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Investigation of atomic and electronic structures of LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$/SrTiO$_3$ interfaces using Cs-corrected STEM and EELS
Abstract

Investigation of atomic and electronic structures of LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$/SrTiO$_3$ interfaces using Cs-corrected STEM and EELS

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Two dimensional electron gas (2DEG) has got an intense interest since it was discovered in the LaAlO$_3$/SrTiO$_3$ interface in 2004. Many researches were carried out to reveal the origin of the 2DEG but there is not any established theory. On the other hand, in the year 2013, there is a report about electrical properties of LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$/SrTiO$_3$. In this report, as the composition of Sr increases, the interfacial conductivity increases by 6 order of magnitude. Difference in the degree of TiO$_6$ octahedral tilt was suggested as the origin of the difference in electrical properties of the interfaces. The research is motivated by this report.

In this work, atomic and electronic structures of the LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ and LaAlO$_3$/SrTiO$_3$ were investigated using Cs corrected TEM and EELS. Each samples showed same tendency in sheet
resistance as that of the previous report. High resolution HAADF and ABF STEM images showed that CaTiO$_3$ has considerable degree of octahedral rotation whereas we could hardly observe octahedral rotation at the SrTiO$_3$ substrate in LaAlO$_3$/SrTiO$_3$ system. However, considerable amount of Ti$^{3+}$ was detected in both samples. From this, we concluded that regardless of the portion of Ti$^{3+}$ at the interface, TiO$_6$ octahedral tilt angle plays a crucial role determining interfacial conductivity. To generalize this statement, we will try the same procedure in the LaAlO$_3$/Sr$_{0.5}$Ca$_{0.5}$TiO$_3$/SrTiO$_3$ system.

**Keywords** : Two Dimensional Electron Gas, Cs corrected transmission electron microscope, octahedral tilt, perovskite oxide

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Chapter 1. Introduction

1.1. Transitional metal oxide in perovskite structure

Researches related to ABO$_3$ perovskite compounds have been of a great interest among scientists and engineers. This is mainly because perovskite oxides have a wide range of physical properties, related to many possible applications such as memory devices.

Perovskite oxides was first discovered in 1839 by Gustav Rose, who gave the name of Russian mineralogist L. Perovski to the CaTiO$_3$ compound. Nowadays, perovskite structure has been observed in non-oxide metal-organic compounds such as (CH$_3$NH$_3$)$_2$PbI$_3$. In this sense, perovskite structure refers to the ABX$_3$ compounds where X is not necessarily oxygen.

In the case of cubic ABO$_3$ perovskite structure, the A cation is located at the corner of the cube and B cation is located at the body center of the cube. Oxygen anions are located at the face center of the cube, hence oxygen anions form an octahedron as shown in Fig 1.1. This ideal cubic structure can be viewed of alternating AO and BO$_2$ planes when ABO$_3$ is viewed on the [100] zone axis.

However, cubic structure of perovskite is an ideal case and generally, perovskite oxides have tetragonal, orthorhombic, monoclinic or rhombohedral structures. The type of lattice structure is governed by the so-called the Goldschmidt tolerance factor,

\[
t = \frac{r_A + r_B}{\sqrt{2(r_B + r_O)}}
\]

(1.1.1)

where $r_A$, $r_B$ and $r_O$ are the ionic radii of A, B and O respectively.[1] If t is equal or
almost 1, $\text{ABO}_3$ becomes cubic like $\text{SrTiO}_3$ and $\text{BaZrO}_3$. On the other hand, if $t$ is less than 1, or the radius A-site cations become smaller, A cation cannot fill the available space in the lattice. $\text{BO}_6$ octahedron then tends to rotate to occupy as much space as possible in the lattice. This lowers crystal symmetry of the perovskite oxide.

Using the tolerance factor, effect of strain on octahedral rotation can be explained although there is not term related to the lattice constant in ‘$t$’. Consider the perovskite film which is in-plane strained on the perovskite substrate. If the film is compressively strained, even if the size of cations are small, there is more available space where A site cation can be filled. Thus, octahedral tilt angle is gets smaller and the rotation is suppressed. Conversely, if the perovskite compound is tensile strained, in-plane lattice constant becomes larger. To occupy space as much as possible, $\text{BO}_6$ octahedron is much more rotated and oxygen anions tend to be closer to A site cations.
Fig 1.1 Schematic illustration of (a) cubic and (b) BO$_6$ octahedral tilted ABO$_3$ perovskite structure. Bonds between B site cation and O anion are described as polyhedrons.
1.2. Complex oxide interfaces and Two Dimensional Electron Gas (2DEG)

Transition metal oxide interfaces have gained intense interest, due to their wide range of structural, electronic and magnetic properties such as ferroelectricity, super-conductivity, magnetism, multiferroism and metal-insulator transitions. Furthermore the formation of an interface between two different oxide compounds shows new type of properties that do not exist in bulk.

A typical example of new physics emerging at oxide interfaces is found in the LaAlO$_3$/SrTiO$_3$ structure. [2] This system, comprised of the band insulators with large band gap (LaAlO$_3$: 5.6eV, SrTiO$_3$: 3.2eV), metallic interface is formed and completely new physics is emerged. This phenomena is called two dimensional electron gas (2DEG). The definition of 2DEG is a gas of electrons free in two dimensional sheets, but the movement is confined in the third dimension. 2DEG is first discovered in devices consist of 3-5 compound semiconductors. However, 2DEG in LaAlO$_3$/SrTiO$_3$ structure showed completely different behavior from that in semiconductor heterostructures.

