensating the polar discontinuity. Therefore the system does not have itinerant electrons and remains insulating [15, 28].

Nakagawa *et al.* observed quantitative evidence for the reconstructed interfaces by means of STEM-EELS. They compared the spectroscopic features of the $LaAlO_3/SrTiO_3$ samples grown on a TiO_2 terminated $SrTiO_3$ substrate (n-type, with interface of LaO/TiO_2) and on a SrO terminated one (p-type, with interface of AlO_2/SrO), where the surface composition was controlled by deposition of a monolayer of SrO onto a TiO_2 terminated $SrTiO_3$ (001) substrate. Significant change of the Ti-L edge was observed in the n-type interface, indicating larger amount of Ti^{3+} component there. On the other hand, the O-K edge at the p-type interface showed a component which could not be matched to that of either bulk $SrTiO_3$ or $LaAlO_3$. They compared it to the shape of O-K edge of oxygen deficient $SrTiO_3$, and concluded that the component indicates the existence of oxygen vacancies.

One of the key corollaries of this explanation is the $LaAlO_3$ thickness dependence. This is because the size of the potential difference arising from the stacking of the dipoles in the unreconstructed structure is finite in thin films, and if it is small enough, the system may be stable without any reconstruction. Indeed, a critical thickness of $LaAlO_3$ was observed for the electronic reconstruction to occur [21], where the n-type $LaAlO_3/SrTiO_3$ interface is insulating if the thickness of $LaAlO_3$ is up to 3 unit cells. When the $LaAlO_3$ thickness is above that, the interface shows metallic conductivity. A similar tendency was

also observed in $SrTiO_3/LaAlO_3/SrTiO_3$ trilayer structures where the distance between the two polar interfaces was varied [20].

Oxygen vacancy formation during kinetic growth

$SrTiO_3$ is known as a material which readily accommodates oxygen vacancies which act as donors to provide itinerant electrons [29–31]. Due to the highly kinetic growth by PLD, bombardment of the substrate by the ablated species can induce oxygen vacancies. Kalabukhov *et al.* studied the optical, transport, and microscopic properties of the interfaces between $SrTiO_3$ and $LaAlO_3$, deposited at different oxygen partial pressure [22]. When the sample was grown at low pressure (10^{-6} Torr), the samples showed blue cathode- and photoluminescence at room temperature, similar to that of the reduced $SrTiO_3$ by Ar bombardment [32]. Also, they showed a similar temperature dependence of the transport properties. Finally, a large strain field at the interface was observed by electron microscopy, which can enhance the diffusion of oxygen, and they considered this enhancement as a possible origin of the high conductivity of $LaAlO_3/SrTiO_3$ interfaces.

Siemons *et al.* performed transport and spectroscopic studies of the $LaAlO_3/SrTiO_3$ interfaces grown by PLD under various oxygen pressures, as well as the samples postannealed in oxygen [23]. They showed that the carrier density is very sensitive to the oxidization condition of the growth as well as the annealing. The high carrier density (sheet carrier density of $\sim 2 \times 10^{16}$ cm^{-2} at 4 K) was achieved by growth under oxygen pressure of 10^{-6} Torr. Postannealing of the sample reduced the sheet carrier density to $\sim 2 \times 10^{13}$ cm^{-2} at 4 K and $\sim 2 \times 10^{14}$ cm^{-2} at 300 K, which is similar to that of the samples grown under oxygen pressure of $\sim 2 \times 10^{-5}$ Torr. Note this sheet carrier density of $\sim 2 \times 10^{14}$ cm^{-2} is close to the nominally expected value from the *polar discontinuity* picture, which is half an electron per 2D unit cell (3.28×10^{14} cm^{-2}), and the samples grown at lower pressure contained much more carriers. Also, photoemission spectra showed larger amount of Ti^{3+} in the samples grown at lower pressure. Their observations imply that the oxygen vacancies formed during kinetic growth by PLD in reducing conditions can introduce large numbers of itinerant electrons in $SrTiO_3$.

Precise transport studies of the $LaAlO_3/SrTiO_3$ interfaces grown under low pressure were presented by Herranz *et al.*, comparing them to the bulk doped $SrTiO_3$ [24]. They found Shubnikov-de Haas oscillations in the magnetoresistance of the low pressure grown sample, and based on their analysis, the itinerant electrons have a three dimensional Fermi surface. Also, they found other oxides deposited on $SrTiO_3$ can generate the high carrier density with bulk-like mobility of $SrTiO_3$ when they were grown at low oxygen pressure.

Recent observation of the conducting channels in $LaAlO_3/SrTiO_3$ by means of conductive tip AFM revealed the decay length of > 1 μm of oxygen vacancies in the samples grown at low pressure [25]. When they annealed the sample, the width of the conductive layer decreased to ~ 7 nm, which was probably limited by the radius of the probing tip.

The clear signature of the oxygen vacancies formed during growth was observed from

Figure 3.8: Conductive tip AFM mapping around the $LaAlO_3/SrTiO_3$ interface of (a) the as grown sample and (b) the postannealed sample (Basletic *et al.* [25]).

the samples grown at very low pressure ($\sim 10^{-6}$ Torr) and the effect diminished in the samples grown at higher pressure or those postannealed in oxygen. However it is difficult to exclude the role of oxygen vacancies even in these samples grown at higher pressure, partially because the oxygen vacancies and other mechanisms such as the polar discontinuity scenario give similar transport and spectroscopic properties, and the direct observation of dilute oxygen vacancies is extremely experimentally difficult, given the small relative atomic number of oxygen. In addition, there can be defects other than the growth induced oxygen vacancies in $SrTiO_3$, for example, point defects in $LaAlO_3$ films. Oxide heterostructures are usually grown by PLD, and the stoichiometry of the films are known to strongly depend on the growth conditions [33]. Such non-stoichiometric films can contain charged point defects, which can be compensated by not only other charges in the film, but also those in the proximate material. Therefore, it is also difficult to determine the effect of atmosphere during the growth or postannealing processes, since it can also affect the film stoichiometry.

Charge accumulation due to the internal field

In situ photoemission spectroscopy (PES) studies were carried out by Yoshimatsu *et al.* to seek for the origin of the metallic behavior and the band structure at the $LaAlO_3/SrTiO_3$ interface [26]. They compared the PES spectra by changing the thickness of $LaAlO_3$ on $SrTiO_3$ [Fig 3.9(a)] and the termination at the interface. Their observation showed a notched structure in $SrTiO_3$, only in the $LaAlO_3/TiO_2$ terminated $SrTiO_3$ samples, but no clear change of the density of states at the Fermi energy was observed within 1 nm from the interface. They claimed that if the origin of the charges is the polar discontinuity, the width of the carrier distribution should be of the order of 1 nm by theoretical calculation [34], as well as by the microscopic observation [19]. Due to the absence of such confined change of Ti valence states in their PES data [Fig 3.9(b)], they concluded that the origin is not the polar discontinuity, but the accumulation of charges provided by the oxygen vacancies in $SrTiO_3$.

One comment to their discussion would be on the flat band in $LaAlO_3$ drawn in the

Figure 3.9: (a) PES spectra obtained from $LaAlO_3/SrTiO_3$ samples with various thickness of $LaAlO_3$, grown on TiO_2-terminated $SrTiO_3$. (b) Comparison of the experimental PES spectrum around the Fermi energy and the simulated spectra assuming the decay length λ of the negative charges with total density of half electrons per 2D unit cell, as suggested by the *polar discontinuity* picture. (c) Energy band diagram of $LaAlO_3/SrTiO_3$ interfaces based on the PES observation (Yoshimatsu *et al.* [26]).

energy band diagram, as shown in Fig 3.9(c). If the negative compensation charges originate from the oxygen vacancies in the $SrTiO_3$, positive charges with the same number as the negative ones remained at the oxygen vacancies in the $SrTiO_3$. The charge neutrality of the system is maintained without any compensation charge at the surface of $LaAlO_3$. This means the electric field induced by the stacking of the dipoles in the $LaAlO_3$ unit cells are not compensated and the band diagram in the $LaAlO_3$ should have a finite slope, which contradicts with their picture. In order to avoid this contradiction, the simplest way is to take the negative charges at the interface as the summation of the compensation charges for the stacking of the dipoles in $LaAlO_3$ and the accumulated charges due to the band bending. Still, the idea of charge accumulation may be relevant, because it can accumulate extra carriers provided by other donors in $SrTiO_3$ (e. g. oxygen vacancies or impurities), which can significantly increase the carrier density of these interfaces.

Finally, let us discuss the difference between the two experimental results by STEM (Nakagawa *et al.*) and PES (Yoshimatsu *et al.*). The STEM measurement was done *ex situ* and the surface reconstruction can be modified by exposure to air, as well as by the thinning process during the sample preparation for STEM. On the other hand, the samples for the PES work was measured just after deposition, *in situ*, but they were grown by the deposition of $LaAlO_3$ films on top of the 20 monolayers of $SrTiO_3$ films on Nb:$SrTiO_3$ substrate to avoid the charge up effect. It is unclear whether this $SrTiO_3$ film is thick enough to decouple the $LaAlO_3/SrTiO_3$ interface and the Nb:$SrTiO_3$ substrate.

Intermixing at the interface

Willmott *et al.* studied precise atomic structure of a five-monolayer film of $LaAlO_3$ on $SrTiO_3$ (001) by means of surface x-ray diffraction [27], with the coherent Bragg

Figure 3.10: (a) Occupancies and (b) cumulative displacements Δ_z of the atoms at the $LaAlO_3/SrTiO_3$ interface. (c) Concentration of Ti^{3+} determined by invoking a minimization of the electric static potential. (d) Predicted cumulative unit cell displacements from bulk $SrTiO_3$ positions, based on the component ionic radii (Willmott *et al.* [27]).

rod analysis (COBRA) method [35] and further structural refinement. Their analyses revealed intermixing of the cations (La, Sr, Al, and Ti) at the interface [Fig. 3.10(a)], with the significant local displacement of atomic positions in the film, as well as in $SrTiO_3$ close to the interface [Fig. 3.10(b)]. The distribution of Ti valence was also obtained by minimizing the electrostatic potential [Fig. 3.10(c)] following the obtained atomic positions, and the displacement of the unit cells were well explained by the larger ionic radii of Ti^{3+} compared to Ti^{4+} [Fig. 3.10(d)]. The observation that Al begins to substitute Ti positions at shallower depths than La with Sr suggests the existence of $La_{1-x}Sr_xTiO_3$ at the interface. Based on this fact, they compared their experimental data to the calculation based on density functional theory (DFT) with interface composition of $La_{1-x}Sr_xTiO_3$, and the data was best reproduced by three transition layers with $x = 0.86$, 0.70, and 0.10.

One of the important findings was that the mixing of La and Sr was observed 6 Å deeper than that of Al and Ti. This is larger than 2 Å, the half length of a perovskite unit cell, which is the value we expect assuming the abrupt termination of LaO/TiO_2 at the interface and allowing symmetric interdiffusion of the atoms. Since the ionic radii of La and Sr are larger than those of Al and Ti and thus La should feel a higher barrier to get into the substrate than Al, simple kinetic bombardment during PLD growth cannot explain this result. They considered the effect of a local thermal spike, which can assist the adatoms to overcome the barrier and realize the atomic positions observed. The origin of the different mixing point of the A site and B site cations in perovskites (ABO_3) is further discussed in Chapter 6.

3.1.5 Challenges to the *polar discontinuity* picture

One of the challenges to the explanation based on the *polar discontinuity* picture has been the question: Where do the electrons come from? In the current proposed model based on polar discontinuity [19, 21, 36], the charges are provided from the surface of the $LaAlO_3$ film to the Ti^{4+} close to the interface, but it is not so obvious that they travel through the insulating films independently of its thickness beyond the critical thickness. There is still debate over whether the stacking sequence of the atomic layers is the origin of the metallic conductivity, although the experimental results show that the interface composition does change the transport properties of oxide interfaces [15, 28, 37]. One of the reasons is because the current model cannot answer this question clearly, promoting the search for other origins. [22, 23, 25–27].

The other difficulty is how to treat the charge density to describe the macroscopic electric field. Based on the *polar discontinuity* picture, the stacking of the dipoles in the unit cells creates a macroscopic electric field, resulting in the change of the potential slope at the discontinuity. In this picture, the unit cells start from the discontinuity, and thus the composition is always the same as that of the bulk, which is charge neutral. It might be strange that the potential starts to bend at the discontinuity although all the unit cells are neutral, because the source of the electric field is charges. In fact, it is the macroscopic bound charge density at the surface that is the source of the electric field, as explained later in Section 3.3.3, but the existence of such implicit charge density has caused confusion in the understanding of the polar nature and made it difficult to draw a proper energy band diagram in the semiconductor sense. In order to treat these charges explicitly, an equivalent but different viewpoint of treating the polar discontinuities is useful. This *local charge neutrality* picture based on the dipole-free unit cells is discussed in the next section.

3.2 The *local charge neutrality* picture

3.2.1 Unit cells in ionic crystals

One of the origins of confusion regarding the stability and the reconstructions of polar discontinuities arises because of the various choices of a unit cell in a crystal, which determines the size and direction of the dipole in it. For example, when we take the unit cell of $LaAlO_3$, one way is to visualize the crystal as a stacking of [(AlO_2) (LaO)]. From an ionic point of view (La^{3+}, Al^{3+}, and O^{2-}), this stacking can be treated as a dipole of [$(AlO_2)^-$ $(LaO)^+$], as shown in Fig. 3.11(a). However, it is also possible to take [$(LaO)^+$ $(AlO_2)^-$] as an unit cell, and the sign of the dipoles is opposite to the previous case, as shown in Fig.3.11(b).

The choice of unit cells should not change the electrostatic potential in the crystal. Indeed, the difference between the two choices is compensated by the potential V_{sur} arising from the surface layer. If the surface is terminated by the $(AlO_2)^-$ layer, it remains as an

Figure 3.11: Schematic illustrations of the various choices of unit cells in $LaAlO_3$, charge distribution ρ, and associated potential $-V$. The filled allows indicate the orientation of the dipoles with size Δ in the unit cells. (a) Taking $[(AlO_2)^-\ (LaO)^+]$ as an unit cell. (b) Taking $[(LaO)^+\ (AlO_2)^-]$ as an unit cell, and the total potential $-V_{\rm tot}$ is the sum of the potential $-V_{\rm dip}$ arising from the stacking of the dipoles and the potential $-V_{\rm sur}$ from the surface charge. (c) Taking a dipole free unit cell $[\frac{1}{2}(LaO)$ - (AlO_2) - $\frac{1}{2}(LaO)]$.

extra negatively charged layer when we take $[(LaO)^+\ (AlO_2)^-]$ as the unit cell, as shown in Fig.3.11(b), and the total electrostatic potential remains the same as in the $[(AlO_2)^-$ $(LaO)^+]$ unit cell case.

Therefore, it is impossible to fix the direction of the dipoles without knowing the surface termination. In other words, it is the surface that determines the stability of the system. So the problem can and should be solved considering the surface locally, and not by counting the number of dipoles in the material. In order to avoid considering the dipoles arising from the stacking of charged layers, the simplest approach is to take the dipole-free unit cells. This can be achieved in any crystal [5], and in the $LaAlO_3$ case, this is achieved by taking $[\frac{1}{2}(LaO)$ - (AlO_2) - $\frac{1}{2}(LaO)]$ (or $[\frac{1}{2}(AlO_2)$ - (LaO) - $\frac{1}{2}(AlO_2)]$) as a unit cell, as shown in Fig. 3.11(c). This is analogous to the unit cell in a type 2 model in Tasker's classification. According to group theory, it is known that spontaneous polarization can be observed only in the direction where the crystal does not have mirror symmetry. Since cubic perovskites do have mirror symmetry in the [001] direction, it is natural to take the dipole free unit cells to reflect the lack of polarization in the bulk.

When we take this unit cell, the stability of a polar surface or interface can be discussed by only considering the charge neutrality of each unit cell, since now there is no net dipole created by the stacking of charged layers. For example, the instability of the (AlO_2) terminated surface of $LaAlO_3$ is naturally derived because the top most unit cell is $[(AlO_2)^-\ \frac{1}{2}(LaO)^+]^{-0.5}$, which violates charge neutrality, as shown in Fig. 3.11(c). Thus the (001) surface of $LaAlO_3$ cannot keep the bulk termination, either by an AlO_2 or LaO layer, and must reconstructs to compensate this charge. Of course, once charge neutrality of the unit cells is kept, the system allows electron / hole modulation or interdiffusion / displacement of the atoms which creates only finite dipoles and does not

Figure 3.12: Schematic illustrations of the charge structure across the two types of *bulk-frozen* $LaAlO_3/SrTiO_3$ interfaces, assuming the ionic charges based on the valence states in bulk $LaAlO_3$ and $SrTiO_3$. Taking dipole free unit cells, the interface unit cell cannot keep charge neutrality, and the simplest neutral interface stoichiometry is written in the right. (a) LaO/TiO_2 terminated $LaAlO_3/SrTiO_3$ interface and (b) AlO_2/SrO terminated $LaAlO_3/SrTiO_3$ interface.

violate neutrality[6]. These perturbations are important because they determine the real charge structure, for example via lattice distortion close to the surface of $LaAlO_3$ [38].

Following these arguments, the polar nature of given *bulk frozen* surfaces and interfaces is clearly defined, considering local charge neutrality in the dipole free unit cells: a *bulk frozen* surface or interface is polar if the unit cell at the surface or interface cannot keep charge neutrality when we take dipole free unit cells in the bulk.

3.2.2 Explanation of the metallic conductivity of $LaAlO_3/SrTiO_3$ by the *local charge neutrality* picture

Now we discuss the stability of the $LaAlO_3/SrTiO_3$ (001) interfaces. Taking dipole free unit cells of perovskites ABO_3 in the [001] direction, namely $[\frac{1}{2}(AO)$ - (BO_2) - $\frac{1}{2}(AO)]$, the interface unit cell can be treated as a δ-dopant at the interface. As shown in Fig. 3.12, the interface unit cell does not keep the stoichiometry of either of the bulk materials, even not a simple mixture of them. This issue is one of the central aims of the interface science of compounds. Namely, the LaO/TiO_2 terminated $LaAlO_3/SrTiO_3$ interface has $La_{0.5}Sr_{0.5}TiO_3$ as the interface unit cell. Considering the formal electronic charges of La^{3+}, Sr^{2+}, and O^{2-}, the Ti ion in this unit cell should take $Ti^{3.5+}$ as a formal valence, which is the same reconstructed state as that of the previous explanations by the *polar discontinuity* picture.

Similarly, the AlO_2/SrO terminated interface has $La_{0.5}Sr_{0.5}AlO_3$ as the interface unit cell, and due to the fixed ionic charges of the elements, such a unit cell is unstable. $LaAlO_3$ is known to be a stable material, but $SrAlO_3$ is not. Instead, a material with a

[6]The effect of diffusion is further discussed in Appendix A as an example of sources of such finite dipoles. Also, note there is another important source of the interface dipoles, and this *quadrupolar discontinuity* is discussed in Appendix B.

Figure 3.13: (a) Schematic band structures of $SrTiO_3$, $LaAlO_3$ and $La_{0.5}Sr_{0.5}TiO_3$, assuming that $SrTiO_3$ and $LaAlO_3$ are intrinsic semiconductors, Oxygen $2p$ states of $SrTiO_3$ and $La_{0.5}Sr_{0.5}TiO_3$ are assumed to be lined up. (b) Schematic energy band diagram of the $LaAlO_3/SrTiO_3$ interface with the δ-dopant $La_{0.5}Sr_{0.5}TiO_3$ at the interface. Note the difficult self consistency to determine the bandgap of the doped material, since in transition metal oxides, strong electron-electron correlation cannot be neglected. For further discussions on the correlation effects, see Section 3.2.6.

composition of $Sr_2Al_2O_5$ is available as a mixture of $Sr_3Al_2O_6$ and $SrAl_2O_4$[7]. Allowing the change of the oxygen number in the interface unit cell, $La_{0.5}Sr_{0.5}AlO_{2.75}$ can be considered as a mixture of $LaAlO_3$ and $Sr_2Al_2O_5$, and the decrease of the oxygen numbers at the interface to stabilize a p-type $LaAlO_3/SrTiO_3$ interface is naturally derived. Note in this case, these oxygen vacancies are introduced to keep charge neutrality, and thus do not provide any free electrons. Following these explanations, the electrons/oxygen vacancies to reconcile the polar instability of the *bulk frozen* $LaAlO_3/SrTiO_3$ interfaces are supplied by the interface unit cell itself[8].

In semiconductors, δ-doping is usually achieved in a symmetric geometry, namely the dopant layer is sandwiched between the same host material. In the $LaAlO_3/SrTiO_3$ case, on the contrary, the two sandwiching materials have different band structure, namely $SrTiO_3$ has narrower bandgap. Therefore, broadening of the charge distribution from the δ-dopant occurs only in the $SrTiO_3$ side. Figure 3.13 shows how the $LaAlO_3/SrTiO_3$ interface can be depicted in a semiconductor energy band diagram. Only the $SrTiO_3$ has notched structure, which well matches the PES results by Yoshimatsu *et al.* [26].

3.2.3 Coupling of polar discontinuities

When two polar discontinuities are brought in proximity to one another, coupling of the charges can occur to minimize the total energy of the system. This can be considered in analogy to the coupling of dopant layers in δ-doped semiconductor heterostructures. This is because polar discontinuities provide an interface unit cell that cannot keep charge neutrality based on the bulk stoichiometry and charge states, which can be treated as a δ-dopant.

[7] In Chapter 5, fabrication of insulating $LaAlO_3/SrTiO_3$ interfaces using this material is described.
[8] See Section 3.2.5 for further discussions.

Figure 3.14: Schematic band diagram of an (a) undepleted and (b) depleted δ-doped semiconductor. The undepleted structure contains free carriers as well as ionized impurities. The depleted structure contains the same amount of donor and acceptor impurities (Gossmann and Schubert [39]).

Coupling of the two δ-doping layers are understood in terms of depleted and undepleted structures. Figure 3.14(a) shows the band diagram of an undepleted semiconductor with one layer of δ-dopant. Since the dopant is positively ionized, an equal number of free electrons are left, and they screen out the potential created by the δ-dopant. As a consequence, the structure is neutral, and has zero electric field sufficiently far away from the δ-dopant layer.

On the other hand, Fig. 3.14(b) shows the band diagram of a depleted δ-doped structure, where the number of donors is equal to that of acceptors, and they are sufficiently close in space. As a result, all the free carriers recombine and the structure is depleted. The critical parameters to treat electronic coupling of two δ-doping layers are the distance between them and the dielectric constant of the medium. When the distance between them are smaller than the length scale of band bending of the undepleted structure, they couple and the system goes to a depleted structure. Note in this case, the charge neutrality in the neighborhood of one dopant layer is not necessarily maintained.

In δ-doped semiconductor heterostructures, only considering modulation of free carriers is sufficient to describe the coupling of the δ-dopant layers. However, when the system allows possibilities of excess charges other than the free carriers, which come from outside of the constructed crystal – e. g., anion or cation vacancies or foreign atoms absorbed to the surface, the electrostatic potential can be minimized via them. For example, the instability of polar AlO_2 terminated $LaAlO_3$ surface can be solved by introducing positively charged surface oxygen vacancies. The $LaAlO_3$ thickness dependence of LaO-TiO_2 terminated $LaAlO_3/SrTiO_3$ can be explained by a simple assumption, where we only consider coupling of the free electrons provided by the $LaAlO_3/SrTiO_3$ interface and the surface oxygen vacancies to keep the local charge neutrality of the polar $LaAlO_3$ surface. Figure 3.15 shows a schematic structure of the $LaAlO_3/SrTiO_3$ heterojunction, where two polar discontinuities exist at the $LaAlO_3/SrTiO_3$ interface and the $LaAlO_3$ surface. When the $LaAlO_3$ film is sufficiently thick [Fig. 3.15(a)] these polar discontinuities are decoupled and charge neutrality is preserved locally by introducing oxygen vacancies at the surface and taking the Ti valence of 3.5+, which keeps local charge neutrality of the interface unit cell. Fractionally filled Ti valence provides itinerant electrons, and

Figure 3.15: Schematic illustration of the charges (ρ) of the dipole free unit cells of atomically abrupt $LaAlO_3/SrTiO_3$ interfaces in (a) the thick $LaAlO_3$ limit with the polar discontinuities locally neutralized and (b) the thin $LaAlO_3$ limit with the depleted polar discontinuities.

therefore the system is metallic in the thick limit.

If the two polar discontinuities are brought closer [Fig. 3.15(b)], the external charges and the free carriers (surface oxygen vacancies and extra electrons in Ti valence) can recombine in the environment with oxygen gas, and the system is depleted and the conductivity disappears[9]. Here, the word "deplete" is used to mean "reduce the amount of charges other than charges bound to the crystal", and the full depletion of the $LaAlO_3$ surface means extinguishing the positively charged oxygen deficiency at the surface – i. e. the surface turns to be an unreconstructed *bulk frozen* state. In real systems, charge modulation can occur through further complex mechanisms, for example lattice distortion or interdiffusion and thus the stable structure is expected to be more complicated.

3.2.4 Modulation doping by a proximate polar discontinuity

Even if the system contains only one polar discontinuity, coupling of the polar discontinuity and the other layers can occur in analogy to modulation doping by a δ-doping layer, as shown in Fig. 3.16. At the semiconductor interface, lineup of the conduction and valence bands should be kept, as well as the continuity of the chemical potential, which causes the modulation of carriers resulting in band bending. Assume an interface between two intrinsic semiconductors A (narrow bandgap) and B (wide bandgap). If the δ-dopant in B is sufficiently far from A, the flat band condition at the interface is maintained [Fig. 3.16(a)]. When A is brought in proximity to the δ-dopant in B, in order to keep the conduction band lineup, the conduction band minimum of A lies at lower

[9]This is an analogy of recombination of free electrons and holes, and the actual recombination can be written by following Kröger-Vink notation [40] as: $\frac{1}{2}O_2 + 2e' + V_O{}^{\cdot\cdot} \rightarrow 0$.

Figure 3.16: Schematic band diagram of the interface between two intrinsic semiconductors A and B, with a layer of δ-dopant in B. (a) A is sufficiently far from the δ-dopant in B. (b) Model with no charge modulation though the distance between A and the δ-dopant is close, resulting in the mismatch of the chemical potential. (c) Charges transfer from B to A, so as to match the chemical potential.

energy than the chemical potential in B [Fig. 3.16(b)]. Since the free carriers around the δ-dopant in B have higher energy than the conduction band minimum of A, they transfer to A and band bending occurs in A [Fig. 3.16(c)]. As a result, the δ-dopant in B is depleted, and A is doped close to the interface. Such modulation doping can occur between a narrow band gap semiconductor and a polar discontinuity in a wider band gap material. In Chapter 4, we describe the recent observation of the charge modulation from a type 3 polar surface of $LaAlO_3$ (001), which acts as a δ-dopant, to a Mott insulator $LaVO_3$ with narrower bandgap, where the $LaAlO_3/LaVO_3$ (001) interface is type III and thus non-polar, assuming full ionicity.

3.2.5 Advantages of the *local charge neutrality* picture

As already discussed, the *local charge neutrality* picture gives clear explanations for the various phenomena at surfaces and interfaces. Following this picture, the stability of given surfaces and interfaces can be simply judged by looking at the local composition. When the interface composition differs from that of the bulk or a simple superposition of them, a different electronic and/or atomic state can be expected. The local charge neutrality at the interface unit cell naturally explains the source of the charges which can change the stoichiometry or the electron number of the constituent atoms from those of the bulk. For example, in a LaO/TiO_2 terminated $LaAlO_3/SrTiO_3$ *bulk frozen* interface,

the interface unit cell is $La_{0.5}Sr_{0.5}TiO_3$ and its Ti valence is naturally derived to be 3.5+ to achieve charge neutrality. Therefore, the difference between the Ti^{4+} in the bulk $SrTiO_3$ and the interface $Ti^{3.5+}$ comes from the interface unit cell itself, and not from anywhere else.

Also, this is a big advantage, especially when considering interfaces with more complex stoichiometry. For example, interdiffusion can occur at real interfaces, which makes it difficult to consider whether the potential diverges far from the interface. Interdiffusion induces a finite dipole, so it does not change the condition for the diverging potential due to the polar discontinuities, but still it is not straight-forward to connect the given diffused interface to the *bulk frozen* interface model, In addition, in a real system, the interface composition may be different from that of the *bulk frozen* interface even after subtracting the effect of the interdiffusion, as experimentally pointed out by Willmott *et al.* [27]. This is because the interface composition can be modified via inserting other materials during growth, or by the change in the stoichiometry of the surface on which another material is deposited to form the interface. For example, the properties of the interface between $SrTiO_3$ and $LaMO_3$, where M is a trivalent metal ion, can strongly depend on the interface stoichiometry, which is described in Chapters 5 and 6. In such cases, drawing all the diagrams of the electric field and the potential to determine the stability is difficult, and it is easier to count the number of charges based on the *local charge neutrality* picture.

The other advantage of taking the *local charge neutrality* picture becomes clear when we discuss the coupling of polar discontinuities, because we can consider the phenomena in analogy to the coupling of δ-dopant layers in semiconductors. The stability of the system can be discussed through the distance between the polar discontinuities and the screening length of the host material. In other words, the stability is determined by the balance of the activation energy of the dopant and the electrostatic energy allowing polarization of the media between the dopant layers. Therefore, the total polarizability of the media can be naturally considered in the calculation, and is connected to the bulk permittivity in the thick limit. Note when the media is thin, the local effective permittivity is not trivial since the local atomic displacements can be different from that in the bulk.

Finally, note the *local charge neutrality* picture is qualitatively equivalent to the charge redistribution model at a valence-mismatched interface, for example, $SrTiO_3$ /$La_{1-x}Sr_xMnO_3$ [41, 42]. In these models, they simply assumed the charge modulation between the neighboring atomic layers, for example, when the MnO_2 plane is surrounded by SrO and $La_{1-x}Sr_xO$ layers, the Mn should take higher valence compared to that in bulk $La_{1-x}Sr_xMnO_3$ due to additional hole doping from the SrO layer. However, their model only considers local charge transfer without considering the unit cells to construct the total structure, and therefore global charge neutrality is neglected. This problem may appear clearly when we treat diffused interfaces, since the neighboring relations can be very complicated within the interdiffusion length scale. In order to treat these charge distributions quantitatively, connecting the local charge distribution and global charge

neutrality is essential, which can be enabled by taking dipole free unit cells.

In summary, the advantage of taking dipole free unit cells arises from the ability to avoid the ambiguity of the (artificial) dipole moment of the unit cell and focus on the local charge neutrality of the unit cells. This guarantees that global charge neutrality is maintained, and avoids ambiguous questions regarding non-local sources of charge.

3.2.6 Further discussions considering correlation effects

So far we have tried to describe the polar discontinuity within the semiconductor language by taking dipole free unit cells and treating the interface unit cell as a δ-dopant. Here, we should note that at the presence of strong electron-electron correlation, for example in transition metal oxides, it is impossible to draw semiconductor energy band diagrams based on the single-particle picture of independent electrons[10] [45, 46]. Also, in order to draw band diagrams, we should know which part of the charges to be assigned as free carriers, and it is non-trivial in the correlated systems, for example, in Mott insulators.

However, still the *local charge neutrality* picture can provide important information on the interface charge structure of transition metal oxides, since the electron correlation cannot change the number of total charge. Therefore it is possible to predict the number of charges in each dipole free unit cell based on *local charge neutrality* even at the presence of the correlation effects. Of course, the finite perturbation to move these charges is allowed, but it does not change the total number of the charges in the system, and still the number of charges can be determined in a cluster consisted of a sufficiently large number of dipole free unit cells. This is because the material outside of the charge modulation region consists of dipole free unit cells of bulk, which are charge neutral and thus stable. When considering how to assign these charges to the states in the actual system, then the effect of correlation becomes important. In other words, taking dipole free unit cells can provide cluster models with fixed electron numbers to discuss the electronic structure at the interfaces or surfaces.

3.3 Equivalence of the two pictures

3.3.1 Maxwell's equations in infinite media

Maxwell's equations are the set of four partial differential equations which describe the properties of electric and magnetic fields and the relationship between them and their sources, current and charge density. Considering the electrostatic potential, the relevant equation is the Gauss-Maxwell's law of electric field:

$$\nabla \cdot \mathbf{D} = \rho_{\text{free}}, \tag{3.3}$$

[10] Owing to the relatively small (still not negligible) correlation effects in $SrTiO_3$ with the Ti $3d^0$ configuration [43] and weak $2p$-$3d$ hybridization in the coherent state of doped $SrTiO_3$ [44] , the schematic band diagram shown in Fig. 3.13 may be still valid, by assuming $SrTiO_3$ to be a band semiconductor.

in media. Here the electric flux density $\mathbf{D}$ is related to the electric field $\mathbf{E}$ and polarization density $\mathbf{P}$ by

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}, \tag{3.4}$$

where ε_0 is the vacuum permittivity and ρ_{free} is the free charge – the part of the macroscopic charge density due to excess charges not intrinsic to the medium. Other charges in the medium are called bound charges ρ_{bound}. Note these definitions do not depend on whether these charges are localized or itinerant, and are just introduced for practical convenience to treat the displacement of the bound charges as the dielectric response of the media to the electric field.

The electric flux density $\mathbf{D}$ was introduced to simplify the calculation of the electric field. It is often very complicated to treat the total charge ρ_{total} based on first principles, which is the Gauss-Maxwell's law of electric field in vacuum

$$\nabla \cdot \mathbf{E} = \frac{\rho_{\text{total}}}{\varepsilon_0}, \tag{3.5}$$

and consider the response self-consistently. Separating the bound charges in the crystal and its response to the electric field $\mathbf{E}$, the Gauss-Maxwell's law of electric field in the media (3.3) was obtained, which relates $\mathbf{D}$ to the free charge density. By taking the divergence of the equation (3.4) we obtain

$$\nabla \cdot \mathbf{D} = \nabla \cdot \varepsilon_0 \mathbf{E} + \nabla \cdot \mathbf{P} \;\Leftrightarrow\; \rho_{\text{free}} = \rho_{\text{total}} + \nabla \cdot \mathbf{P} \;\Leftrightarrow\; -\rho_{\text{bound}} = \nabla \cdot \mathbf{P}, \tag{3.6}$$

and $\mathbf{P}$ is related to the bound charge density.

In infinite crystals, only the divergence of $\mathbf{E}$, $\mathbf{P}$, and $\mathbf{D}$ has physical meaning, and the dipole density $\mathbf{P}_{\text{unit}}$ arising from the dipole moment of the unit cells is neglected since it merely adds a constant value to $\mathbf{P}$. This is because Gauss-Maxwell's law of electric field is written in differential form, as previously shown.

3.3.2 Gauss-Maxwell's law of electric field in finite crystals

When the crystal is finite, the polarization density $\mathbf{P}$ containing $\mathbf{P}_{\text{unit}}$ discontinuously drops to zero at the surface. This suggests that the choice of the unit cells is important in Maxwell's equations in finite media, since it can change $\mathbf{P}_{\text{unit}}$, and thus its discontinuity at surfaces. According to equation (3.6) it is also clear that the magnitude of the polarization discontinuity at the surface is determined by the bound charge density there. Since the total amount of charge at the surface does not depend on the choice of the unit cells, uncertainty in the dipole moment in the unit cell is compensated by whether the charges at the surface are defined to be free or bound. This consideration naturally requires a clear definition whether the charges at the surface of a crystal is free or bound, depending on the choice of the unit cells – the surface charge is bound when it belongs to a bulk unit cell, and free when not, and this definition does not depend on the origin of the charges [6].

To make the calculation simple, let us adopt the bulk dielectric constant ε to connect the electric field $\mathbf{E}$ and the induced polarization $\mathbf{P}_{\text{ind}}$ by the field, namely

$$\mathbf{P}_{\text{ind}} = (\varepsilon - \varepsilon_0)\mathbf{E}, \tag{3.7}$$

and the total dipole density $\mathbf{P}$ is given by

$$\mathbf{P} = \mathbf{P}_{\text{ind}} + \mathbf{P}_{\text{unit}}. \tag{3.8}$$

Substituting them to equation (3.4) we obtain

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P} = \varepsilon_0\mathbf{E} + (\varepsilon - \varepsilon_0)\mathbf{E} + \mathbf{P}_{\text{unit}} = \varepsilon\mathbf{E} + \mathbf{P}_{\text{unit}}. \tag{3.9}$$

Note equations (3.4) and (3.9) have a similar structure, but the dipole moment $\mathbf{P}_{\text{ind}}$ due to the dielectric response is included in the $\mathbf{P}$ term in the former and in the $\varepsilon\mathbf{E}$ term in the latter. Based on these definitions, let us calculate the value of $\mathbf{E}$, $\mathbf{P}_{\text{unit}}$, $\mathbf{D}$, and the charge density ρ, considering the (AlO_2) terminated (001) surface of $LaAlO_3$ as an example.

Taking [$(AlO_2)^-$ $(LaO)^+$] as an unit cell – the *polar discontinuity* picture

Let us take the z axis as perpendicular to the (001) plane of the $LaAlO_3$. Consider only the z-component of the vectors $\mathbf{D}$, $\mathbf{E}$, and $\mathbf{P}$, and write them as D, E, and P, respectively. As shown in Fig. 3.17(a), all the ionic charges are included in the unit cells, and thus bounded. To fix the constant in E, let us take the vacuum to be the reference, namely $E = 0$ there. Due to the absence of free charges, $D = 0$ from equation (3.3). In this case, the [$(AlO_2)^-$ $(LaO)^+$] unit cell has a dipole moment of $\frac{q_0 a}{2}$, where q_0 is the elementary charge and a is the pseudocubic lattice constant of $LaAlO_3$. This can be derived by considering two oppositely charged layers separated by $a/2$, which is the distance between the $(AlO_2)^-$ and $(LaO)^+$ layers. Considering the unit cell volume a^3, the dipole density P_{unit} satisfies $P_{\text{unit}} = \frac{q_0}{2a^2}\theta(z)$, where $\theta(z)$ is the step function. Equation (3.9) immediately derives E as a function of the position, namely $E = -\frac{q_0}{2\varepsilon a^2}\theta(z)$. The total dipole moment P is given by $P = \left((\varepsilon - \varepsilon_0)\cdot\frac{-q_0}{2\varepsilon a^2} + \frac{q_0}{2a^2}\right)\theta(z) = \frac{\varepsilon_0}{\varepsilon}\frac{q_0}{2a^2}\theta(z)$, following equations (3.7) and (3.8). According to equation (3.6), bound charge density is derived by differentiating P, $\rho_{\text{bound}} = -\frac{\mathrm{d}}{\mathrm{d}z}P = -\frac{\varepsilon_0}{\varepsilon}\frac{q_0}{2a^2}\delta(z)$, where $\delta(z)$ is the Dirac's δ function. This indicates that the system has bounded charges of $-\frac{\varepsilon_0}{\varepsilon}\frac{q_0}{2a^2}$ at the surface.

Taking [$\frac{1}{2}$(LaO) - (AlO_2) - $\frac{1}{2}$(LaO)] as an unit cell – the *local charge neutrality* picture

When we take dipole free unit cells [Fig. 3.17(b)], the topmost unit cell is [(AlO_2) - $\frac{1}{2}$(LaO)] , which is not a bulk unit cell. Therefore, the half negative charge which belongs to this unit cell is free, and the free charge density is described by $-\frac{q_0}{2a^2}\delta(z)$. By integrating equation (3.3) and using the boundary condition that $D = 0$ in the vacuum, we obtain

Figure 3.17: Schematic illustration of macroscopic D, P_{unit}, P, E, ρ_{bound},ρ_{free}, and ρ_{tot} close to the (001) surface of $LaAlO_3$. (a) Taking $[(AlO_2)^-\ (LaO)^+]$ as an unit cell and (b) taking $[\frac{1}{2}(LaO)$ - (AlO_2) - $\frac{1}{2}(LaO)]$ as an unit cell.

$D = -\frac{q_0}{2a^2}\theta(z)$. Since $P_{\text{unit}} = 0$, E is obtained as $E = \frac{D - P_{\text{unit}}}{\varepsilon} = -\frac{q_0}{2\varepsilon a^2}\theta(z)$. According to equation (3.4), the total polarization density is $P = D - \varepsilon_0 E = \frac{\varepsilon - \varepsilon_0}{\varepsilon}\frac{q_0}{2a^2}\theta(z)$, and the bound charge density is obtained by equation (3.6), namely $\rho_{\text{bound}} = \frac{\varepsilon - \varepsilon_0}{\varepsilon}\frac{q_0}{2a^2}\delta(z)$. This bound charge density appeared as a response to the electric field E arising from ρ_{free}.

3.3.3 Equivalence of the two pictures considering total charge density

Comparing the obtained values from the two pictures, one can see that $E = -\frac{q_0}{2\varepsilon a^2}\theta(z)$ and $\rho_{\text{total}} = -\frac{\varepsilon_0}{\varepsilon}\frac{q_0}{2a^2}\delta(z)$ are independent of the choice of the unit cells. This fact may be trivial from the viewpoint of Maxwell's equations because the electric field and the total charge density are always connected by Gauss-Maxwell's law. This equivalence bridges the gap between the *polar discontinuity* picture based on the ionic charges and the *local charge neutrality* picture which can treat the interface unit cells as δ-dopants and enable to depict them in semiconductor energy band diagrams. However, it may be still surprising that the microscopic choice of unit cells does not change the macroscopic electric field, even though they have different explanations for its origin. This seemingly strange difference arises from the definitions of the free and bound nature of charge which were introduced merely to describe Maxwell's equations in media.

3.4 Summary

As pointed out by Tasker, the order of the ionic charge stacking plays an important role for the stability of the surfaces and interfaces, and sometimes they show a diverging potential when following bulk compositions and electronic states. In semiconductors where the number of ionic charges are fixed, they are usually stabilized by atomic reconstructions, as shown by Harrison *et al.*, and the polar nature of the discontinuities does not appear in the electronic structure. However, in transition metal oxides, change of the electronic structure provides another possibility to reconcile the instability.

In order to treat the instability of such polar discontinuities, two different pictures were introduced – one based on the stacking of dipole shifts due to the dipole moment in the unit cells which start from the discontinuity, and the other due to the broken local charge neutrality at the discontinuity. The former picture well explained the metallic conductivity of the $LaAlO_3/SrTiO_3$ interfaces, but ambiguities remained due to the mismatch with semiconductor language, where the dipoles in the bulk unit cells are neglected. By taking the latter picture, the polar discontinuities can be treated as δ-dopants, and it connects the instability of polar discontinuities better to semiconductor energy band diagrams.

The long journey guided by Tasker ended by showing the equivalence of the two pic-

tures based on Maxwell's equations. We believe that this trivial but not-well-understood equivalence can solve the deepest root of the confusions in the understanding of the stability of polar discontinuities. It guarantees that once the stability of a given system is determined based on one picture, it is also determined in the other picture. This implies that the stability of polar discontinuities is independent of whether the charge is free or bound, itinerant or localized, and electronic or ionic, because these definitions were introduced as a matter of practical convenience, and cannot change the total charge density, hence, the physics.

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Chapter 4

Modulation doping of a Mott quantum well

When a narrower bandgap material is brought close to the $LaAlO_3$ polar surface, transfer of the compensation charge to the other material can enable electronic reconstructions, in analogy to modulation doping. In this Chapter, we present evidence for hole-injection into $LaAlO_3$ (cap) /$LaVO_3$ /$LaAlO_3$ (substrate) quantum wells near the polar surface of AlO_2-terminated $LaAlO_3$ (001). When the $LaAlO_3$ cap is thin, an exponential drop in resistance, a decreasing positive Seebeck coefficient, and loss of satellite diffraction streaks due to the $LaAlO_3$ surface reconstruction were observed below a characteristic coupling length of 10-15 unit cells (uc). We attribute this behavior to a crossover from an atomic reconstruction of the $LaAlO_3$ surface to an electronic one of the vanadium valence. A striking point is that the doped carriers are holes. This excludes the role of electron-donor oxygen vacancies, which make the origin of itinerant electrons at the $LaAlO_3/SrTiO_3$ interfaces controversial.

4.1 Possibility of hole-doping using polar discontinuities

Surfaces and interfaces of oxides have been of growing interest, partially because of the rich variety of bulk oxide functionalities [1], as well as their unique reconstruction mechanisms [2–4] not found in conventional semiconductors [5, 6]. The observation of metallic interfaces between two perovskite insulators, $LaAlO_3$ and $SrTiO_3$ [2], has motivated many studies on the origin of this conductivity, as explained in Chapter 3. Discriminating between these two proposed scenarios has been controversial, in part because both mechanisms could give similar transport and spectroscopic signatures.

The $LaAlO_3/SrTiO_3$ system actually involves two polar discontinuities – the type II polar interface between $LaAlO_3$ and $SrTiO_3$, which require a net of $-q_0/2$ per 2D uc from the *bulk frozen* state, as well as the type 3 polar AlO_2-terminated surface of $LaAlO_3$, which requires a net of $+q_0/2$ per 2D uc. Recently it was found that the conducting $LaAlO_3/SrTiO_3$ interface exhibited a transition to an insulating state when the

$LaAlO_3$ was thinner than a critical thickness of 4 uc, bringing the two polar discontinuities close together [7]. (A similar tendency was also observed for proximity coupling of two $LaAlO_3/SrTiO_3$ interface polar discontinuities with opposite sign [8].) This critical thickness may be interpreted as the threshold dipole shift below which it is energetically favorable to remain in an unreconstructed state for both the surface and the interface [9], based on the *polar discontinuity* picture. A different but equivalent perspective is that the polar AlO_2-terminated surface of $LaAlO_3$ is compensating the electrons at the $LaAlO_3/SrTiO_3$ interface by hole-doping on short length scales, and the polar discontinuities are depleted. Far above the critical thickness (including bulk $LaAlO_3$), the polar $LaAlO_3$ (001) surface atomically reconstructs via surface off-stoichiometry and surface relaxation; electronic reconstructions are unavailable because of the fixed valence of La, Al, and O [10–12]. Below a characteristic coupling distance, however, hole-doping provides an alternative electronic reconstruction if it is energetically favorable.

In order to test this possibility of hole-doping, we have studied the transport properties of the Mott insulator $LaVO_3$ embedded in $LaAlO_3$ in trilayer structures [Fig. 4.1(a)]. $LaVO_3$ is an attractive candidate since it can be readily hole-doped by chemical substitution [13], and because of its structural and thermodynamic compatibility with $LaAlO_3$ for the growth of atomically precise thin film structures. Although $LaVO_3$ has the same polar structure as $LaAlO_3$, and hence their interface is type III and non-polar, we find an exponential drop in resistance when a polar AlO_2-terminated surface of $LaAlO_3$ is brought in close proximity to the $LaVO_3$ quantum well. Furthermore, the positive thermopower voltage measured indicates hole-like carriers, which scales with the doping dependence of bulk $LaVO_3$. These results indicate that polar discontinuities can be utilized for the tunable doping of holes, which cannot arise by growth induced oxygen vacancies.

$LaAlO_3$(n uc)/$LaVO_3$(m uc)/$LaAlO_3$((001), substrate) heterostructures [LAO(n)/LVO(m)] were fabricated by PLD, using a KrF excimer laser with a laser fluence of 1.0 J/cm^2, a spot size of 1.6 mm^2, and a repetition rate of 8 Hz. The thickness of each layer was monitored by RHEED oscillations [Fig. 4.1(b)]. AlO_2-terminated $LaAlO_3$ (001) single crystal substrates were preannealed at 950 °C for 30 minutes, and m uc ($m = 1$ to 30) $LaVO_3$ layers were deposited, followed by n uc ($n = 1$ to 50) $LaAlO_3$ capping layers using $LaVO_4$ polycrystalline and $LaAlO_3$ single crystal targets, respectively. The growth temperature was 600 °C and the oxygen partial pressure was 1.0×10^{-6} Torr for all processes. These conditions follow our previous optimization of high quality $LaVO_3$ thin film growth in the layer-by-layer growth mode [14], with one exception. Note the different laser conditions: we now use a 4 lens afocal zoom stage to accurately image an aperture, rather than a single lens just off of the focusing condition. This is far less sensitive to the divergence characteristics of the laser, and hence much more reproducible between systems. We confirmed that one RHEED oscillation corresponds to the formation of one perovskite unit cell by characterizing the superlattices of $LaAlO_3$ and $LaVO_3$ using XRD.

The stoichiometry of $LaVO_3$ films grown in these conditions has been confirmed from several different perspectives in previous studies. The film lattice volume was found to

Figure 4.1: (a) Schematic band diagram and crystal structure of LAO(n)/LVO(3) quantum wells grown on AlO_2-terminated $LaAlO_3$ (001) substrates. Filled and empty bands correspond to the valence and conduction bands, respectively, and O $2p$ bands are assumed to be aligned. (b) Typical RHEED oscillations during growth of LAO(8)/LVO(3). (c) AFM image of LAO(50)/LVO(3) showing a clear step and terrace surface with step height of $\sim$ 0.4 nm.

be close to the bulk (accounting for the compressive strain by the substrate) – usually, in the presence of significant cation defects, there is a significant expansion of the lattice [14]. $LaVO_3$ films were also studied extensively by STEM-EELS [15]. The insulating $LaVO_3$ films have a clear V^{3+} valence, as observed in the V-$L_{2,3}$ edge. Any significant doping by off-stoichiometry would have shown clear deviations from V^{3+} spectra. Thus the stoichiometry of our $LaVO_3$ films has been well established in these previous studies. $LaAlO_3/LaVO_3/LaAlO_3$ quantum wells could not be grown at higher oxygen partial pressures than those used here, due to the competing formation of polycrystalline $LaV^{5+}O_4$ [14, 15]. Furthermore, the $LaVO_3$ layers in the as-grown quantum wells converted to the insulating, transparent (d^0) $LaV^{5+}O_4$ phase upon oxygen post annealing.

The film surface was investigated by AFM, and all structures were atomically flat with a clear step and terrace structure reflecting the slight miscut angle of the substrate [Fig. 4.1(c)]. The step size ($\sim$ 0.4 nm) was consistent with the height of one $LaAlO_3$ uc (pseudocubic lattice constant a_{LaAlO_3} = 0.379 nm). Ohmic contacts were made to the buried quantum well layers using indium ultrasonic soldering, which penetrated more than 40 nm from the surface as confirmed using buried $SrVO_3$ test structures.

4.2 $LaAlO_3$ cap thickness dependence

4.2.1 Transport properties

The in-plane sheet resistance was dramatically dependent on the $LaAlO_3$ cap thickness as shown in Fig. 4.2(a), where the thickness of the $LaVO_3$ layer was fixed to 3 uc. Below a

Figure 4.2: (a) Sheet resistance and (b) activation energy of LAO(n)/LVO(3) as a function of $LaAlO_3$ cap thickness n. The curve is a guide to the eye. Inset of (b) shows Arrhenius plots of the sheet resistance.

characteristic thickness of around 10-15 uc, the sheet resistance decreased exponentially. For all samples the sheet resistance showed Arrhenius-type thermally activated behavior as shown in the inset of Fig. 4.2(b). The activation energy was $\sim$ 0.7 eV for the thick capping layer samples, and decreased to $\sim$ 0.1 eV with decreasing thickness. Since $LaAlO_3$ is such a robust insulator (both in bulk and as measured in our thin films), the resistance of the embedded $LaVO_3$ layer could be measured to the very high values shown.

These results are well explained by the electrostatic coupling of reconstructions of the polar surface and the quantum well, as illustrated in Fig. 4.3. Since we fabricated the quantum well structures by perovskite unit cell deposition on AlO_2-terminated $LaAlO_3$ substrates, the surface of the $LaAlO_3$ cap preserves AlO_2-termination, which requires a net charge of $+q_0/2$ per 2D uc to avoid the potential divergence arising from the surface polar discontinuity. Here we consider two reconstruction mechanisms for this system. The first possibility is hole injection into the $LaVO_3$ quantum well layer. In this case we have no divergence, but still a finite dipole shift $\Delta(n)$ arising from the polar $LaAlO_3$ cap. Thus the total energy of this electronic reconstruction is the sum of the energy cost to change the vanadium valence E_{val} and $\Delta(n)$. The second process is the normal surface reconstruction of $LaAlO_3$ where an atomic reconstruction is dominant (oxygen vacancies and lattice distortions) to provide the positive charges. This reconstruction

Figure 4.3: Schematic diagrams of possible reconstruction processes. (a) Without reconstruction the structure is composed of negatively and positively charged (ρ) layers from the surface, which induces a non-negative electric field (E), leading to a divergence in potential ($-V$). (b) Electronic reconstruction at the $LaVO_3$ quantum well layer with a net of half hole per 2D unit cell induced. The potential divergence is canceled, but a finite shift $\Delta(n)$ in the potential remains. (c) Atomic reconstruction of the $LaAlO_3$ polar surface.

requires an energy cost E_{sur} which is nominally independent of the thickness of the cap layer. Note that this is the same E_{sur}, calculated in Ref. [16] with respect to E_{val} for Ti, where the conducting $LaAlO_3/SrTiO_3$ interface is toggled by manipulating the surface reconstruction. The difference in E_{val} for Ti and V leads to the different critical thickness observed in the two systems.

In the simplest form, $\Delta(n)$ increases linearly as a function of the $LaAlO_3$ cap thickness: $\Delta(n) = nq_0/2\varepsilon a_{\text{LaAlO}_3}$ (ε is the dielectric constant of $LaAlO_3$ [17]). If the cap is sufficiently thin (and $E_{\text{val}} < E_{\text{sur}}$), then $E_{\text{val}} + \Delta(n) < E_{\text{sur}}$ and hole injection is dominant, which decreases the resistance of the quantum well. On the other hand, when the cap is very thick, $E_{\text{val}} + \Delta(n) > E_{\text{sur}}$, and the surface of the $LaAlO_3$ cap is reconstructed, while the $LaVO_3$ layers are undoped and insulating. Between these limiting cases, hole injection into the $LaVO_3$ layer gradually decreases and the resistance increases as a function of the cap thickness, as observed in the transport measurements. Taking the $LaAlO_3$ bulk dielectric constant $\varepsilon = 24\varepsilon_0$ (ε_0 is the vacuum permittivity), the dipole shift is $\Delta(10) = 9.9$ eV, exceeding the $LaAlO_3$ bulk bandgap of ~ 5.6 eV [18]. In the actual system this is greatly reduced by the strong polarization of the $LaAlO_3$ lattice as observed by surface x-ray diffraction in $LaAlO_3$ thin films on $SrTiO_3$ [19]. Thus the detailed response is far more complex than that represented in Fig. 4.3, and the energy cost $\Delta(n)$ is likely dominated by the polarization energy of $LaAlO_3$. A further discussion of the contrast in $LaAlO_3$ thickness dependence of the conductivity observed here (conductivity in the thin limit), with prior results for the (001)-oriented $LaAlO_3/SrTiO_3$ and $LaVO_3/SrTiO_3$ interfaces [7, 20] (conductivity in the thick limit), is given in Section 4.4.

Note that Fig. 4.3 only shows the near surface region with the $LaVO_3$ quantum well.

Figure 4.4: Schematic reconstructions of the top and bottom polar surfaces of (001)-oriented $LaAlO_3$ for two different terminations of the bottom surface.

To formally confirm that global charge neutrality is maintained for the total system in all cases of reconstructions, the structure of the bottom surface must be known. This can best be illustrated in the schematic shown in Fig. 4.4, where we discuss only polar surfaces of $LaAlO_3$ for simplicity.

As is well established in surface science, the polar surfaces are unstable to reconstructions driven to keep the electrostatic potential bounded. For case A, each surface requires $+q_0/2$ charge to achieve this. The net $+q_0$ is compensated by the extra $(AlO_2)^-$ layer in the total structure, thus preserving global charge neutrality. For case B, the top surface requires $+q_0/2$ charge, the bottom surface $-q_0/2$ charge, and since the number of $(AlO_2)^-$ layers and $(LaO)^+$ layers are equal, here again global charge neutrality is conserved. Note that in case B, one could say that the $q_0/2$ was transferred from the bottom to the top surface, while in case A, $q_0/2$ may be considered to arise locally. In either case, the reconstruction of the top $(AlO_2)^-$ surface is identical, although to formally conserve total charge, knowledge of the bottom interface is needed. Practically, these two surfaces are completely decoupled (the thickness of our substrates is 0.5 mm, and certainly changing the termination layer on one surface does not affect the other across this macroscopic distance), so we address only the top surface in Fig. 4.3, as is conventional in such discussions of polar surfaces. Therefore our conclusions are independent of the assignment of charge transfer. Only when polar surfaces are microscopically close [7, 8, 20] do they couple.

4.2.2 Effect of further capping by $SrTiO_3$

Similar results were found for these LAO(n)/LVO(3) trilayer structures further capped with 10 uc of $SrTiO_3$, which has charge neutral stacking, as shown in Fig. 4.5 Here the measurements were limited to a lower range of resistance values ($n \leq 8$) by the higher intrinsic conductivity of $SrTiO_3$. This suggests that the conductivity of the $LaVO_3$ layer only depends on the distance to the polar surface ($LaAlO_3$ surface) or interface ($SrTiO_3/LaAlO_3$) and not on the total thickness of the material deposited on top of it. Therefore, the role of $LaVO_3$ defects created during growth of the cap can be neglected here.

Figure 4.5: (a) Sheet resistance of LAO(n)/LVO(3) and $SrTiO_3$-capped LAO(n)/LVO(3) measured at 360 K as functions of the $LaAlO_3$ cap thickness n. The dashed line shows the measurement limit for the $SrTiO_3$ capped samples, and the curves are guides to the eye. Schematic structure of (b) uncapped and (c) $SrTiO_3$-capped $LaVO_3$ quantum wells.

4.2.3 Thermoelectric power

A critical test of the model of coupled surface and interface reconstructions is whether the carriers induced by the electronic reconstruction are holes and not electrons as in all previous examples [2, 7, 8, 21–23]. They should further be tunable with the $LaAlO_3$ cap layer thickness. To determine the sign of the transport carriers, the Seebeck coefficient S of the LAO(n)/LVO(3) structures was measured, as shown in Fig. 4.6. Intrinsic voltage fluctuations at high impedance limited the measurements to higher temperatures and thin $LaAlO_3$ cap samples. The positive sign of S confirms hole-doping, and it systematically increased as a function of increasing $LaAlO_3$ capping layer thickness, indicating a decreasing hole density and mirroring the evolution of the sheet resistance shown in Fig. 4.2. These results agree well with thermopower measurements of bulk $La_{1-x}Sr_xVO_3$ and $La_{1-x}Ca_xVO_3$, where S was positive for $0 < x < 0.2$ and decreased as the dopant concentration x increased [24–27].

Given the compressive strain arising from the $LaAlO_3$ substrate, the reduced electronic bandwidth, and interface scattering, a comparison between the $LaVO_3$ quantum wells and bulk values is an approximate one. Nevertheless, this comparison indicates that the maximum equivalent hole density achieved in the single uc $LaAlO_3$ cap sample is just below the bulk metal-insulator transition, occurring at $x = 0.18$ in $La_{1-x}Sr_xVO_3$ [13]. A recent theoretical proposal suggests that doped holes at $LaVO_3$ interfaces are susceptible to charge ordering due to the artificial confined geometry [28], which may be relevant here.

The temperature dependence S of the LAO(n)/LVO(3) structures was also measured, as shown in Fig. 4.6(c). The Seebeck coefficient S of a material is known to have completely different behavior as a function of temperature, depending on whether the Fermi energy E_F is degenerate or not [29]. A semiconductor, which does not have states between the bandgap, shows thermopower due to the extrinsic conduction with an activa-

Figure 4.6: (a) Thermoelectric voltage measured as a function of applied temperature difference between the two electrodes on LAO(n)/LVO(3) quantum wells at room temperature. (b) Seebeck coefficient of LAO(n)/LVO(3) as a function of n (filled circles), plotted in comparison with bulk values for $La_{1-x}Sr_xVO_3$ (Refs. [24–26]) and $La_{1-x}Ca_xVO_3$ (Ref. [27]) at 300 K. (c) Temperature dependence of the Seebeck coefficient.

tion energy $E_{\mathrm{A}n}$ of the carrier density and its magnitude is obtained as a function of the temperature T

$$S(T) = \frac{k}{q}\left[\frac{E_{\mathrm{A}n}}{kT} + A\right], \tag{4.1}$$

where q is the charge of a carrier, A is a constant reflecting the scattering process, and k is the Boltzmann constant. On the other hand, when E_{F} is degenerate, S has the magnitude of

$$S(T) = \frac{\pi^2}{3}\frac{k^2T}{q}\left[\frac{\mathrm{d}\ln\sigma(E)}{\mathrm{d}E}\right]_{E=E_{\mathrm{F}}}, \tag{4.2}$$

where σ is the conductivity. Even though the material has states at E_{F}, if it has a significant amount of disorder, the electrons at the Fermi energy are localized, and hopping process dominates the conduction mechanism [30]. The cutoff energy E_{cut} of the itinerant and localized electrons is specified uniquely, and if $kT \ll E_{\mathrm{cut}} - E_{\mathrm{F}}$, σ is given by $\sigma = e\mu(E_{\mathrm{F}})N(E_{\mathrm{F}})kT$, where μ is the mobility and N is the density of state. When μ has activation type temperature dependence $\mu(E) = \mu_0(E)\exp(-E_{\mathrm{A}\mu}/kT)$, by substituting these equations to the equation (4.2), we obtain

$$S(T) = \frac{\pi^2}{3}\frac{k}{q}\left[kT\left[\frac{\mathrm{d}\ln(\mu_0 N)}{\mathrm{d}E}\right]_{E=E_{\mathrm{F}}} - \left[\frac{\mathrm{d}E_{\mathrm{A}\mu}(E)}{\mathrm{d}E}\right]_{E=E_{\mathrm{F}}}\right]. \tag{4.3}$$

Both extrinsic conduction in semiconductors and the hopping conduction in degenerate semiconductors show activation type temperature dependence of the conductivity, but S has different forms. Namely, S has the form of $A + B\frac{1}{T}$ in the former case, and $A + BT$ in the latter. Although the temperature range of the measurement was limited, the experimental S of the LAO(n)/LVO(3) samples were well explained by hopping conduction. In bulk $La_{1-x}Sr_xVO_3$, linear temperature dependence of S was observed in the heavily doped samples ($x = 0.05$ and $x = 0.20$), while the pure $LaVO_3$ showed band semiconductor like

Figure 4.7: RHEED patterns obtained from (a) $LaAlO_3$ substrate, (b) LAO(3)/LVO(3), and (c) LAO(30)/LVO(3). The arrows show the subpeak corresponding to the diffraction due to the larger 2D unit cells at the surface.

behavior [24]. These comparisons to the bulk further support that the hole-doping in the LAO(n)/LVO(3) samples was achieved just at the edge of the metal-insulator transition.

4.2.4 Surface observation by RHEED

One critical test for the possibility of charge modulation from polar surfaces to buried layers is to check the reconstructions of the surface structures. RHEED was employed not only for the thickness control by monitoring its oscillations, but also for observing the surface structure from the diffraction patterns. To obtain clear diffraction, LAO(n)/LVO(3) samples were further annealed *in situ* at 950 °C for 30 minutes after deposition, and the RHEED patterns were recorded after cooling the sample to 600 °C. The oxygen partial pressure was 1.0×10^{-6} Torr through the whole process. The transport properties were confirmed to be unchanged by the annealing, indicating the charge structure of the $LaVO_3$ layers are maintained.

Figure 4.7 shows the RHEED patterns of the annealed $LaAlO_3$ (001) substrate and LAO(3)/LVO(3) and LAO(30)/LVO(3), recorded with the incident beam direction of [10]. The penetration depth of electrons in RHEED is very short (< 1 nm) due to the shallow incident angle ($0.5° \sim 3°$), and the diffraction patterns are strongly sensitive to the surface [31, 32]. Between the main streaks corresponding to the 2 dimensional square lattice at the surface, characteristic sub streaks were observed from the substrate, suggesting the existence of ordered structure with larger unit cells. Due to the limited information, it is difficult to determine the complete structure at the surface, but as is well established, the polar (001) surface of $LaAlO_3$ is known to reconstruct via various mechanisms [10–12], and these ordered structures indicate that the surface structure was reconstructed from that of the *bulk frozen* surface. A similar reconstructed RHEED pattern appeared from LAO(30)/LVO(3), indicating a reconstructed surface similar to that of the substrate. By contrast, the surface of LAO(3)/LVO(3) did not show strong streaks other than these for the simple square lattice, which suggests the surface remained unreconstructed.

These observations of the surface reconstructions are consistent with the schematic model in Fig. 4.3. The system prefers valence reconstruction in the $LaVO_3$ layer when the $LaAlO_3$ cap is thin, resulting in the unreconstructed $LaAlO_3$ surface, but when the $LaAlO_3$ cap is thick enough, surface reconstruction is preferable. It is remarkable that the model of the reconstructions were confirmed both from the atomic structure of the surface and the valence structure of the buried layers.

4.3 $LaVO_3$ well thickness dependence

In the regime of a thin $LaAlO_3$ cap layer, a V^{4+} component giving rise to these holes should be observable. This has indeed been seen recently by x-ray photoemission spectroscopy (XPS) on LAO(3)/LVO(m) structures (grown on $SrTiO_3$ substrates) [33, 34]. In particular, the spatial distribution was highly asymmetric, with the V^{4+} predominantly in the topmost $LaVO_3$ layer. This non-uniformity naturally arises in Fig. 4.3(b), since $\Delta(n)$ would thus be minimized. The detailed charge distribution is a balance between $\Delta(n)$ and the electronic compressibility. This issue was further studied by measuring the transport properties of LAO(3)/LVO(m) quantum well structures. As shown in Fig. 4.8, the sheet resistance was strongly dependent on the $LaVO_3$ layer thickness m. The data did not scale with $1/m$, as would be expected for a uniform three-dimensional (3D) resistivity. For $m > 10$, there was little change in the sheet resistance, but for $m < 6$ it increased more rapidly than $1/m$, indicating the length scale for strong perturbation of the charge distribution by confinement effects. Thus the thickness dependent resistance indicates that the conducting holes were distributed primarily at the top of the $LaVO_3$ layer, as would be expected for doping arising from the polar $LaAlO_3$ surface.

4.4 Comparison of $LaAlO_3$ thickness-dependent conductivity in $LaAlO_3/LaVO_3/LaAlO_3$ (001) with $LaAlO_3/SrTiO_3$ (001) and $LaVO_3/SrTiO_3$ (001)

It is worth contrasting the $LaAlO_3$ thickness dependence for the interface hole-doping we find here, with prior results for electron-doping at the (001)-oriented $LaAlO_3/SrTiO_3$ interface [7] (and (001)-oriented $LaVO_3/SrTiO_3$ interface [20]). For the $LaAlO_3/SrTiO_3$ structures, there are two polar discontinuities, the $LaAlO_3$ surface (type 3) and the $LaAlO_3/SrTiO_3$ interface (type II). Without any reconstruction, the finite shift Δ remains, as shown in Fig. 4.9(a). When the $LaAlO_3$ layer is thick, the large Δ makes the system unstable, and the polar discontinuities are reconstructed in order to solve the instability [the $LaAlO_3$ surface shown in Fig. 4.9(b)], and the $LaAlO_3/SrTiO_3$ interface by inducing Ti valence changes and associated metallic behavior as shown in Fig. 4.9(c). However, one reconstruction just by the $LaAlO_3$ surface or by the $LaAlO_3/SrTiO_3$ interface alone is insufficient and the electrostatic potential diverges. Therefore, when the two polar discontinuities are far from each other in which case the potential shift

Figure 4.8: (a) Sheet resistance and (b) activation energy of LAO(3)/LVO(m) as functions of $LaVO_3$ layer thickness m. Inset of (a) shows Arrhenius plots of the sheet resistance. The curve is a guide to the eye.

Δ in Fig. 4.9(a) becomes large, both must reconstruct simultaneously, as shown in Fig. 4.9(d). Only when they are brought close together can they couple and remain unreconstructed [7, 8, 20]. Thus the $LaAlO_3/SrTiO_3$ interface is insulating for thin $LaAlO_3$ layers [Fig. 4.9(a)], and metallic in the thick limit [Fig. 4.9(d)].

For the $LaAlO_3/LaVO_3/LaAlO_3$ structures, there is only one polar discontinuity, the type 3 polar $LaAlO_3$ surface. For a $LaVO_3$ layer embedded in $LaAlO_3$ far from any surface, there are no discontinuities to resolve, and thus no reconstructions induced. Only when the $LaVO_3$ layer is brought in proximity to the polar $LaAlO_3$ surface does it provide an alternative reconstruction mechanism, by V valence change. Therefore conductivity appears only in the thin limit, which is opposite to that for the $LaAlO_3/SrTiO_3$ interface.

From a different, but equivalent view point, these polar discontinuities can be treated as δ-dopant layers, as discussed in Chapter 3. In the semiconductor language, these phenomena can be understood as the difference between the depletion of the two δ-dopant layers with opposite signs ($LaAlO_3/SrTiO_3$) and modulation doping from the δ-dopant layer to the material with narrower bandgap ($LaAlO_3/LaVO_3/LaAlO_3$). In the $LaAlO_3/SrTiO_3$ case, the two polar discontinuities are decoupled, and the system remains undepleted and thus conducting. On the other hand, in the $LaAlO_3/LaVO_3/LaAlO_3$ case, modulation doping only occurs when the $LaVO_3$ layer and the polar $LaAlO_3$ surface are brought in a proximity, and thus conductivity appears only in the thin limit.

Figure 4.9: Schematic reconstructions of the polar $LaAlO_3$ (001) surface and the polar $LaAlO_3/SrTiO_3$ (001) interface. (a) No reconstruction, (b) only the $LaAlO_3$ surface is reconstructed, (c) only the $LaAlO_3/SrTiO_3$ interface is reconstructed, and (d) both are reconstructed.

4.5 Summary

We have found a strong electrostatic coupling between the AlO_2-terminated $LaAlO_3$ (001) surface and an embedded $LaVO_3$ quantum well. When they were separated by less than 4-6 nm, transport and thermopower measurements indicated a systematically increasing hole-doping with decreasing separation, and associated changes of the surface reconstruction were observed. We propose that these results reflect a competition between atomic and electronic reconstructions, driven by the need to resolve the divergent surface energy arising from the polar surface termination. An important aspect of this study is that the electronic reconstruction involves holes and not electrons. Therefore the role of polar discontinuities can be more clearly distinguished from that of electron-donor oxygen vacancies, in contrast to previous examples. They further demonstrate that oxide heterostructures can be designed to introduce carriers without local chemical substitution, in analogy to modulation doping in compound semiconductor heterostructures.

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Chapter 5

Physical properties of $LaAlO_3/SrTiO_3$ heterostructures

The metallic conductivity of the $LaAlO_3/SrTiO_3$ interface strongly depends on the interface composition. In this Chapter, [$LaAlO_3$/ $SrTiO_3$] superlattices were grown with different interface compositions. In the superlattices, we have two types of interfaces: $LaAlO_3$ above $SrTiO_3$ (L/S type), or the opposite (S/L). By changing the composition of the L/S type interfaces by inserting $Sr_2Al_2O_5$, the metallic conductivity and the photoluminescence intensity were suppressed, suggesting a strongly asymmetric nature between these two types of interfaces. Structural and spectroscopic studies by scanning transmission electron microscopy revealed that the L/S type interfaces had a larger interdiffusion length and lower Ti valence states which can contribute to the metallic conductivity. This observation was further supported by soft x-ray resonant scattering, where the model with transition layers only at the L/S interfaces best explained the results.

5.1 Interface compositions in $LaAlO_3/SrTiO_3$ superlattices

5.1.1 Changing interface compositions

The interface composition strongly affects the metallic conductivity of $LaAlO_3/SrTiO_3$ interfaces – inserting one monolayer of SrO in between makes the system insulating [1, 2]. One possible explanation by the *polar discontinuity* picture is that switching the termination to SrO flips the sign of the compensation charge, resulting in excess positive charge, which can be realized by formation of oxygen vacancies, not itinerant holes [3]. In order to further study this phenomenon, [$LaAlO_3$/ $SrTiO_3$] superlattices were grown with varying interface compositions. In the superlattices, we have two types of interfaces: $LaAlO_3$ above $SrTiO_3$ (L/S type), or the opposite (S/L), as shown in Fig. 5.1(a).

Assuming abrupt interfaces with the nominal compositions and taking dipole free unit cells, the L/S type has the interface unit cell of $La_{0.5}Sr_{0.5}TiO_3$, which requires the Ti

Figure 5.1: Schematic illustrations of the nominal atomic stacking in the $LaAlO_3/SrTiO_3$ superlattices, assuming the absence of interdiffusion and stoichiometric layer-by-layer growth preserving BO_2-terminated surfaces. One way to take dipole free unit cells is drawn on the right of the structures, with the composition and valence states of the possible reconstructed interface unit cells. (a) Superlattice grown by alternate stacking of $LaAlO_3$ and $SrTiO_3$, (b) superlattice with one monolayer of $Sr_2Al_2O_5$ at the L/S type interface, and (c) superlattice with one monolayer of $LaTiO_3$ at the S/L type interface.

valence of 3.5+ to keep the charge neutrality[1]. Unlike previous studies, a material with nominal composition of $Sr_2Al_2O_5$ (a mixture of $Sr_3Al_2O_6$ and $SrAl_2O_4$) was used to change the interface compositions of the L/S type interfaces in the superlattices without losing the A and B site cation number balance in the perovskites ABO_3. The $Sr_2Al_2O_5$ target was sintered from the initial materials, $SrCO_3$ and Al_2O_3 with nominal compositions of Sr : Al = 1 : 1 via solid state reaction in air at 1400 °C for 14 hours, twice. The target was confirmed to be a mixture of $Sr_3Al_2O_6$ and $SrAl_2O_4$ by means of powder XRD and no other phase was observed. By inserting one monolayer of this material ($SrAlO_{2.5}$) to the L/S interface, the interface composition is expected to change to $La_{0.5}Sr_{0.5}AlO_3$, and due to the fixed electron numbers of the ions, oxygen deficiency may be preferred to form $La_{0.5}Sr_{0.5}AlO_{2.75}$ [Fig. 5.1(b)].

As a point of comparison, the interface composition of the S/L type can also be changed by inserting one monolayer of $LaTiO_3$ [Fig. 5.1(c)]. Here, the nominal interface composition changes from $La_{0.5}Sr_{0.5}AlO_3$ to $La_{0.5}Sr_{0.5}TiO_3$, and enhanced carrier density is expected by further doping electrons at the interface.

The designed heterostructures described in Table 5.1 were fabricated by PLD, using a KrF excimer laser with a laser fluence of 1.2 J/cm^2, a spot size of 2.3 mm^2, and a repetition rate of 4 Hz. The heterostructures were grown on TiO_2-terminated $SrTiO_3$ (001) substrates preannealed at 950 °C under an oxygen partial pressure (P_{O_2}) of 5.0×10^{-6} Torr for 30 minutes. During deposition, the substrate temperature (T_{sub}) was 700 °C or 800 °C , and P_{O_2} was 1.0×10^{-5} Torr. The buffer layers were deposited before

[1]This explanation is equivalent to the *polar discontinuity* picture, as discussed in the Chapter 3.

Table 5.1: Details of the fabricated heterostructures. R indicates the repetition of the units.

Sample description	One unit	R	Buffer	T_{sub}
Superlattice	[$SrTiO_3$ (12 uc) /$LaAlO_3$ (6 uc)]	7	$SrTiO_3$ (12 uc)	700 °C
Superlattice with $Sr_2Al_2O_5$ at (every) L/S	[$SrTiO_3$ (12 uc) /$LaAlO_3$ (5 uc) /$SrAlO_{2.5}$ (1 uc)]	7	$SrTiO_3$ (12 uc)	700 °C
Superlattice with $LaTiO_3$ at (every) S/L	[$SrTiO_3$ (11 uc) /$LaTiO_3$ (1 uc) /$LaAlO_3$ (6 uc)]	7	$SrTiO_3$ (12 uc)	700 °C
Superlattice with $Sr_2Al_2O_5$ at first L/S	[$SrTiO_3$ (12 uc) /$LaAlO_3$ (6 uc)]	7	$SrAlO_{2.5}$ (1 uc) /$SrTiO_3$ (12 uc)	700 °C
Superlattice grown at 800 °C	[$SrTiO_3$ (12 uc) /$LaAlO_3$ (6 uc)]	7	No buffer	800 °C
$LaAlO_3$/$SrTiO_3$ single interface	$LaAlO_3$ (32 uc)	1	$SrTiO_3$ (10 uc)	700 °C

the growth of heterostructures at the same condition to calibrate the deposition rate during growth. Clear reflection high-energy electron diffraction (RHEED) oscillations were observed during the deposition, indicating the layer-by-layer growth of the films, and the thickness of each layer was monitored by its oscillations [Fig. 5.2(a)]. We confirmed that one RHEED oscillation corresponds to the formation of one perovskite unit cell by characterizing the superlattices using XRD [Fig. 5.2(b)]. The spacing between the fringes in the XRD patterns corresponding to the superlattice period d was in accordance within error of 2 % with the expected value of 69.36 Å, obtained from the $SrTiO_3$ lattice parameter of 3.905 Å and the strained $LaAlO_3$ lattice parameter of 3.75 Å[2].

5.1.2 Transport properties

The in-plane sheet resistance was strongly dependent on the interface composition, as shown in Fig. 5.3(a). The superlattice with no insertion showed metallic conductivity, but it disappeared after inserting $SrAlO_x$ at all of the L/S type interfaces, and the contribution of the L/S type interfaces to the conduction was confirmed. On the other hand, the superlattice with $LaTiO_3$ at the S/L showed much lower resistance.

When comparing the superlattice and the $LaAlO_3$/$SrTiO_3$ single interface, both showed almost similar values of sheet resistance, although the superlattice has seven conducting interfaces in total. This result suggests the possibility of different conductivity between the L/S type interfaces in the superlattice and the first interface in proximity to the substrate. To detect the conduction in the superlattice by eliminating the conduction at the first interface, the sheet resistance of the superlattice with $Sr_2Al_2O_5$ at the first L/S interface was measured, which showed a temperature invariant value of $\sim$ 100 kΩ, which was far higher than that of the single interface.

[2]The strained $LaAlO_3$ lattice parameter was obtained by characterizing a single film of $LaAlO_3$ deposited on $SrTiO_3$ substrate under the same conditions.

Figure 5.2: (a) RHEED oscillation patterns during growth of one period of the superlattices. (b) XRD 2θ-ω scans of the superlattices, showing clear superlattice fringes (indicated by triangles). The calculated superlattice periods d are also included.

To further study the transport properties we measured the Hall resistance R_{xy} of the samples with sufficient conductivity for the measurement [Fig. 5.3(b)]. All the sample showed non-linear Hall effect as a function of the magnetic field. The Hall coefficient R_{H} and the mobility was calculated from the Hall resistance by taking their slope at the low (-1 T< μH <1 T) and the high (-7 T< μH <-8 T and 7 T< μH <8 T) fields [Fig. 5.3(c, d)]. Here, the value $-1/R_{\mathrm{H}}q_0$ corresponds to the sheet carrier electron density assuming uniform mobility of the carriers. One possible explanation of this nonlinearity is the anomalous Hall effect related to magnetism, and another possibility is multiple layer conduction with different carrier density and mobility, but the origin is currently ambiguous. Still, it is clear that the the superlattice with $LaTiO_3$ at S/L showed large sheet carrier density, suggesting insertion of $LaTiO_3$ added more valence electrons in the Ti, resulting in the increase of the number of itinerant carriers.

5.1.3 Photoluminescence of the $LaAlO_3/SrTiO_3$ superlattices

The blue ($\lambda \sim 450$ nm) photoluminescence (PL) of $SrTiO_3$ at room temperature is known to be dramatically enhanced by electron doping [4–7]. In the $LaAlO_3/SrTiO_3$ superlattices, we observed changes in the blue PL by varying the interface compositions, consistent with the transport measurements, where the number of free carriers was strongly dependent on the composition. Figures 5.4(a, b) show the PL spectra of the three superlattices. The $LaAlO_3/SrTiO_3$ superlattice showed blue PL at room temperature. Insertion of $LaTiO_3$ at S/L enhanced the PL intensity, suggesting the increase of doped electrons in the superlattice. On the other hand, by inserting $Sr_2Al_2O_5$ at L/S, the PL intensity was strongly suppressed and a new peak appeared around $\lambda \sim 800$ nm.

Figure 5.3: (a) Sheet resistance, (b) antisymmetrized and normalized Hall resistance at 2 K, (c) inverse Hall coefficient corresponding to the total sheet carrier density, and (d) carrier mobility of the $LaAlO_3/SrTiO_3$ heterostructures.

Figure 5.4: PL measured at 300 K with different excitation wavelengths: by (a) $\lambda = 266$ nm and (b) $\lambda = 351$ nm light. The sharp lines in (b) correspond to the bright lines in the pumping lamp for the Ar gas laser. PL spectra of the superlattices excited by $\lambda = 266$ nm light, measured at 10 K plotted in (c) linear and (d) log scales. Inset in (c) shows the PL around $\lambda = 800$ nm of the superlattice with $Sr_2Al_2O_5$ at the L/S interfaces.

The PL was also measured at 10 K, and the peak around $\lambda \sim 800$ nm appeared with sharp peak structures [Fig. 5.4(c, d)]. It is known that even in nominally pure $SrTiO_3$, weak PL by Cr impurities is observed at this wavelength and they are strongly enhanced by Cr-doping [8–10]. The shape of the Cr fluorescence lines and satellite peaks due to the the electron-phonon coupling matched well to the observed peaks from the superlattices with $Sr_2Al_2O_5$ at L/S. Since the $Sr_2Al_2O_5$ target did not show any fluorescence of Cr, the Cr concentration in the superlattices should be the same, independent on the insertion. Indeed, Cr fluorescence lines were observed from the $LaAlO_3$ single crystal substrate, with the same composition as the crystal we used for the PLD targets, and the most likely origin of these Cr ions are from the $LaAlO_3$ layers. By doping electrons in $SrTiO_3$, the absorption by the free carriers [11, 12] diminishes the Cr fluorescence [13]. The result that Cr lines were only observed in the superlattice with $Sr_2Al_2O_5$ at L/S indicates that in this structure the Cr fluorescence survived due to the lack of free carriers, which is consistent with the transport measurements. In addition, other superlattices showed sharp near band edge structure in PL around $\lambda \sim 380$ nm, which is often observed in electron-doped $SrTiO_3$ at low temperature [5, 6].

5.2 Structural studies

5.2.1 STEM study

The atomic and electronic structures of the superlattices were studied by STEM-EELS. Figure 5.5(a, b) shows the cross-sectional ADF images around the superlattice grown at 800 °C. The ADF intensity roughly scales with $Z^{\sim 1.7}$, where Z is the atomic number, and in this image, $LaAlO_3$ appeared brighter due to the presence of La, which has the largest Z in the constituent elements. At the interfaces, the ADF intensity changes as the probing electrons scan across different materials. As shown in Fig. 5.5(c), the line scan profile of the ADF intensity across the interfaces showed strong asymmetry in the interdiffusion length between the L/S and the S/L type interfaces, namely the L/S type showed ~ 3 transition layers while S/L type showed ~ 1 layer.

Spatially resolved core-loss EELS was performed across the two types of interfaces to study the electronic nature of these asymmetric interfaces [Fig. 5.6(a, b)]. Each element has its own transition energies for core electrons, and thus the edge structures can be used as fingerprints of the elements. The EELS near edge structure is strongly affected by the chemical and valence states of the element. For example, the shape of the Ti $L_{2,3}$ edge dramatically changes as its valence shifts from 4+ to 3+ by electron doping, associated with the lowering of the peak positions [14, 15]. Considering the perspectives obtained by the transport studies, the Ti valence state was also expected to change asymmetrically in the superlattices, and indeed, only the Ti $L_{2,3}$ edge at the L/S type interface showed a signature of the lowered Ti valence compared to the Ti^{4+} in the substrate.

To further clarify the distribution of the lower Ti valence component, principal com-

Figure 5.5: (a) Cross-sectional ADF-STEM image of the [$LaAlO_3$/$SrTiO_3$] superlattice grown at 800 °C. (b) Higher magnification image and (c) ADF line profile across the superlattice shown in (b).

Figure 5.6: (a) ADF-STEM image showing the scan direction of the spatially resolved EELS spectra. (b) Raw EELS spectra across the $LaAlO_3$ layer. Two spectra are highlighted to show the EELS features recorded at the marked positions in (a). (c) EELS spectra after background subtraction by power functions, showing the lower energy features (arrows) in the Ti $L_{2,3}$ edge of the L/S type interface compared to the $SrTiO_3$ substrate and the S/L interface.

Figure 5.7: (a) Principal components obtained from the measured data and (b) reference EELS spectra of bulk $SrTiO_3$ and $LaTiO_3$ (Ref. [16]). (c) ADF-STEM image showing the scanning direction of the EELS, composition, concentration profiles of the PCA coefficients $C_{1,i}$ and $C_{2,i}$, and the size of the residue r_i.

ponent analysis (PCA)[3] on the Ti $L_{2,3}$ edge was carried out. Two principal components ($\Phi_1(E_j)$ and $\Phi_2(E_j)$ [Fig. 5.7(a)]) were found to reproduce the measured data. They were compared to the reference spectra, $\Phi_{\mathrm{SrTiO_3}}(E_j)$ and $\Phi_{\mathrm{LaTiO_3}}(E_j)$, of $SrTi^{4+}O_3$ and $LaTi^{3+}O_3$ [Fig. 5.7(a)], and the best fitting by a linear combination of the reference was obtained by

$$\begin{bmatrix}\Phi_1(E_j)\\ \Phi_2(E_j)\end{bmatrix} = \begin{bmatrix}0.80 & 0.16\\ 0.41 & 0.53\end{bmatrix}\begin{bmatrix}\Phi_{\mathrm{SrTiO_3}}(E_j)\\ \Phi_{\mathrm{LaTiO_3}}(E_j)\end{bmatrix} + \begin{bmatrix}R_1(E_j)\\ R_2(E_j),\end{bmatrix} \tag{5.1}$$

where the residual vectors $R_1(E_j)$ and $R_2(E_j)$ were minimized and their size was $R_1(E_j) = 0.059$ and $R_2(E_j) = 0.115$. Assuming the EELS near edge structure of $Ti^{(3+x)+}$ can be represented by the linear combination of those for Ti^{4+} and Ti^{3+} [14, 17], the second component $\Phi_2(E_j)$ contains a larger amount of the lower valence features, and the distribution of $\Phi_2(E_j)$ provides the information of the spatial change of the Ti valence.

Subsequently, the measured spectra $\Psi_i(E_j)$ were fitted by the two principal components via least square fitting, namely $\Psi_i(E_j) = C_{1,i}\Phi_1(E_j) + C_{2,i}\Phi_2(E_j) + r(E)$, and the linear coefficients $C_{1,i}$ and $C_{2,i}$ were plotted, compared with the composition distribution obtained by integrating the edge intensities of the elements [Fig. 5.7(c)]. The coefficient $C_{2,i}$ for the lower valence component $\Phi_2(E_j)$ was only observed at the L/S type interface.

Note the difficulty of the local composition analysis due to the lack of the composition standards in the diffused superlattices and of the information about Al and Sr since their edge positions are not suitable for the current EELS measurement. Therefore, we can only apply qualitative discussions on the composition distribution in Fig. 5.7(c) that may be still available to explain the observed asymmetric distribution of the lower valence components. It is noticeable that the La was observed deeper into the $SrTiO_3$ at the L/S type interface than at S/L. This suggests the L/S type interface contains more $LaTiO_3$ as the virtual composition at the interface, which can provide extra electrons in the Ti valence.

5.2.2 Soft X-ray resonant scattering (SXRS)

The asymmetric nature of the interfaces in the superlattices were further studied by soft x-ray resonant scattering (SXRS) investigations[4], which has recently been used to study $LaMnO_3/SrMnO_3$ [19]. In the ideal superlattices with atomically abrupt interfaces, the forbidden peaks in the elastic scattering disappears due to the extinction rule. When the energy of the incident x-ray is identical to the electron transition energy in the material, the scattering is enhanced via resonant processes. If the spatial distribution of electronic states does not follow the extinction rule, the corresponding resonant scattering appears even at the forbidden peaks. Indeed, in the $LaMnO_3/SrMnO_3$ case, the intensity of elastic scattering at the forbidden peaks was suppressed, and the scattering in resonance with the electronic states degenerating with the Fermi energy appeared, showing a clear evidence of electronic reconstruction at the interfaces.

[3]For details of PCA, see Section 6.2.3.

[4]This section is based on the results reported in Ref. [18].

Figure 5.8: Peak-position analyses by taking into account the effects of refraction (δ). (a) (002) at the Ti $2p$ edge, (b) (003) at the Ti $2p$ edge, (c) (002) at the O $1s$ edge, (d) (003) at the O $1s$ edge, (e) (003) at the La $3d$ edge (Wadati *et al.* [18]).

In this study, the forbidden (003) peak of the [$LaAlO_3$(6 uc)/$SrTiO_3$(12 uc)] superlattice was observed at all photon energies, indicating reconstructions at the interface. From the on-resonant peak position analyses considering the effect of refraction based on the real part δ of the atomic scattering factors, the (002) peaks at the Ti $2p$ and O $1s$ edges were well reproduced, but the (003) peaks (interface sensitive peaks) were not, indicating the electronic states distribution was different from the atomic distribution at the interfaces [Fig. 5.8]. On the other hand, the (003) peak at the La edge was well reproduced, and this can be explained by the robust electronic states of La ions due to their fixed trivalent nature. These results strongly suggests the existence of electronic reconstruction at the interfaces, which are different from the atomic one.

To further study the spatial distributions of scattering centers, reflectivity analyses were performed, and we conclude that the L/S type and S/L type interfaces have different distributions of atomic scattering factors [Fig. 5.9]. Namely, four models were considered for the analyses: model A has abrupt interfaces, and others have 3 uc interface layers with averaged scattering factors (real part: δ and ideal part: β) of $SrTiO_3$ and $LaAlO_3$ at only L/S type in model B1, only S/L type in model B2, and both L/S and S/L types in model C. In these models, A and C have symmetric distribution, and thus still the (003) peak should follow the extinction rule, which did not agree with the experimental data. On the other hand, the other asymmetric models reproduced the data, indicating the asymmetric nature of the two types of interfaces, and the thickness of the interface layers were determined to be 3 uc.

Figure 5.9: Comparison of the reflectivity spectra between experiment and calculation (Wadati *et al.* [18]). (a) Ti 2p on-resonance, (b) Ti 2p off-resonance, (c) O 1s on-resonance, (d) O 1s off-resonance, (e) La 3d on-resonance, and (f) La 3d off-resonance. (g) Models of the distributions of β for the calculations.

5.3 Summary

A monolayer of $Sr_2Al_2O_5$ inserted at the L/S type interface made the [$LaAlO_3$/$SrTiO_3$] superlattices insulating, confirming the importance of L/S type interfaces in metallic conduction. The atomic and electronic structures of the superlattices were studied by STEM-EELS. A clear signature of reduced Ti valence was observed only at the L/S interface, associated with deeper interdiffusion of the cations. These observations were further supported by soft x-ray resonant scattering (SXRS) measurements. A model with 3 unit cells of interfacial layers only at L/S interfaces best reproduced the SXRS data. It is remarkable that the existence of interfacial layers were confirmed in both real space (STEM) and reciprocal space (SXRS), and the emergence of the novel properties were indeed produced by the change of the interface stoichiometry.

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Chapter 6

Microscopic studies of manganite films

Difficulty in control of interface electronic states and precipitates formed during growth of manganite thin films by pulsed laser deposition have been obstacles for fabricating high quality devices incorporating these ferromagnetic metals. To study the role of interface composition, we have investigated the spectroscopic and structural properties of $LaMnO_3/SrMnO_3/SrTiO_3$ heterostructures by means of scanning transmission electron microscopy. Systematic change of the Mn valence was observed by varying the thickness of $SrMnO_3$, suggesting the possible control of electronic states by changing interface compositions. In addition, the nature of these precipitates are analysed. For $LaMnO_3$ films, crystallites of Mn_3O_4 are found to segregate out from stoichiometric films, further capped by Mn-deficient $LaMnO_3$. These features indicate that the film microstructure arises to accommodate a net cation off-stoichiometry during growth.

6.1 Growing interests in manganite heterostructures and current obstacles

The perovskite manganese oxides $R_{1-x}A_xMnO_3$ (R: rare earth, A: alkaline earth) show rich physical properties, for example colossal-magnetoresistance in $La_{1-x}Sr_xMnO_3$ ($x = 0.175$) associated with magnetic phase transitions [1] or multiferroic $TbMnO_3$ showing the coupling of antiferromagnetic and ferroelectric properties [2]. Device applications using these materials have been one of the main goals of the oxide electronics community.

The ferromagnetic metal $La_{1-x}Sr_xMnO_3$ ($0.16 < x < 0.5$) is a leading candidate for ferromagnetic electrodes, due to its high Curie temperature, full spin polarization, and good lattice match with other perovskites [3–5]. PLD is a widely used growth technique for the fabrication of perovskite oxide heterostructures, and with continual improvements operation of $La_{1-x}Sr_xMnO_3/SrTiO_3/La_{1-x}Sr_xMnO_3$ magnetic tunneling junctions has been reported [6]. However, there are a number of obstacles for improving the efficiency and the reproducibility of these devices; one of the primary concerns is the so-called dead layer formation close to the interface [7], where the half-metallic behavior is lost

far below the bulk T_C. The enhancement of interface magnetization by changing the interface composition was reported [8], but the full understanding of the role of interface composition is still unclear. Another obstacle is the formation of precipitates ~100 nm in diameter during film growth. Although these precipitates can be somewhat managed by pre-patterned substrates providing artificial nucleation sites [9], little is known about their precise structural and electronic properties.

In this Section, we present microscopic studies of the interface $LaMnO_3/SrTiO_3$ to show the role of polar nature of these interfaces, which can be changed by varying the interface composition. Also, the observation of these nano-particles in $LaMnO_3$ thin films grown by PLD is described, with a conclusion that they are microcrystals of Mn_3O_4 capped with Mn-deficient $LaMnO_3$.

6.2 Nanoscale doping of the $LaMnO_3/SrTiO_3$ interface

6.2.1 Changing interface composition by insertion of $SrMnO_3$

To further study the importance of the interface composition, the atomic and electronic structure of $LaMnO_3/SrTiO_3$ (001) interfaces were studied microscopically with varying thickness of $SrMnO_3$ inserted at the interface, which can provide a systematic variation of interface composition. The parent compound of $La_{1-x}Sr_xMnO_3$, $LaMnO_3$, was chosen because the polar nature is expected to be enhanced in nondoped systems, due to the larger difference of the ionic charges in LaO and MnO_2 layers in $LaMnO_3$ (001).

$LaMnO_3$ films were deposited on TiO_2 terminated $SrTiO_3$ (001) substrates following the deposition of the $SrMnO_3$ ($0 \sim 2$ uc) layers by PLD using a KrF laser. $LaMnO_3$ and $SrMnO_3$ polycrystalline targets were used, and the growth conditions and the thicknesses of these materials are shown in Table 6.1. Two different conditions were used for the $LaMnO_3$ films, to see its effect on the interface compositions. Five samples were grown and denoted LMO[SMO(n), $\#_G$(A or B)], where (n, m) = (0, A), (1, A), (2, A), (0, B), and (1, B), based on the $SrMnO_3$ thickness n uc and the $LaMnO_3$ growth condition $\#_G$(A or B). The thickness of the $SrMnO_3$ was determined by the combination of RHEED and AFM characterizations [10], where the ideal growth of $SrMnO_3$ in the layer by layer mode was confirmed up to 2 uc. They were further capped by amorphous Al_2O_3, to protect the surface from damage during STEM sample preparations.

Since the samples were grown on top of the TiO_2 layer of $SrTiO_3$ (001), the nominal interface termination was LaO/TiO_2 without $SrMnO_3$ inserted, and metallic conductivity was expected in analogy to the previous observations in $LaAlO_3/SrTiO_3$ (001) [11, 12] and $LaVO_3/SrTiO_3$ (001) [13]. However, none of the $LaMnO_3/SrTiO_3$ samples showed conductivity as grown, independent of the $SrMnO_3$ insertion [14]. This clearly contrasts the importance of this work, and microscopic studies were expected to reveal the nature of this characteristic result.

Table 6.1: Growth conditions and thickness of $SrMnO_3$ and $LaMnO_3$ ($\#_G$(A or B)).

	P_{O_2}	T_{sub}	Laser fluence	Spot size	Repetition	Thickness
$SrMnO_3$	1 mTorr	850 °C	0.3 J/cm^2	10 mm^2	4 Hz	0 ∼ 2 uc
$\#_G$(A)	1 mTorr	750 °C	3.8 J/cm^2	1.6 mm^2	4 Hz	16 nm
$\#_G$(B)	1 mTorr	850 °C	0.40 J/cm^2	10 mm^2	4 Hz	40 nm

Figure 6.1: (a) Cross-sectional STEM-ADF image around the $LaMnO_3$ film in LMO[SMO(0), $\#_G$(A)]. (b) Higher magnification images and (c) averaged line profiles across the interfaces of (1) LMO[SMO(0), $\#_G$(A)], (2) LMO[SMO(1), $\#_G$(A)], (3) LMO[SMO(2), $\#_G$(A)], (4) LMO[SMO(0), $\#_G$(B)], and (5) LMO[SMO(1), $\#_G$(B)]. The size of the images in (b) is the same as the box in (a).

6.2.2 Structural observations of the interfaces

The microscopic structure of these films was studied by ADF in STEM. Figure 6.1(a) shows the ADF images around the interfaces of $LaMnO_3/SrTiO_3$ with the sample oriented along a substrate [100] crystallographic axis. Since La is the heaviest element in this system, the $LaMnO_3$ film appeared brighter than the $SrTiO_3$ substrate in the Z-contrast images by ADF.

In higher magnification images [Fig. 6.1(b)], the epitaxial relation between the $LaMnO_3$ and the $SrTiO_3$ was confirmed in all the samples. By averaging the ADF intensity, ADF line profiles were obtained across the interfaces, as shown in Fig. 6.1(c). When considering the role of $SrMnO_3$ insertion, it is clear that the diffusion of cations with large Z at the interface was suppressed by the insertion of $SrMnO_3$ in the samples

grown under $\#_{\mathrm{G}}$(B), while in the samples grown under $\#_{\mathrm{G}}$(A), no significant change was observed.

Comparing the growth conditions, samples grown under $\#_{\mathrm{G}}$(A) had abrupt change of ADF intensity at the interface compared to those under $\#_{\mathrm{G}}$(B). Although the stronger laser fluence in $\#_{\mathrm{G}}$(A) predicts larger diffusion length if the kinetic bombardment during PLD growth enhances the interdiffusion, in fact, the results were opposite to this scenario. Therefore, the other parameter, the substrate temperature is suspected to be the responsible parameter, namely higher temperature enhancing interdiffusion. It should be noted however, that when the growth conditions change, other effects related to the changes in the parameter should be taken into account, e.g., the change of the film stoichiometry.

A darker region in the substrate close to the interface was observed in the samples grown under $\#_{\mathrm{G}}$(A). This may suggest the existence of strong strain field due to the lattice mismatch, which can change the crystallographic axis locally to reduce the ADF intensity [15][1]. This elastic effect is expected to be suppressed when the interface is more diffused, since the change in the lattice constant becomes less abrupt. Indeed, the dark region disappeared in the samples grown under $\#_{\mathrm{G}}$(B).

6.2.3 Chemical composition and valence states studied by EELS

In order to study the chemical composition, spatially resolved EELS was carried out. Figure 6.2(a) shows a typical trajectory, and each EELS spectrum was recorded along a line (∼10 nm of length) perpendicular to the scan direction (parallel to the interface plane), to avoid the damage due to the long exposure to the high-energy electrons. Figure 6.2(b) shows the EELS spectra recorded from LMO[SMO(0), $\#_G$(A)] including the Ti-$L_{2,3}$ ($\sim$ 455 eV), O-K ($\sim$ 530 eV), Mn-$L_{2,3}$ ($\sim$ 640 eV), and La-M_5 ($\sim$ 830 eV) edges, which are well separated in energy. By normalizing the integrated edge intensity taking the $SrTiO_3$ substrate and $LaMnO_3$ film as the composition standards[2], the composition distribution was obtained, as shown in Fig. 6.2(c).

The useful information of the valence state appears in the near edge structure of the Ti-$L_{2,3}$ and Mn-$L_{2,3}$ edges with the change of their peak positions, as well as their shapes. The EELS spectra close to the interface and deep in the substrate / film were compared after subtracting the background with the form of a power function, to seek the change of valence states at the interface. As shown in Fig. 6.2(d), the Ti-$L_{2,3}$ edge did not show much difference between the interface and the substrate other than the broadening of the peaks at the interface, which might correspond to the poorer signal-noise ratio due to the lower signal counts[3]. This result suggests that the Ti valence remained Ti^{4+} at the interface. On the other hand, the Mn-$L_{2,3}$ edge showed clear decrease in the peak positions at the interface, suggesting the lower valence of Mn [Fig. 6.2(e)].

[1]The effect of channeling, where the direction of the electron beam and the crystallographic axis plays an important role, is discussed later in Section 6.3.3.

[2]The stoichiometry of the $LaMnO_3$ film was confirmed by comparing its EELS to that of the bulk polycrystalline $LaMnO_3$, which is discussed in Section 6.3.2.

[3]Also, the Ti-$L_{2,3}$ edge did not show a clear second component in the principal component analysis.

Figure 6.2: (a) High resolution STEM-ADF image around the $LaMnO_3/SrTiO_3$ interface of LMO[SMO(0), $\#_G$(A)] and (b) EELS spectra recorded along the arrow in (a). The three spectra corresponding to the $SrTiO_3$ substrate, the interface, and the $LaMnO_3$ film were highlighted. (c) Composition map obtained by integrating the edge intensity in (b). Comparison of the EELS spectra of (d) Ti (between the substrate and the interface) and of (e) Mn (between the film and the interface) are also shown.

To further study the valence state of Mn, principal component analysis (PCA) was performed. PCA is a vector transformation used to reduce the dimension of the data set, by finding a small number of principal base vectors and represent the data by their linear combinations. In this study, we chose the spectra $\Psi_i(E_j)$ to represent the Mn $L_{2,3}$ edge, where i is the spectrum number representing the recorded positions, and E_j is the discrete energy within the region between 635.8 eV and 655.8 eV with the energy dispersion of 0.2 eV. The vectors $\Psi_i(E_j)$ were normalized by taking the $LaMnO_3$ as the composition standard, namely the average of $\sqrt{\sum_j \Psi_i(E_j)^2}$ in the film to be 1, and all the spectra were scaled proportionally. Figure 6.3 shows the two principal components $\Phi_1(E_j)$ and $\Phi_2(E_j)$ for the Mn-$L_{2,3}$ edge chosen to reproduce the EELS spectra through the $LaMnO_3$ film and the interface. The first component $\Phi_1(E_j)$ is almost identical to that of the trivalent Mn^{3+} in bulk $LaMnO_3$, while the second one $\Phi_2(E_j)$ has similar peaks to those of the divalent Mn^{2+} in MnO. The size of the components were normalized by their size, $\sqrt{\sum_j \Phi_k(E_j)^2}$ $(k = 1, 2)$ to be 1.

Taking these two components as references, the entire data set was fitted by their linear combinations with fitting coefficients $C_{1,i}$ and $C_{2,i}$, namely $\Psi_i(E_j) = C_{1,i}\Phi_1(E_j) + C_{2,i}\Phi_2(E_j) + r(E)$, where $r(E_j)$ is the residual function, and its size $R_i = \sqrt{\sum_j r_i(E_j)^2}$ was minimized through least square fitting. Note LMO[SMO(2), $\#_G$(A)] did not show a clear second component due to the lack of lower valence features, instead the $\Phi_2(E_j)$ for LMO[SMO(0), $\#_G$(A)] was used as the second component for the fitting.

Figure 6.4 shows the data of the five samples, including the fitting coefficient $C_{2,i}$ for the lower valence component and the fitting residue R_i, as well as the compositions of La, Mn and Ti obtained in the same manner as Fig. 6.2(c). $C_{2,i}$ distributed only in the vicinity of the interface, and the amount was reduced as the amount of the inserted $SrMnO_3$ increased.

Figure 6.3: (a) Principal components $\Phi_1(E_j)$ and $\Phi_2(E_j)$ obtained from each sample. LMO[SMO(2), $\#_G$(A)] did not show a clear second component, only an effective broadening of the first component. (b) Reference EELS spectra around Mn $L_{2,3}$ edges obtained from manganese oxides with different oxidation states (Kurata and Colliex [16]). Note that energy offset was added to Mn_2O_3 reference to align it to the $LaMnO_3$ film, to correct the difference between measurements. Also, the MnO and Mn_3O_4 spectra were shifted so that the Mn_3O_4 spectrum is best fitted by a linear combination of MnO and Mn_2O_3 (indicated as MnO+Mn_2O_3), based on the assumption that the Mn $L_{2,3}$ edge changes linearly as a function of the valence between the divalent and trivalent states.

Figure 6.4: Compositions of La, Mn and Ti, fitting coefficient $C_{2,i}$ for the lower valence component of Mn, and the fitting residue R_i of (a) LMO[SMO(0), $\#_G$(A)], (b) LMO[SMO(1), $\#_G$(A)], (c) LMO[SMO(2), $\#_G$(A)], (d) LMO[SMO(0), $\#_G$(B)], and (e) LMO[SMO(1), $\#_G$(B)]. The curves are guides to the eyes.

Figure 6.5: (a) Schematic charge structure of the LaO/TiO_2 terminated $LaMnO_3/SrTiO_3$ interface. (b) By inserting one monolayer of $SrMnO_3$ to (a), the interface termination switches to MnO_2/SrO.

6.2.4 Polar discontinuity doping of manganese at $LaMnO_3/SrTiO_3$ interfaces

Since the $LaMnO_3$ films were grown on a TiO_2 terminated $SrTiO_3$ (001) substrates, the nominal interface termination is LaO/TiO_2, as shown in Fig. 6.5(a). $LaMnO_3$ consists of alternate stacking of $(LaO)^+$ and $(MnO_2)^-$, while $SrTiO_3$ has charge neutral (SrO) and (TiO_2) layers, thus this *bulk frozen* interface is type II polar, and there is charge instability. To find the amount and sign of the compensation charge, dipole free unit cells are taken. The interface unit cell is $La_{0.5}Sr_{0.5}TiO_3$ and to keep the local charge neutrality, this Ti is expected to take a valence state of 3.5+, which is lower than that of the bulk $SrTiO_3$.

However, due to the lower energy of the valence $3d$ states of Mn compared to Ti, these extra valence electrons in the Ti $3d$ states may prefer the proximate Mn site. This scenario well explains the observation of the lower valence state of Mn in the vicinity of the interface. This explanation is consistent with the previous studies of $La_{0.6}Sr_{0.4}MnO_3/SrTiO_3$ junctions by means of PES, where they also observed the robust Ti^{4+} state at the interface [17][4].

These observations of the robust Ti^{4+} and the lowering of Mn valence can explain the lack of conductivity of $LaMnO_3/SrTiO_3$ interfaces. In the previous case of $LaAlO_3/SrTiO_3$, the metallic conductivity was achieved by the itinerant electrons in the Ti $3d$ valence, however in the $LaMnO_3/SrTiO_3$ case, the electrons were accommodated by the Mn site, to form localized Mn^{2+} state.

By inserting one unit cell of $SrMnO_3$, the interface termination is expected to switch to MnO_2/SrO, and increase of Mn valence at the interface is expected, as shown in Fig. 6.5(b). However, in fact, lower Mn valence states were also observed in LMO[SMO(1), $\#_G$(A)] or LMO[SMO(1), $\#_G$(B)], as shown in Fig. 6.4(b) and (e). In the real system, we

[4]Note they did not show the Mn valence lowering even though their $La_{0.6}Sr_{0.4}O/TiO_2$ terminated interface is expected to show lower valence, and we will discuss the origin of this lack of information later in Section 6.2.7.

Figure 6.6: Schematic illustration of the *integral intervals* to count the AB-difference in $LaMnO_3/SrTiO_3$ interfaces with various interface compositions. (a) An abrupt LaO/TiO_2 terminated interface, interfaces with (b) one and (c) two monolayers of $SrMnO_3$ inserted in (a), and (d) an interdiffused interface. (e) Shows the composition function of La and Mn in (d), and the area S of the domain bounded by the curves corresponds to its AB-difference.

have many perturbations from the ideally abrupt interfaces, for example, interdiffusion or change of the cation balance at the interface, and it is important to take these effects into account to understand the real charge structure. In order to treat local charge neutrality at the interfaces with interdiffusion or various interface compositions, counting the number of cations in a selected region is useful. This AB-difference is explained in the next section.

6.2.5 Local composition analysis

Definition of AB-difference

To further study the local compositions quantitatively, we introduce a parameter, AB-difference d_{A-B}. The idea of this parameter is to count the net cation numbers around the diffused interface formed between two semi-infinite perovskite materials, ABO_3 and $A'B'O_3$ in the [001] direction, assuming perfect oxygen stoichiometry. Also, it is assumed that the A sites are always occupied by A or A', while the B sites by B or B'. First, a sufficiently large number of dipole-free unit cells was chosen for the *integral interval*, to include the whole region of the interface as shown in Fig 6.6(a). The remainder consists of the dipole free unit cells of either bulk material, thus local charge neutrality is already maintained without any reconstructions from the bulk. Therefore, in order to maintain the stability of the system, local charge neutrality in the *integral interval* is sufficient.

The AB-difference d_{A-B} is defined by the difference in the numbers of the A cations and the B cations in the *integral interval*. For example, in the case of $LaMnO_3/SrTiO_3$ taken as $ABO_3/A'B'O_3$, an abrupt LaO/TiO_2 terminated interface has $d_{\mathrm{La-Mn}} = 0.5$ [Fig. 6.6(a)], a MnO_2/SrO terminated one has $d_{\mathrm{La-Mn}} = -0.5$ [Fig. 6.6(b)]. One more

$SrMnO_3$ layer inserted to the MnO_2/SrO terminated interface, makes $d_{\mathrm{La-Mn}}$ to be -1.5 [Fig. 6.6(c)]. Considering the abrupt interface model based on a TiO_2 terminated substrate and the deposition of the films, $d_{\mathrm{La-Mn}}$ is expected to behave as a function of $SrMnO_3$ thickness $t_{\mathrm{SrMnO_3}}$ [uc]:

$$d_{d_{\mathrm{La-Mn}}} = \frac{1}{2} - t_{\mathrm{SrMnO_3}} \tag{6.1}$$

Even when the interface is interdiffused [Fig. 6.6(d)], d_{A-B} can be uniquely defined in a similar manner, by integrating the composition functions [Fig. 6.6(e)]. Here we should note that the interdiffusion of atoms in the *integral interval* can provide finite dipoles, but does not change the total number of cations there[5]. Also, since the numbers of A and B cations are equal outside of the *integral interval*, this value is uniquely defined, independent of the choice of the *integral interval* if both ends are outside of the interface region. Subsequently, the AB-difference in the measured samples were calculated from the value plotted in Fig. 6.4[6].

AB-difference and the local charge neutrality

If $d_{A-B} = 0$, the number of A equals that of B, and the interface composition is equivalent to a mixture of ABO_3 and $A'B'O_3$. Therefore the total number of valence electrons are invariant and equal to the sum of the charges from the bulk valences. Note the modulation of these charges in the valence states can occur as perturbations, but it should occur conserving the number of charges.

On the other hand, if d_{A-B} is non-zero, that means there is non bulk-like configuration at the interface, and may change the total number of valence electrons. For example, in the case of $LaMnO_3/SrTiO_3$, positive $d_{\mathrm{La-Mn}}$ gives the virtual amount of $LaTiO_3$, while negative $d_{\mathrm{La-Mn}}$ gives the virtual amount of $SrMnO_3$, when we assume all the other cations forms either $LaMnO_3$ or $SrTiO_3$. Even when they are mixed at the interface, charge neutrality cannot be violated, and the total number of valence electrons is invariant. Thus counting the number of these virtual materials ($LaTi^{3+}O_3$ and $SrMn^{4+}O_3$) different from either $LaMnO_3$ or $SrTiO_3$ can tell the difference from the original valence states, namely Mn^{3+} and Ti^{4+} in their bulks. Therefore, the $d_{\mathrm{La-Mn}}$ should satisfy the following relation:

$$d_{\mathrm{La-Mn}} = e^{\mathrm{ex}}, \tag{6.2}$$

where e^{ex} is the total number of extra electrons in the valence states in the vicinity of the interface.

Estimation of the total extra valence charge from the PCA results

The total amount of lower valence component $C_2^{\mathrm{tot}} = \sum_i C_{2,i}\Delta_z/a_{\mathrm{per}}$ was calculated from the data shown in Fig 6.4, where Δ_z is the sampling width of the measurement and

[5]For further discussion on the effect of interdiffusion, see Appendix A.

[6]To find the practical methods to calculate d_{A-B} for interdiffused interfaces, see Appendix C.

Figure 6.7: Plots of the summation C_2^{tot} of the lower valence component as a function of (a) the AB-difference and (b) the inserted $SrMnO_3$ thickness. (c) Plot of the AB-difference as a function of the inserted $SrMnO_3$ thickness. Different symbols indicate the different growth conditions, and the solid line shows the expected value considering the abrupt interface models.

$a_{\mathrm{per}} = 4.0$ Å is the typical perovskite lattice parameter, assuming the change of the lattice parameter across the interface is negligible. Figure 6.7(a) shows the value of C_2^{tot} plotted as a function of $d_{\mathrm{La-Mn}}$. In order to compare C_2^{tot} obtained by PCA to the extra valence electrons, the $\Phi_1(E_j)$ and $\Phi_2(E_j)$ components were assumed to be identified as the Mn^{3+} and Mn^{2+} EELS spectra[7]. Also, the EELS spectrum $\Phi_{\mathrm{Mn}^{(2+x)+}}$ of the mixed valence state between Mn^{2+} and Mn^{3+} is assumed to be represented as a linear combination of the end members $\Phi_{\mathrm{Mn}^{2+}}$ and $\Phi_{\mathrm{Mn}^{3+}}$, namely $\Phi_{\mathrm{Mn}^{(2+x)+}} = (1-x)\Phi_{\mathrm{Mn}^{2+}} + x\Phi_{\mathrm{Mn}^{3+}}$[8]. Following these assumptions, C_2^{tot} can be taken as the number of extra electrons e^{ex} in the Mn valence:

$$C_2^{\mathrm{tot}} = e^{\mathrm{ex}}. \tag{6.3}$$

Local composition and electronic states – discrepancy from the abrupt interface model

Following equations (6.2) and (6.3), we obtain the equation,

$$C_2^{\mathrm{tot}} = d_{\mathrm{La-Mn}}, \tag{6.4}$$

and indeed, such a relation was observed in Fig. 6.7(a), although there remained a finite offset between them. This result suggests the value $d_{\mathrm{La-Mn}}$ is a good measurable parameter to determine the total number of extra valence charges.

The value C_2^{tot} was also plotted as a function of the inserted $SrMnO_3$ thickness $t_{\mathrm{SrMnO_3}}$ [Fig. 6.7(b)]. Although it can be predicted that the insertion of $SrMnO_3$ decreases the number of extra valence electrons based on the abrupt interface model, and indeed such

[7] This is a strong assumption, since these two components were generated numerically from the measured spectra, and do not physically have to be the same as those of the pure Mn^{3+} and Mn^{2+} states. In order to survey the number of valence electrons, fitting by the reference spectra of Mn^{3+} and Mn^{2+} measured simultaneously is better. However, due to the absence of a proper reference for Mn^{2+} during the measurement, we adopted PCA, and compared the principal components to the known EELS reference in the literature to find the best physical meaning of these components.

[8] The validity of this assumption is further explained in Section 6.2.7.

decreasing behavior was observed, there remained a large gap between C_2^{tot} and the value expected from the thickness of the inserted $SrMnO_3$ in the abrupt interface:

$$C_2^{\mathrm{tot}} = \frac{1}{2} - t_{\mathrm{SrMnO_3}}, \tag{6.5}$$

which is obtained from equations (6.1) and (6.4)

The value of $d_{\mathrm{La-Mn}}$ was also different from what was expected from the abrupt interface model [eq. (6.1)], where the effect of the interdiffusion is neglected by considering $d_{\mathrm{La-Mn}}$ [Fig. 6.7(c)]. These observations suggests there are some mechanisms to change the local stoichiometry at the interface from the nominal termination based on the abrupt interface picture. As discussed previously, simple interdiffusion cannot change the number of cations, and thus is not sufficient to explain this difference.

6.2.6 Possible origins of the difference from the expectations for abrupt interfaces

Compared to the expected value from the abrupt interface model, too many extra valence electrons were observed. There are two main differences from the abrupt interface model. One is the discrepancy from the expected relation $d_{A-B} = \frac{1}{2} - t_{\mathrm{SrMnO_3}}$, as shown in Fig. 6.7(c), which requires the difference in the cation numbers (difference #1). The other is the discrepancy from $C_2^{\mathrm{tot}} = d_{A-B}$, as observed in the difference of the plot intercept in Fig. 6.7(a), and this can be explained by a process to change the number of valence electrons (difference #2). In this section, some of the possible mechanisms accounting for these two differences are presented.

Sr segregation during growth

If the $LaMnO_3$ film is grown epitaxially on TiO_2 terminated $SrTiO_3$ (001), the value of $d_{\mathrm{La-Mn}}$ should be $a_{\mathrm{per}}/2$, reflecting the half unit cell difference of the positions of the first MnO_2 and LaO layers. The observation of $d_{\mathrm{La-Mn}}$ larger than $a_{\mathrm{per}}/2$ at the interface of LMO[SMO(0), $\#_G$(A)] and LMO[SMO(0), $\#_G$(B)] can be explained by a scenario where some amount of the Sr close to the interface was lost and their sites were filled by La during the growth process. This mechanism can explain the difference #1.

The most probable phenomenon to realize such loss of Sr is the segregation of Sr to the surface of the film, which was indeed observed in $La_{1-x}Sr_xMnO_3/SrTiO_3$ grown by PLD [18]. Also, in $LaVO_3/SrTiO_3$ heterostructures, the change of interface composition was reported, and they proposed explanations based on Sr segregation during growth [19]. Such Sr segregation during growth may be relevant for the observation of a better surface morphology of the perovskite films on SrO-terminated $SrTiO_3$ substrates compared to those on TiO_2-terminated ones [20], since the segregated Sr can work as a surfactant which mediates the growth of films with flat surfaces [21].

Direct observation of such segregation by EELS would be the best confirmation of this scenario, but due to the weak signal of Sr in EELS overlapping other spectral features, we

could not obtain sufficient information for Sr. To further study this issue, measurement of $LaMnO_3/CaTiO_3$ is a good candidate, since Ca and Sr has similar chemical properties and Ca edges can be clearly observed by EELS.

Off-stoichiometric surface of $SrTiO_3$ substrates

Another possibility to change the amount of Sr is the off-stoichiometric surface of $SrTiO_3$. Significant efforts have been made to prepare TiO_2 terminated $SrTiO_3$ surfaces using pH-controlled NH_4-HF solution [22] or combining a boiling water dip and HF solution [23], based on the strategy to etch the SrO monolayer selectively. The surface termination of these prepared substrates was confirmed to be TiO_2 terminated by means of AFM, surface ion scattering, or clear RHEED oscillations during subsequent thin film growth.

However, it is also known that the surface stoichiometry of $SrTiO_3$ is strongly sensitive to the gas environment, pressure, and temperature [24, 25][9]. When the surface is Ti-rich, it can even form a double-TiO_2 terminated surface, confirmed by scanning tunneling microscopy (STM) [26]. These observations suggest that even after the chemical preparation to form a TiO_2 terminated surface, it is very difficult to exclude the slight off-stoichiometry at the surface. In particular, when such off-stoichiometry is accommodated by the formation of vacancies close to but not at the surface [27], it is difficult to detect them by means of surface sensitive measurements. When we assume Sr vacancies at the $SrTiO_3$ surface, the observation of larger $d_{\mathrm{La-Mn}}$ value can be explained. Also, this hypothesis may be relevant for the observation of a large $d_{\mathrm{La-Al}}$ value (6 Å) at the $LaAlO_3/SrTiO_3$ interface, where no Sr segregation was observed [28]. This mechanism can explain the difference #1.

In order to seek the possibility of off-stoichiometric surfaces of $SrTiO_3$, comparison of the $LaMnO_3/SrTiO_3$ on substrates prepared by various methods (e. g. etched or not etched, annealed in different conditions) would give important information. Also, comparison of the interfaces on $SrTiO_3$ substrates and on films may make the role of surfaces clear. These observations are proceeding for further investigation.

Charge accumulation due to band bending

As discussed in the section 3.1.4, charge accumulation by the possible bending of the band may change the number of charges at the interface, and this mechanism may be relevant to the difference #2, although the effect is expected to be small. Note in this case, the same amount of charge with the opposite sign to the accumulated one remains in the rest of the system, but usually they are too sparsely distributed to be observed.

Elastic effects

When an epitaxial film is grown on a substrate with a different lattice constant, strain fields can act on the film and change its physical properties. Such effect has been stud-

[9] To find a good summary of the examples of the $SrTiO_3$ surface observations, see Ref. [25] and Table I therein.

ied in manganite films, since the magnetic and transport properties of manganites are known to strongly depend on the lattice parameters, especially via change of the bonding angles [29]. For example, the magnetic and transport properties of $Nd_{0.5}Sr_{0.5}MnO_3$ films on $SrTiO_3$ substrates were changed when they were deposited on different surfaces of $SrTiO_3$, namely on (001), (110), or (111) [30]. Also, $La_{2/3}Ca_{1/3}MnO_3$ films on $SrTiO_3$ (001) and (110) substrates were compared by Infante *et al.*, and the (110) films showed higher Curie temperature compared to the (001) ones [31]. The possible reconstructions associated with the strain field through changes of atomic and electronic structures, chemical and mechanical properties, as well as magnetic and orbital states are of course highly complicated.

One interesting comment by Infante *et al.* is one strain-assisted segregation of Ca in $La_{2/3}Ca_{1/3}MnO_3$ due to the difference of the ionic radii of Ca ($\sim$ 1.12 Å) and La ($\sim$ 1.16 Å). Since $La_{2/3}Ca_{1/3}MnO_3$ has smaller pseudocubic lattice parameter ($a = 3.863$ Å) than that of $SrTiO_3$ ($a = 3.905$ Å), the tensile strain from the substrate prefers larger ionic radii in the film, and in this case, La is preferable. These elastic effects might be relevant to the $LaMnO_3/SrTiO_3$ interfaces in this study, and related to the difference #1.

Invisible off-stoichiometry

When considering *AB*-difference, we neglected the off-stoichiometry of oxygen. This is because the oxygen vacancy formation during growth of these $LaMnO_3/SrTiO_3$ samples is expected to be neglected, since they were grown under sufficiently high pressure of oxygen (1 mTorr), which is often used to remove the oxygen vacancies in $SrTiO_3$. Also, there is no space for interstitial oxygen ions in the perovskite lattice. However still the kinetic bombardment during PLD growth may introduce oxygen vacancies, which can add extra valence electrons, and this can be relevant to the difference #2. Since the O-K edge at the interface consisted of various features reflecting the mixing of materials, it was impossible to determine the oxygen stoichiometry at the interface in this study.

Also, in the local composition analyses, we assumed the perfect stoichiometry of the cations. However, $LaMnO_3$ is known to be a material which readily accommodates cation vacancies, with associated change of magnetic and transport properties [32–34]. Potential slight off-stoichiometry of the $LaMnO_3$ films can affect the local composition analysis. Also these stoichiometry can change the transport properties of the $LaMnO_3/SrTiO_3$ interfaces, which can be relevant to the observation of the insulating transport properties of these interfaces, independent of $SrMnO_3$ insertion.

Overestimation of the lower valence component by PCA

We estimated the amount of the extra valence electrons by equation (6.3) taking the principal components derived by PCA to be the reference of Mn^{3+} and Mn^{2+}, but as already noted, these components are numerical products. Therefore, even though the principal components were similar to the reference in the literature, there still remains a possibility for the overestimation by this analysis. Also, the change of the EELS spectra

was assumed to change linearly on the valence states, but due to the large hybridization of the Mn 3d and the O 2p states, this dependence can be non-linear[10]. This can change the number of electrons and thus account for the difference #2.

6.2.7 Comparison of $LaMnO_3/SrTiO_3$ and $La_{1-x}Sr_xMnO_3/SrTiO_3$ – spectroscopically invisible higher valence states

The observation of lower Mn valence component in EELS shows a significant difference from the previous spectroscopic observations in $La_{1-x}Sr_xMnO_3/SrTiO_3$, where clear report on the lowering of the valence state has not been made, although it is expected from a viewpoint of local composition. However, from a viewpoint of transport properties, change of the Schottky barrier height of the doped system, $La_{0.7}Sr_{0.3}MnO_3$ on TiO_2-terminated Nb:$SrTiO_3$, was observed by varying the amount of the inserted $SrMnO_3$ coverage on the Nb:$SrTiO_3$ [10]. This result can be explained by the change of the interface dipole which suggests that the amount of the electrons doped to Mn at the interface decreased as a function of $SrMnO_3$ coverage.

On the other hand, the increasing behavior of the Mn valence expected from the interface composition was observed, namely the occupation in the Mn e_g state decreased, when $SrTiO_3$ was deposited on top of $La_{0.6}Sr_{0.4}MnO_3$ to form a SrO/MnO_2 terminated interface [17]. This observation is consistent with the improved interface magnetic properties by inserting $LaMnO_3$ at the $SrTiO_3/La_{0.6}Sr_{0.4}MnO_3$, to reconcile the loss of electrons at this interface.

The spectroscopic features of Mn with various valence states have been extensively studied by means of XPS [35], XAS [36], XPS and XAS [37], and EELS [38]. One of the striking features of these observations was that the Mn $L_{2,3}$ edge behaved insensitively between the nominal valence state of Mn^{3+} and $Mn^{3.4+}$, while it gradually changed as the valence increased beyond $Mn^{3.4+}$, and converged to the Mn^{4+} spectra. This result can be understood considering the strong coupling between the Mn 3d states and the O 2p states [39]. If the chemically doped holes are assigned to the O ligand sites, the local electronic states around the Mn ions do not change significantly, hence they are spectroscopically insensitive. Indeed, the observation of the prepeaks in the O-K XAS spectra revealed hole doping in O 2p states in $La_{1-x}Sr_xMnO_3$ [40].

When electrons are further doped to $LaMnO_3$, this electron is expected to occupy the e_g state of Mn, since the O 2_p state is almost filled. Therefore, this change of electron number can be observed by looking at the spectroscopic features of Mn, as we did in this study. Even in this case, couplings between the 3d and 2p, as well as the covalent character of these materials cannot be neglected, but still these effects are expected to be small.

In summary, the lack of spectroscopic information about the lowering of the Mn valence has caused confusion over inconsistency between hole and electron doping, al-

[10]The strong hybridization is described in Section 6.2.7.

though both are expected to be achieved by changing the interface compositions. However, considering the insensitive doping dependence of the spectroscopic features of Mn in $La_{1-x}Sr_xMnO_3$, electron doping is expected to be difficult to observe. Our observations of the Mn valence lowering in $LaMnO_3/SrTiO_3$ suggest such observation of electron doping to $LaMnO_3$ at the interface is possible, owing to the higher sensitivity of the Mn-$L_{2,3}$ EELS spectra.

6.3 Atomic and electronic structure of Mn_3O_4 precipitates in laser-ablated manganite films

6.3.1 Precipitates formed during kinetic growth of manganite films

$LaMnO_3$, the parent compound of $La_{1-x}Sr_xMnO_3$, was chosen to study the structure of the precipitates on manganite films, so that the complete cation stoichiometry could be examined in detail by electron energy-loss spectroscopy (EELS) – such an analysis in $La_{1-x}Sr_xMnO_3$ is hindered due to weak Sr-$M_{4,5}$ edges. 40 nm thick $LaMnO_3$ films were deposited on (001)-oriented $SrTiO_3$ substrates by PLD under the condition $\#_G$(A) in Table 6.1. The surface of a typical film was investigated by atomic force microscopy (AFM), as shown in Fig. 6.8(a), and particles ~100 nm in diameter were observed on the flat surface of the $LaMnO_3$ film.

Figure 6.8(b) shows a cross sectional ADF image of a $LaMnO_3$ film around a precipitate with the sample oriented along a substrate [100] crystallographic axis. In Fig. 6.8(b), the precipitate was dark, and a brighter region (cap) was observed on top of it. Three precipitates were observed by STEM, and all of them had a similar structure with caps.

6.3.2 Compositions obtained by STEM-EELS

In order to study the composition, spatially resolved EELS was performed along a line as shown in Fig. 6.8(b). Figure 6.8(c) shows the EELS spectra including the Ti-$L_{2,3}$, O-K, Mn-$L_{2,3}$, and La-M_5 edges, which are well separated in energy. The elemental distribution, as shown in Fig. 6.8(d), was obtained by integrating the La and Mn intensities and using the $LaMnO_3$ film as the composition standard. No La was detected in the precipitate, which suggests that it consists of pure manganese oxide, MnO_x. The cap, on the other hand, showed both La and Mn edges, but with a La concentration slightly higher than that of Mn.

In considering differences associated with chemical bonding around O sites, the most useful information is contained in the near edge structure of the O-K edges, as shown in Fig. 6.9(a). The O-K edge is determined by transitions from O 1s to unoccupied molecular orbitals with O 2p character, and it is known to be strongly affected by the oxidization state of the Mn in MnO_x [16, 41, 42]. When comparing the spectrum obtained from the precipitate with reference spectra of MnO_x, the O-K edge of Mn_3O_4 gives the

Figure 6.8: (a) AFM image of a $LaMnO_3$ film grown on $SrTiO_3$, showing precipitates (∼100 nm in diameter) on the flat surface of $LaMnO_3$. (b) Cross-sectional STEM ADF image around a precipitate. A brighter region (cap) on top of the precipitate was observed. (c) EELS spectra recorded at the filled points in (b). Four representative spectra were chosen from the $SrTiO_3$ substrate, the $LaMnO_3$ film, the precipitate, and the cap, respectively. (d) Concentration profiles of La and Mn along the line scan in (b).

Figure 6.9: (a) O-K and (b) Mn-$L_{2,3}$ EELS near edge structure after background subtraction and normalization. Reference data for Mn_3O_4 from Ref. [42] are also plotted for comparison, where the energy offsets were added to match the leading edge positions to those of the precipitate, in order to correct the difference between the measurement systems. Inset in (b) shows the Mn-L_3 peak positions of the cap and the $LaMnO_3$ film.

best match of the peak positions and the near edge fine structure.

Additional information about the Mn valence state can be obtained from the Mn-$L_{2,3}$ edge. As shown in Fig. 6.9(b), the Mn-L_3 edge from the precipitate is shifted to lower energy compared to the fingerprint of the formal Mn^{3+} in $LaMnO_3$, reflecting the lower valence of the Mn. This is consistent with the result for the O-K edges because Mn_3O_4 has a formal $Mn^{2.67+}$ valence. In fact, the spectra from Mn_3O_4 and the precipitate also showed a similar Mn-$L_{2,3}$ fine structure. Based on these spectroscopic studies, the stoichiometry of the precipitate was determined to be Mn_3O_4.

The EELS fine structure of the O-K and Mn-$L_{2,3}$ edges of the $LaMnO_3$ film and the cap was also compared to that of bulk polycrystalline $LaMnO_3$, which was measured using a spectrometer dispersion of 0.1 eV per channel. Both the O-K and the Mn-$L_{2,3}$ edges of the $LaMnO_3$ film were well matched with those of the bulk, indicating that the film, aside from the precipitates, was grown maintaining the target stoichiometry. On the other hand, the cap showed a quite different structure, and the Mn-L_3 edge was observed at higher energy than the bulk and the film, suggesting a higher Mn valence. Considering the previous observation of the cation off-stoichiometry, the increase of the valence indicates Mn deficiency in the cap.

Figure 6.10: (a) High resolution ADF image of the epitaxial interface between $LaMnO_3$ and $SrTiO_3$, and (b) lower magnification image of the film around the precipitate, both taken along the (100) zone axis of the $SrTiO_3$ substrate. (c) ADF image aligned to the cap boxed in (b). (d) Perovskite crystal structure observed in the area marked by the box in (c).

6.3.3 Crystal structures

Although the film and the cap have a similar composition, the cap was much darker in the ADF image since there is no coherence of crystal orientation between the cap and the substrate. When the sample is aligned, so that a zone axis is parallel to the incident electron beam direction, channeling of the electron probe along the column of atoms occurs, resulting in enhancement of the ADF intensity [43]. As shown in Fig. 6.10(a), the $LaMnO_3$ film was grown epitaxially on the substrate, and therefore shows an enhanced ADF intensity compared to the cap [Fig. 6.10(b)]. By rotating the sample, the cap can be aligned along a zone axis, which results in an increase of the ADF intensity [Fig. 6.10(c)]. Clear crystal lattice fringes of the cap were obtained in this direction, exhibiting the perovskite lattice as shown in Fig. 6.10(d).

This effect of channeling also reduced the ADF intensity of the precipitate. As shown in Fig. 6.11(a), the precipitate could be aligned using the CBED pattern [Fig. 6.11(b)]. In this direction the clear crystal structure of the precipitate was observed, as shown in Fig. 6.11(c), where the heavier Mn ($Z = 25$) lattice dominates over O ($Z = 8$). Both the CBED pattern and the Fourier transformation of the lattice image [Fig. 6.11(d)] show two dimensional symmetry of $c2mm$, which matches the (100)-projection of the tetragonal space group $I41/amd$, appropriate for the Mn_3O_4 distorted spinel structure [Fig. 6.11(e)].

6.3.4 Possible origins of the precipitation

Similar precipitation (distinct from ablated particles from the target) has been reported, especially in transition metal oxides such as cuprates or manganites [9, 45]. Recently, it has been established that precise tuning of the ablation conditions, especially the laser spot size and fluence, is necessary to achieve cation stoichiometry in PLD grown

Figure 6.11: (a) ADF image of the $LaMnO_3$ film aligned to a segment of the precipitate. (b) CBED pattern obtained from the precipitate. (c) High resolution lattice image and (d) Fourier transformation of the image taken from the precipitate. (e) Crystal structure of Mn_3O_4 in a (100)-projection [44].

films [46, 47]. If the chemical condition during growth is optimal for the $LaMnO_3$ film, deficiency or excess of the cations cannot be stabilized as defects in the film, and therefore are easy to form precipitates on the surface. This scenario well matches to the observation of the precipitate on the the $LaMnO_3$ film keeping its stoichiometry. Considering the Gibbs free energy for the oxidation reaction, the stable oxidation number tends to decrease as a function of the temperature under the constant partial pressure of oxygen. The ablated materials have high kinetic energy, which can increase the local temperature on the surface, and they are cooled down to the temperature of the substrate to form films. Also, strain energies can be different among the $LaMnO_3$ film strained to the substrate, the precipitate, and the cap. These variations of the local conditions, including temperature or strain, may explain the coexistence of the different valence states of Mn in one system.

6.4 Summary

To study the precise electronic structure of the manganite junctions, $LaMnO_3/SrTiO_3$ was chosen due to its wide variability by inserting $SrMnO_3$. Unlike $LaAlO_3/SrTiO_3$, $LaMnO_3/SrTiO_3$ interfaces were insulating, independent of the $SrMnO_3$ insertion (0 to 2 uc). The lack of conductivity even without $SrMnO_3$ was explained by the STEM-EELS observations of lower valence Mn ($< 3+$), which do not contribute to metallic transport. At the interface, the mixing of La and Sr was observed deeper into $SrTiO_3$ than that of Mn and Ti, suggesting the existence of $LaTiO_3$ as the interface composition which provides the lower valence of Ti compared to that of $SrTiO_3$. These additional electrons in the Ti $3d$ states may prefer the Mn sites due to the lower energy of their $3d$ level, hence explaining the Mn lower valence features. As the inserted $SrMnO_3$ layers increased, the lower valence features decreased, suggesting the possible control of electronic states by changing interface compositions.

Precipitates formed in PLD grown $LaMnO_3$ films were determined to be Mn_3O_4 crystallites thorough spectroscopic and structural observations. Our observation of Mn_3O_4 precipitates within stoichiometric $LaMnO_3$ films suggests that they form to accommodate a net cation off-stroichiometry in the ablation plume, and this is a key factor currently limiting particle-free manganite films needed for device structures.

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Chapter 7

RVO$_4$:Eu^{3+} (R=La or Y) phosphor films grown by PLD

Eu^{3+} doped rare-earth orthovanadates are known to be good red phosphor materials. Especially, LaVO$_4$:Eu^{3+} is a promising candidate due to the poor point symmetry around the Eu^{3+} site, and thus high probability of dipole transitions is expected according to Judd-Ofelt theory. However, the poor solid solubility limit ($<$ 3 mol%) of Eu^{3+} in LaVO$_4$:Eu^{3+} prevented its efficiency as a phosphor. In this Chapter, we present optical evidence of the enhanced Eu^{3+} solubility as high as 10 mol% in LaVO$_4$:Eu^{3+} thin films grown by pulsed laser deposition. The photoluminescent intensity exceeds that of YVO$_4$:Eu^{3+} thin films when excited by the light 351 nm of wavelength, indicating the stronger direct emission of Eu^{3+}.

7.1 RVO$_4$:Eu^{3+} as a phosphor

Rare-earth orthovanadate RVO$_4$ has been of particular interest and utilized due to its wide applications as phosphors[1, 2], lasers[3, 4], and amplifiers for fiber-optic communication[5]. Especially, RVO$_4$:Eu^{3+} is known as an excellent phosphor with bright red emission, where the Eu^{3+} works as an activator and its quantum yield is as high as 70 % in YVO$_4$ [2]. Phosphors have wide applications for cathode ray tube (CRT) or flat panel displays, as well as fluorescent lamp or white light-emitting diodes, and phosphors with the three primary colors, including red, have been of particular importance. This red luminescence mainly corresponds to the transitions of the Eu $4f$ multiplet states, from the ^{5}D$_0$ level to the ^{7}F$_J$ states (J = 1, 2, 3, 4, 5), which are dipole prohibited due to the same parity of the multiplet states of the initial and the final states. However, according to Judd-Ofelt theory, dipole transitions are allowed by the perturbation via crystal fields with odd parity [6, 7]. In RVO$_4$:Eu^{3+}, the Eu^{3+} substitutes the R site due to their matched valence and ionic radii, and due to the poor point symmetry around the R site, high transition probability is achieved via electric dipole transitions. In addition, the large energy transfer from the VO$_4$ tetrahedrons to the Eu^{3+} enhances indirect luminescent processes, resulting in the strong emission from the Eu^{3+} ions.

Table 7.1: Effective ionic radii of La, Y, and Eu (Shannon [11]).

Element	La		Y		Eu	
Coordination number	8	9	8	9	8	9
Effective ionic radii (Å)	1.160	1.216	1.019	1.075	1.066	1.120

Figure 7.1: Crystal structure of monazite type $LaVO_4$ [8] and zircon type YVO_4 [9].

The ionic radii of the R element [Table 7.1] is known to determine the crystal structure of RVO_4. $LaVO_4$ usually shows monazite structure due to the large ionic radii of La [8], while YVO_4 shows a more packed zircon structure reflecting the smaller Y [9]. Theses crystal structures are shown in Fig. 7.1, and their structural properties are described in Table 7.2 Note $EuVO_4$ also has zircon structure [10].

The difference of the crystal structures changes their optical properties. From the viewpoint of point symmetry around the R site, monazite type $LaVO_4$ is expected to be the better host material due to its poor symmetry, and thus has higher dipole transition probability. However, there are two main obstacles to prevent the strong emission from $LaVO_4$:Eu^{3+}. One is the poor solubility limit of Eu^{3+} (< 3 mol%) due to the large mismatch of the ionic radii. The excess Eu^{3+} in highly doped $LaVO_4$:Eu^{3+} forms phase-separated zircon $EuVO_4$, which has poor luminescent properties. On the other hand, YVO_4 has the same zircon structure as $EuVO_4$, achieving perfect solubility. Another is the smaller energy transfer from the VO_4 tetrahedrons to the Eu^{3+} ions in $LaVO_4$, which reduces the indirect emission of Eu^{3+}. This is because the larger spacing between Eu^{3+} and VO_4, as expected from the unit cell volume, and the overlapping of their wave functions is suppressed in $LaVO_4$.

Efforts to improve the luminescent properties of $LaVO_4$:Eu^{3+} have been made by changing its crystal structure. Meta-stable zircon $LaVO_4$ was synthesized via hydrothermal process under high pressure [12], and enhanced luminescent properties of $LaVO_4$:Eu^{3+} was achieved in its zircon nano-crystals [13]. However, in these zircon crystals, only the disadvantage of larger spacing between Eu^{3+} and VO_4 remained, and the main advantage, i. e. the poor symmetry around Eu^{3+} site was lost.

In this Chapter, fabrication of RVO_4:Eu^{3+} thin films by PLD and their structural and photoluminescent properties are described, with comparison to those of the bulk polycrys-

Table 7.2: Structural properties of monazite type $LaVO_4$ [8] and zircon type YVO_4 [9].

	$LaVO_4$	YVO_4
Crystal structure	Monazite	Zircon
Space group	$P2_1/c$	$I4_1/amd$
Coordination number of R	9	8
Point symmetry around R	C_1	D_{2d}
Unit cell volume (Å^3)	331	319
Solubility limit of Eu^{3+}	< 3 mol%	100 mol%

talline targets for PLD. In the films grown by PLD, a different meta-stable structure was achieved, namely the solution of Eu^{3+} in monazite $LaVO_4$ exceeding its bulk solubility limit was observed. Due to the higher dipole transition probability, the direct absorption by Eu^{3+} was enhanced, resulting in the photoluminescence even stronger than that of YVO_4:Eu^{3+} when excited by $\lambda = 351$ nm light.

7.2 Polycrystalline RVO$_4$:Eu^{3+}

7.2.1 Solid state reaction

Four polycrystalline PLD targets, $LaVO_4$:Eu^{3+} (1 mol%), $LaVO_4$:Eu^{3+} (10 mol%), YVO_4:Eu^{3+} (10 mol%), and $EuVO_4$, were synthesized from the initial materials La_2O_3, Y_2O_3, Eu_2O_3, and V_2O_5. They were baked at 500 °C in Ar (95 %)-H_2(5 %) mixed gas flow for 10 hours to reduce V_2O_5 to V_2O_3, in order to avoid melting of V_2O_5 (melting point = 690 °C) before the reaction. Subsequently, they were reacted at 1000 °C in Ar (95 %)-H_2(5 %) mixed gas flow for 48 hours, to form a black RVO$_3$:Eu^{3+} pellet. The RVO$_3$:Eu^{3+} was then oxidized at 1000 °C in O_2 flow for 24 hours, and a white pellet of RVO$_4$:Eu^{3+} was obtained. As PLD targets, hard pellets are desired and the RVO$_4$:Eu^{3+} was further baked at 1400 °C in air for 24 hours, twice. In each step between the sinter processes, the pellet was ground to fine powder, and shaped again to a cylinder with diameter of 20 mm under pressure of 40 MPa.

The crystal structure of the pellets was determined by powder x-ray diffraction (XRD), as shown in Fig. 7.2. $LaVO_4$:Eu^{3+} (1 mol%) showed a single phase with the monazite structure, while $LaVO_4$:Eu^{3+} (10 mol%) showed other peaks than the monazite ones. These extra peaks had similar peak positions and intensity ratios to those of zircon $EuVO_4$ or YVO_4:Eu^{3+} (10 mol%), reflecting phase separation since the amount of Eu^{3+} exceeded its solid solubility limit in $LaVO_4$. Note the zircon-like peak positions in $LaVO_4$:Eu^{3+} (10 mol%) were observed at slightly smaller angle than $EuVO_4$, which may suggest this phase-separated zircon phase was not pure $EuVO_4$, but $La_{1-x}Eu_xVO_4$ with high enough Eu concentration to stabilize the zircon phase.

Figure 7.2: Powder XRD patterns of the polycrystalline pellets. Reference patterns of the monazite and zircon type $LaVO_4$ are also plotted. Triangles indicate the peaks corresponding to the zircon phase in $LaVO_4$:Eu^{3+}.

Figure 7.3: Measured PL spectra of the polycrystalline pellets and normalized spectra taking the maximum as the standard. (a) Excited by $\lambda = 266$ nm and (b) $\lambda = 351$ nm light.

7.2.2 Photoluminescence

The photoluminescence of the polycrystalline pellets was measured using excitation lasers with two different wavelengths, $\lambda = 266$ nm and $\lambda = 351$ nm, as shown in Fig. 7.3. The shape of the Eu^{3+} PL spectrum is very sensitive to the local structure around the Eu^{3+} in the material, especially the splitting of the peaks and the ratio between the different peaks change dramatically. YVO_4:Eu^{3+} (10 mol%) and $EuVO_4$ showed a similar PL shape, reflecting the same zircon structure of the host material.

As examined by XRD, $LaVO_4$:Eu^{3+} (1 mol%) consisted of single phase monazite, and its PL spectra was completely different from that of the zircon ones. On the other hand, the shape of PL from $LaVO_4$:Eu^{3+} (10 mol%) had a similar shape to a linear combination of the $LaVO_4$:Eu^{3+} (1 mol%) and the $EuVO_4$ spectra. This is consistent with the structural study by XRD, which indicated that polycrystalline $LaVO_4$:Eu^{3+} (10 mol%) has two separated phases with the zircon and monazite structures, and Eu^{3+} is distributed to both phases. Note the PL intensity is more sensitive to the local symmetry, rather than the bulk symmetry. If the R site is randomly occupied by La and Eu, the distribution of these two elements introduces disorder in crystal, and can reduce the local symmetry. If the separated zircon phase is $La_{1-x}Eu_xVO_4$, the PL is expected to be enhanced compared to that for $EuVO_4$, since the transition is more likely to follow the dipole selection rule.

Figure 7.4: Growth phase diagram for $LaVO_x$ thin films by PLD (Hotta *et al.* [16]).

7.3 RVO$_4$:Eu^{3+} thin films

7.3.1 Fabrication and structural characterization

Thin film growth by PLD

RVO$_4$ films were grown via two different processes: one is the conversion of an epitaxial RVO$_3$/SrTiO$_3$ structure by postannealing in oxygen (converted films), and the other is the direct deposition of RVO$_4$ by PLD under high partial pressure of oxygen during growth (films grown at 10^{-2} Torr). Vanadium ions can take different oxidation numbers in RVO$_x$, for example, $x = 3$ in perovskite LaVO$_3$ or YVO$_3$ [14], $x = 3.5$ in pyrochlore $Y_2V_2O_7$ [15][1], and $x = 4$ in monazite LaVO$_4$ [8] or zircon YVO$_4$ [9]. When the films of RVO$_x$ are grown by PLD, their structure is very sensitive to the growth condition. The growth phase diagram of LaVO$_x$ by PLD has been extensively studied by Hotta *et al.* [16], and selected growth of RVO$_4$ and RVO$_3$ was achieved by controlling P_{O_2} and T_{sub} during growth. From the viewpoint of Gibb's free energy, the thermodynamic condition to stabilize V^{3+}, V^{4+}, and V^{5+} is expected to be similar in RVO$_x$, since the valence state of R is likely to be fixed to trivalent, and the most variable valence state is that of vanadium in these compounds [17]. Following this assumption, the same growth conditions as those for the LaVO$_x$ were used to selectively grow RVO$_3$ and RVO$_4$.

In this study, 40 nm thick RVO$_x$ films were grown on SrTiO$_3$ (001) substrates by PLD, using a KrF excimer laser with a laser fluence of 1.0 J/cm^2, a spot size of 1.6 mm^2, and repetition rate of 8 Hz. The polycrystalline targets described in the previous section were used. The substrates were preannealed at $T_{sub} = 950$ °C and $P_{O_2} = 5 \times 10^{-6}$ Torr, and during deposition, T_{sub} was 600 °C and $P_{O_2} = 5 \times 10^{-7}$ Torr (P_{RVO_3}) or $P_{O_2} = 1 \times 10^{-2}$ Torr (P_{RVO_4}). Clear RHEED oscillations were observed during growth of RVO$_3$ at P_{RVO_3}, and the thickness of the layers was monitored by the oscillations in the growth [Fig. 7.5(a)]. The same pulse number was used for the deposition at P_{RVO_4},

[1]Note pyrochlore $R_2V_2O_7$ is very unstable at ambient pressure and can be synthesized via high pressure growth processes.

Figure 7.5: (a) Typical RHEED oscillations during growth of RVO$_3$ films. (b) XRD 2θ-ω scan of the as grown LaVO$_3$:Eu^{3+} (10 mol%) film and the annealed one. AFM topography of (c) LaVO$_x$:Eu^{3+} (10 mol%) and (d) YVO$_3$:Eu^{3+} (10 mol%) films. Three images are shown for each samples, corresponding to the surfaces of (1) the as grown RVO$_3$, (2) the same ones as (1) but postannealed, and (3) the films grown at 10^{-2} Torr.

assuming the pressure does not change the deposition rate during growth[2].

Structural changes of films grown at $P_{R\mathrm{VO}_3}$ by postannealing

The films grown at $P_{R\mathrm{VO}_3}$ were then postannealed in oxygen flow for 24 hours to convert the structure to RVO$_4$, and the structural change was confirmed by means of XRD and AFM. As shown in Fig. 7.5(b), the peak in the XRD 2θ-ω scan corresponding to the perovskite RVO$_3$ disappeared after postannealing, indicating that the film lost the coherent relation to the substrate. The absence of the peaks from RVO$_4$ is likely due to the small grain size and small total volume of the converted compound insufficient for powder x-ray detection. The conversion of the films was also studied by AFM [Figs. 7.5(c), (d)], and the postannaling was confirmed to change the surface topography completely. The as-

[2]In fact, the deposition rate depends on the pressure, due to the difference of the mean free path of the vapor phase. However, the thickness of these films could not be calibrated directly because of the rough surface of the $P_{R\mathrm{VO}_4}$ films, and the pulse number obtained during growth was adopted to approximate the thickness.

Figure 7.6: STEM ADF images around (a) as grown and (b) postannealed $LaVO_x$:Eu^{3+} (10 mol%)/$SrTiO_3$ superlattices. (c) EELS spectra obtained from the $LaVO_x$:Eu^{3+} in the superlattices. The reference EELS spectra are also plotted (Fitting Kourkoutis *et al.* [18]).

grown RVO_3 films showed the step-and-terrace structures on the surfaces, reflecting the slight miscut angle of the substrate, while the annealed samples showed rough surfaces, which were also different from those of the films grown at 10^{-2} Torr.

STEM-EELS study of $LaVO_x$:Eu^{3+} (10 mol%)/$SrTiO_3$ superlattices

To further study the atomic and electronic structures, STEM-EELS studies of the superlattice of $LaVO_3$:Eu^{3+} (10 mol%) and $SrTiO_3$, grown at the same condition ($P_{O_2} = P_{RVO_3}$) were performed. Figure 7.6(a) show the Z-contrast STEM-ADF image around the superlattice, and the perovskite lattices epitaxial to the substrate was observed. Here the $LaVO_3$:Eu^{3+} (10 mol%) was brighter in the image. When it was postannealed, the structure of $LaVO_x$:Eu^{3+} changed, and the lack of the channeling of the probing electron beam reduced its ADF intensity [Fig. 7.6(b)].

The information of the vanadium valence appears in the EELS fine structure. The measured EELS spectra from the $LaVO_x$:Eu^{3+} layers[3] were compared to the reference, and the as grown $LaVO_3$:Eu^{3+} (10 mol%) film showed a similar spectrum to that of the polycrystalline $LaVO_3$ and the converted one to the polycrystalline $LaVO_4$ [Fig. 7.6(c)]. Through these structural and spectroscopic studies, the crystal structure of the converted films were confirmed to be RVO_4.

Figure 7.7: Measured PL spectra of the converted films and normalized spectra taking the maximum as the standard. (a) Excited by $\lambda = 266$ nm and (b) $\lambda = 351$ nm light. Note in (b), bright lines of the laser pumping lamp overlapped the spectra above $\lambda = 700$ nm.

7.3.2 Photoluminescence

The PL of the converted films [Fig. 7.7] and the films grown at 10^{-2} Torr [Fig. 7.8] were measured using excitation lasers with two different wavelengths, $\lambda = 266$ nm and $\lambda = 351$ nm. The spectra of the $LaVO_4$:Eu^{3+} (10 mol%) films showed almost identical shapes to those of the $LaVO_4$:Eu^{3+} (1 mol%) films, as well as that of the $LaVO_4$:Eu^{3+} (1 mol%) polycrystalline pellet. Since Eu^{3+} substitutes at the La site in $LaVO_4$:Eu^{3+} (1 mol%) with a single monazite phase, this accordance of the shapes indicates that the 10 mol% of Eu is fully doped to the La site in the monazite $LaVO_4$ films.

It is striking that $LaVO_4$:Eu^{3+} (10 mol%) consisted of a single monazite phase in the PLD grown films, even though the Eu concentration exceeded its bulk solid solubility in $LaVO_4$. In the PLD process, the films grow in a non-equilibrium process, namely the ablated materials with high energy quenched on the substrate surface with lower temperature than the melting point of the deposited material [19, 20]. We attribute this enhancement of Eu solubility as a result of the freezing of the atoms before the phases are separated by their migration at the surface of the films, which clearly emphasizes the non-equilibrium nature of the PLD growth.

Another possible origin of the lack of the phase separation would be the effect of small

[3]The EELS spectra were measured at the center of the layers, in order to avoid the influence from the other layers or the interfaces.

Figure 7.8: Measured PL spectra of the films grown at 10^{-2} Torr and normalized spectra taking the maximum as the standard. (a) Excited by $\lambda = 266$ nm and (b) $\lambda = 351$ nm light. Note in (b), bright lines of the laser pumping lamp overlapped the spectra above $\lambda = 700$ nm.

volume of the films. Crystal growth kinetics often appears to depend on the crystal size [21], and in thin films phase separation can be suppressed, because the energy gain by phase separation is smaller compared to the large grains obtained by solid state reactions. On the other hand, diffusion at the surface can occur at lower energy than in the bulk, due to the small number of binding atoms around the surface atoms [22]. As observed in Chapter 6, such diffusion can cause formation of Mn_3O_4 precipitates in $LaMnO_3$ films following the stoichiometry and the thermodynamic conditions. Here, the precipitation can be accelerated by the different chemical potential of the Mn valence states in the film and the precipitate. In the $LaVO_4$:Eu^{3+} films case, the same V valence in $LaVO_4$ and $EuVO_4$ might suppress such migration of atoms to form uniformly doped films.

7.4 Excitation wavelength dependence

The activator ions in phosphor materials can be excited via two different mechanisms. One is the direct excitation of the activator ions, and the other is the indirect excitation process via energy transfer from the excited host material. Considering the different energy dependence of these excitation mechanisms, the excitation wavelength dependence of the PL intensity may be different between these two materials. In addition, the penetration depth of the excited light is expected to depend on its photon energy, and especially in thin films it can be relevant to the PL efficiency.

Figure 7.9: Relative PL intensity of the RVO$_4$:Eu^{3+} samples excited by (a) $\lambda = 266$ nm and (b) $\lambda = 351$ nm light. (c) PLE spectra obtained from the converted LaVO$_4$:Eu^{3+} (10 mol%) and YVO$_4$:Eu^{3+} (10 mol%) films. The PLE spectra was normalized by the intensities at $\lambda = 266$ nm, so that they match to the spectral intensities in Fig. 7.7.

Figure 7.9(a) and (b) shows the relative PL intensity corresponding to the ^{5}D$_0$ $\rightarrow$^{7}F$_2$ transition[4] in the RVO$_4$:Eu^{3+} samples excited by $\lambda = 266$ nm and $\lambda = 351$ nm light, respectively. By comparing LaVO$_4$:Eu^{3+} (10 mol%) and YVO$_4$:Eu^{3+} (10 mol%), the relative ratio of their PL intensities differs by the excitation wavelength, as well as whether they are polycrystalline pellets or thin films. It is quite noticeable that the PL intensity of LaVO$_4$:Eu^{3+} (10 mol%) exceeds that of YVO$_4$:Eu^{3+} (10 mol%) when the thin film samples were excited by $\lambda = 351$ nm light.

This can be understood based on the difference of the direct and indirect excitations [2, 23]. When they are excited by light with energy higher than the bandgap, 3.8 eV ($\lambda = 326$ nm) in LaVO$_4$ and 3.7 eV ($\lambda = 335$ nm) in YVO$_4$ [24], due to the stronger energy transfer from VO$_4$ to Eu^{3+}, YVO$_4$ shows stronger PL, which was indeed observed when excited by $\lambda = 266$ nm light.

If the excitation photon energy is smaller than the host bandgap, namely in the case of $\lambda = 351$ nm excitation, such indirect emission is suppressed, and only the absorption by the activator Eu^{3+} can survive. Even though YVO$_4$:Eu^{3+} shows weaker absorption via dipole transitions in Eu^{3+} due to the higher symmetry, if the sample is thick enough, all the light can be eventually absorbed, and converted to fluorescence from Eu^{3+}, and indeed in bulk samples, it shows stronger emission than LaVO$_4$:Eu^{3+}. However, this excitation is transparent for the host materials, and in the 40 nm thin films, only the direct absorption by Eu^{3+} is relevant, hence the LaVO$_4$:Eu^{3+} films showed stronger emission.

To further study the wavelength dependence of the PL intensity, the photoluminescence excitation (PLE) spectra were recorded from the converted LaVO$_4$:Eu^{3+} (10 mol%) and YVO$_4$:Eu^{3+} (10 mol%) films, using the grated light from a Xe lamp for the excitation ([Fig. 7.9(c)]). The LaVO$_4$:Eu^{3+} (10 mol%) film showed a larger tail of PLE spectra above the bandgap, suggesting the strong direct emission of Eu^{3+}.

[4]The PL intensities between 600 nm and 630 nm in Figs. 7.3, 7.7, and 7.8 were integrated to obtain the intensity of these emissions.

7.5 Summary

The $LaVO_4$:Eu^{3+} (10 mol%) thin films grown by PLD showed an identical shape of the PL spectra as that of 1 mol% doped one, suggesting the enhancement of the solid solubility limit of Eu in the PLD grown films up to as high as 10 mol%. Especially when excited by $\lambda = 351$ nm light, the PL intensity exceeds that of the YVO_3:Eu^{3+} (10 mol%) with the same thickness, reflecting the stronger direct emission of Eu^{3+} via dipole transitions. The non-equilibrium growth process in PLD has been thought to be an obstacle to fabricate high quality thin films. From an opposite viewpoint, this fact can be utilized to stabilize a material which cannot exist in bulk. In addition, by annealing epitaxial superlattices of $LaVO_3$:Eu^{3+}/$SrTiO_3$, well-ordered superlattices of $LaVO_4$:Eu^{3+}/$SrTiO_3$ with abrupt interfaces were obtained. These techniques may pave a road to fabricate high quality optical superlattices including possible laser applications, with the advantage of the high dipole transition probability of Eu^{3+} in $LaVO_4$.

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Chapter 8

Conclusions

When there is a change in the dipole moment of the unit cells starting from the interface, the electrostatic potential diverges, and thus the ionic charges and stoichiometry cannot be maintained. This instability of a polar discontinuity is equivalent to that of the dipole free unit cell at the interface not keeping the stoichiometry of the bulk constituent materials. This issue is one of the central aims of the interface science of compounds. In transition metal oxides, due to multi-valency, electronic reconstructions are available to reconcile this instability. Following these arguments, we described three phenomena related to the changes of the electronic states in PLD-grown oxide heterostructures.

In the $LaVO_3$ quantum well near the polar surface of AlO_2-terminated $LaAlO_3$ (001), clear evidence for the modulation doping of holes from the polar surface was observed by changing the distance from the surface, as well as the well thickness. This behavior was attributed to a crossover from an atomic reconstruction of the polar $LaAlO_3$ surface to an electronic reconstruction of the vanadium valence. A striking point is that the doped carriers are holes, which emphasizes the importance of this work. This is because the role of electron-donor oxygen vacancies are excluded, which has made the origin of conducting electrons at the $LaAlO_3/SrTiO_3$ interfaces controversial.

The metallic conductivity of $LaAlO_3/SrTiO_3$ strongly depended on the interface composition. In the [$LaAlO_3$/ $SrTiO_3$] superlattices, there are two types of interfaces: $LaAlO_3$ above $SrTiO_3$ (L/S type), or the opposite (S/L). The conductivity of the [$LaAlO_3$/ $SrTiO_3$] superlattices disappeared when $Sr_2Al_2O_5$ was inserted at the L/S type interfaces, indicating the strongly asymmetric nature between these two types of interfaces. Structural and spectroscopic studies by scanning transmission electron microscopy revealed that the L/S type interfaces had a larger interdiffusion length scale and lowered Ti valence states, which can contribute to the metallic conductivity. This observation was further supported by soft x-ray resonant scattering, where the model with transition layers only at the L/S interfaces best fit the results. It is remarkable that the existence of interfacial layers were confirmed in both real space (STEM) and reciprocal space (SXRS), and the emergence of the novel properties were indeed produced by the change of the interface stoichiometry.

To further study the role of interface composition, we have investigated the spectro-

scopic and structural properties of $LaMnO_3/SrTiO_3$ interfaces with varying thickness of inserted $SrMnO_3$. By means of scanning transmission electron microscopy, systematic change of the Mn valence was observed by varying the thickness of $SrMnO_3$, suggesting the possible control of electronic states by changing interface compositions.

In addition, the non-equilibrium nature of the PLD growth process can realize off-stoichiometric material transfer or growth of meta-stable materials. Precipitates formed during kinetic growth of $LaMnO_3$ were revealed to be Mn_3O_4 nano-crystals in stoichiometric $LaMnO_3$, indicating that these precipitates are formed to accommodate net cation off-stoichiometry during PLD growth. When RVO$_4$:Eu^{3+} (R=La, Y) films were grown by PLD, the enhanced solubility limit of Eu^{3+} was observed in the LaVO$_4$:Eu^{3+} films, and its photoluminescence brightness excited by $\lambda = 351$ nm light exceeded that of the YVO$_4$:Eu^{3+} films, which is used as commercial phosphors. Understanding these phenomena can further provide useful information on the atomic scale control of oxide heterostructures, as well as potential synthesis of materials with novel crystal structures.

There has been a number of obstacles to reveal and control the nature of complex heterostructures. Through this research, dramatic changes of the physical properties of the atomic-scale oxide heterostructures were observed by tuning the important parameters. These results can be leveraged as general prescriptions to approach unconventional atomic and electronic states in artificial structures, which are fertile soil for the possible germination of unpredictable physical phenomena. Some say "the devil is in the details," meaning solutions collapse when they are examined closely. However, at the same time, it is true that there appear opportunities for discoveries and creativity by digging to the bottom of the issue. Indeed, God is in the details, and we hope these atomic scale perspectives will broaden the horizon of physics.

Appendix A

Effect of interdiffusion

In real systems, interdiffusion of atoms across the interface is inevitable, and we should note the effect of interdiffusion on the electrostatic stability of the system. Interdiffusion is a process where atoms are locally exchanged, and does not change the charge neutrality conditions around the interface, except for the finite dipoles induced by the modulation of charges. Since the instability of polar interfaces can be derived from the lack of charge neutrality around them, as discussed in Chapter 3, simple interdiffusion in a finite region cannot compensate it. In this Appendix, detailed discussions on the role of the interdiffusion are described by considering a simple model of interdiffusion.

Figure. A.1(a) shows the charge structure ρ and the calculated electrostatic potential $-V$ of an abrupt polar interface. By taking dipole-free unit cells, the interface unit cell has a half positive charge per 2D unit cell, and the system does not keep charge neutrality as it is, and is unstable. Figure. A.1(b) shows an example of interdiffusion, where half of the negatively charged layer and half of the charge neutral layer close to the interface are swapped, compared to the model in Fig. A.1(a). In this case, the extra positive charge appears at a different position, but the amount of the charge is conserved, and the similar instability in $-V$ arises as in the abrupt case.

In order to show that interdiffusion does not violate the stability or instability of a polar interface, it is useful to consider charge neutrality in a cluster consisted of a sufficiently large number of dipole free unit cells covering the interface region. By taking dipole free unit cells, the electrostatic structure in the bulk can be neglected to determine the the stability of the system, as shown in Chapter 3. This idea can be available when considering not only the local charge neutrality of the interface unit cell of an abrupt polar interface, but also that of a cluster with a finite size. As an example, let us take an cluster shown in Figs. A.1(a) and (b). Since the modulation of the charge to achieve the interdiffused model occurs inside the cluster, the total amount of the charge in the cluster is naturally conserved, and thus the similar instability appears in the both cases.

For comparison of these models, let us focus on the difference of the charge distributions $\rho(\mathrm{b}) - \rho(\mathrm{a})$ in the two models, as shown in Fig. A.1(c), where a dipole with a finite size appears. Since $-V$ is calculated by spatially integrating the charge distribution twice, and integration is a linear operation, the difference of $-V$ in Figs. A.1(a) and (b)

Figure A.1: Schematic charge structure ρ and electrostatic potential $-V$ of (a) an abrupt interface and (b) an interface with interdiffusion. Five dipole free unit cells are taken as an example of clusters including the interface regions. The dashed line in (b) is the duplication of $-V$ in (a). (c) Difference $\rho(\mathrm{b}) - \rho(\mathrm{a})$ of the charge distributions in (a) and (b), and created potential shift $-V_{\mathrm{dip}}$ by the dipole indicated by the shaded arrow.

should be equal to the potential shift created by the dipole in Fig. A.1(c). Indeed, $-V$ in Fig. A.1(b) has a shift from that in Fig. A.1(a), which is the same amount as the dipole shift in Fig. A.1(c).

Finally, we should note the difference between the simple interdiffusion and the change of the interface composition. In the interdiffusion process, only exchanging atoms in the finite interface region is allowed, and therefore total number of atoms of each element in the region is conserved. On the other hand, interface composition can be changed, for example by inserting other materials, segregation of atoms, or creating vacancies. In this case, the number of ionic charges in the interface region changes associating with the change of numbers of the atoms, and thus the total charge number to stabilize the system can be different from the original system. As an example, the reconstruction model in Fig. 3.5(b) to compensate the instability of a polar Ge/GaAs interface cannot be achieved by a simple roughening at the interface: the numbers of Ge, Ga, and As atoms are different compared to those in the abrupt model [Fig. 3.5(a)].

In summary, the effect of the interdiffusion appears as the extra interface dipole moment at the interface from a viewpoint of electrostatics. Interdiffusion does not change the total number of charges at the vicinity of the interface, and thus cannot screen the charge imbalance at any polar interfaces. In order to compensate the instability of a polar interface, therefore, the introduction of a compositional change or other compensation charge is required. This discussion further emphasizes the importance of the interface composition, as we discussed in the main text of this Thesis. Based on the local composition analysis in in Chapters 5 and 6, all interfaces were, at least to some degree, diffused. Still, however, the total amount of charge to stabilize the system can be treated in a same manner as that for the interface unit cell of an abrupt interface, and can be judged quantitatively by counting the number of atoms around the interface, as described in Chapter 6.

Appendix B

Quadrupolar discontinuity

In Chapter 3, we considered the stability of polar discontinuities, and showed that the number of charge of the interface unit cell to stabilize the system can be determined by taking dipole free unit cells and considering local charge neutrality in each unit cell. Of course, finite charge modulation is allowed once the neutrality is maintained, since it does not violate the total charge neutrality. This dipole energy arising from the modulation of charges determines the real charge distribution in the system.

Here, we should note that there is an intrinsic dipole shift at the interface arising from the charge stacking sequence, which should be distinguished from the charge modulation. For example, consider a $LaAlO_3/SrTiO_3$ (001) interface with $Ti^{3.5+}$ at the interface to solve the instability of the polar interface, as shown in Fig. B.1(a). Although there is no potential divergence, a finite shift Δ remains between the two materials when considering the averaged electrostatic potential in both sides.

The origin of this potential shift can be understood based on the discontinuity of the quadrupole moment of the unit cells. In one dimension, quadrupole moment density Q is defined as $\frac{\mathrm{d}}{\mathrm{d}x}Q = P$, where P is the dipole moment density. It has the same form as that of the Gauss Maxwell's law connecting the dipole moment and the charge – i. e. the source of the quadrupole moment is the dipole moment. Therefore, following the same argument in Section 3.3, a finite interface dipole moment appears at a quadrupolar discontinuity, where the quadrupole moment is different on the two sides.

Moreover, this quadrupole moment is proportional to the potential shift at that point in the absence of free charge, since $D = 0$ and thus $\varepsilon_0 E = -P$. Therefore if the unit cell has a finite quadrupole moment, that means the averaged potential in the unit cell is shifted by the corresponding value. Note the quadrupole moment does not induce potential shift outside the unit cell, while the dipole moment does change.

For example, $[(\frac{1}{2}LaO)^{+1/2}\text{-}AlO_2^{-1}\text{-}(\frac{1}{2}LaO)^{+1/2}]$, a dipole free unit cell of $LaAlO_3$ (001) [Fig. B.1(b)], has a finite quadrupole moment, while the charge neutral stacking of $SrTiO_3$ creates no quadrupole moment in the unit cells[1]. This difference of quadrupole moment between the two sides adds a finite potential shift to the averaged potential in the unit cell.

[1] Absence of covalency is assumed.

Figure B.1: (a) Schematic structure, charge density ρ, and electrostatic potential V of a $LaAlO_3/SrTiO_3$ interface with a $Ti^{3.5+}O_2$ interface layer, showing a finite shift Δ. Taking (b) $[(\frac{1}{2}LaO)^{+1/2}\text{-}AlO_2^{-1}\text{-}(\frac{1}{2}LaO)^{+1/2}]$ and (c) $[(\frac{1}{2}AlO_2)^{-1/2}\text{-}LaO^{+1}\text{-}(\frac{1}{2}AlO_2)^{-1/2}]$ as a unit cell. The blue and pink shaded areas in (b) and (c) show the unit cells with opposite signs of quadrupole moment, respectively, and the green shaded area in (b) shows the unit cell with a finite dipole moment. (d) An example of di-/quadru-pole free unit cells.

Figures B.1(b) and (c) show two ways of taking dipole free unit cells in cubic perovskites, where the sign of the quadrupole moment is opposite. The choice of unit cells cannot change the electrostatic potential, and indeed this difference of the quadrupole moment of the unit cells is compensated by the dipole moment of the interface unit cell in Fig. B.1(b).

The ambiguity of the quadrupole moment in the unit cells is reminiscent of the uncertainty of the dipole moment, as discussed in Section 3.2.1, and we can take the same prescription as we did – taking quadrupole free unit cells. It is more complicated since these quadrupole free unit cells should not have a dipole moment at the same time, in order to avoid the instability of the polar discontinuity, and Fig. B.1(d) shows one way to take such unit cells. Note it is always possible to take unit cells which do not have either dipole or quadrupole moment in one direction in any bulk crystal[2]. Once we take this di-/quadru-pole free unit cell, the size of the interface dipoles can be determined by considering the dipole moment in the interface unit cell(s), since there is no shift in the averaged potential in the bulk unit cells due to the absence of quadrupole moment.

[2]This can be easily proved from the periodicity of the charge structure and the macroscopic charge neutrality of the lattice by using the intermediate-value theorem.

Appendix C

Practical methods to obtain AB-difference

In Chapter 6, we defined AB-difference by counting the number of cations in a selected region. Practically, the AB-difference can be obtained by fitting the composition functions of A and B for the position z[1] with two constants D_1^i and D_2^i ($i = A$ or B):

$$f^i(z) = \frac{1}{2} + \frac{1}{2}\tanh\left(\frac{z - D_1^i}{D_2^i}\right), \tag{C.1}$$

and calculating the difference in the positions $z = D_1^A$ and D_1^B, where $f^i(z) = 1/2$. Since $f(z)$ satisfies the following relation:

$$\int_a^b f^i(z)\mathrm{d}z \approx \left(b - D_1^i\right), \tag{C.2}$$

by taking sufficiently large integral interval, d_{A-B} is obtained as

$$d_{A-B} \equiv \lim_{a\to-\infty}\lim_{b\to+\infty}\frac{1}{a_{\mathrm{per}}}\left[\int_a^b \left(f^A(z) - f^B(z)\right)\mathrm{d}z\right] = \frac{-D_1^A + D_1^B}{a_{\mathrm{per}}}. \tag{C.3}$$

It is important that d_{A-B} is independent of the values D_2^i, which reflect the diffusion length scale of the elements. This result is natural because d_{A-B} represents the difference in the numbers of two kinds of cations, and interdiffusion does not change its value. As a corollary, interdiffusion does not change the total amount of excess charge in the valence around the interface, since the amount is determined by d_{A-B}.

Note the unit of the composition functions is "number of atoms per unit cell" since they are normalized by the bulk compositions. Therefore the lattice constant a_{per} is required to connect the integration of the composition functions and the number of atoms.

[1] Here we set the z-direction by taking ABO_3 to the positive end and $A'B'O_3$ to the negative end. The sign of D_2^i is positive for A and B, while negative for A' and B'.