Since the discovery of 2DEG in oxide interfaces, the origin of 2DEG is disputable. Several hypothesis are suggested, however, all of them has been unsound. In the next section, several hypotheses related to the origin of 2DEG were introduced.
Fig 1.2 Schematic description of a 2DEG at the LaAlO$_3$/SrTiO$_3$ interface. 2DEG in oxide interface was firstly discovered by Othomo and Hwang [2]
1.3. Origin of 2DEG: hypotheses

1.3.1. Polarization catastrophe

The polarization catastrophe, or electronic reconstruction is initially suggested theory to explain the origin of metallic LaAlO$_3$/SrTiO$_3$ interface.

If we look ABO$_3$ perovskite along [001] direction, it can be divided into two parts, AO and BO$_2$ planes. The cation valence of A and B can be $A^{5+}B^{1+}$, $A^{4+}B^{2+}$, $A^{3+}B^{3+}$, $A^{2+}B^{4+}$, and $A^{1+}B^{5+}$ to maintain charge neutrality. SrTiO$_3$ which has an $A^{2+}B^{4+}O_3$ has nonpolar planes whereas LaAlO$_3$ has polar planes. When film with polar planes is grown on the nonpolar planes of substrate, the electrostatic potential diverges unless any interfacial reconstruction does not occur. This phenomenon is called polarization catastrophe (See Fig 1.3). Ohtomo and Hwang suggested electronic reconstruction which shows how interface reconstruction occurs [2]. As shown in the left side of Fig 1.3, when SrTiO$_3$ is Ti-terminated, about 0.5 electrons per unit cell are injected at the interface. When electrons are injected at the interface, only Ti ions can receive electron because Ti has multi valence ions. In other words, about a half of Ti$^{4+}$ ions at the interfacial TiO$_2$ planes become Ti$^{3+}$. On the other hand, charge injection at the interface indicates that the concentration of electrons increases. Thus, when LaAlO$_3$ is grown on SrTiO$_3$ substrate, several amount of charge carriers are concentrated at the interface, forming 2DEG.

This electron reconstruction scenario had been experimentally proved using electron energy loss spectroscopy as shown in Fig 1.4. Nakagawa et al. acquired Ti L edge EELS(Electron Energy Loss Spectroscopy) spectra, proving that several
amount of Ti$^{3+}$ exist at the LaAlO$_3$/SrTiO$_3$ interface.[3] Existence of Ti$^{3+}$ indicates high concentration of charge carriers, which is the main origin of 2DEG.

However, this scenario has some controversies. First, this theory cannot explain the metallic interface between nonpolar-nonpolar oxides. For example, LaAlO$_3$ film grown on SrTiO$_3$ (110) substrate showed metallic interface. [4] This contradicts the charge injection hypothesis. In addition, interface with conductivity was observed between amorphous LaAlO$_3$ film and SrTiO$_3$. [5]
Fig 1.3 Polarization catastrophe model for atomically sharp (001) interfaces between LaAlO$_3$ and SrTiO$_3$. (a) The unreconstructed interface has neutral (001) planes in SrTiO$_3$, but the (001) planes in LaAlO$_3$ have alternating net charges ($\rho$). If the interface plane is AlO$_2$/LaO/TiO$_2$, this produces a non-negative electric field ($E$), leading in turn to an electric potential ($V$) that diverges with thickness. (b) If the interface is placed at the AlO$_2$/SrO/TiO$_2$ sequence instead, the potential negatively diverges. (c) The divergence of electrical potential at the AlO$_2$/LaO/TiO$_2$ interface can be avoided if half an electron is added to the last Ti layer. (d) Polarization catastrophe AlO$_2$/SrO/TiO$_2$ interface can also be avoided by removing half an electron from the SrO plane in the form of oxygen vacancies.
Fig 1.4 Schematic description of the electronic reconstruction at the (a) AlO$_2$/LaO/TiO$_2$ and (b) AlO$_2$/SrO/TiO$_2$ interfaces. (c) EELS intensity profile showing the fractions of Ti and La from the Ti L and La M edges at the AlO$_2$/LaO/TiO$_2$ interface. Ti$^{3+}$ fraction was determined from a least-squares fit to the Ti-L edge from Ti$^{3+}$ and Ti$^{4+}$ reference spectra. There is excess Ti$^{3+}$ on the substrate side of the interface. (d) Corresponding Ti and La M edge profiles for the AlO$_2$/SrO/TiO$_2$ interface, showing almost no excess Ti$^{3+}$
1.3.2. Inter diffusion across the interface

The other suggested hypothesis as the origin of 2DEG is that inter diffusion between LaAlO$_3$ and SrTiO$_3$. The LaAlO$_3$/SrTiO$_3$ interface is far from being atomically abrupt and inter diffusion must be occur as shown by Nakagawa et al. [3]. In addition, Quao et al. argued that interfaces with inter diffusion are more thermodynamically stable using first principles calculations.[5]

On the other hand, it is commonly known that several amount of charge carriers are provided to SrTiO$_3$ when La is doped to SrTiO$_3$. Even a small amount of La can increase the amount of charge carriers in SrTiO$_3$. Such a mixing can give the same effect as La doping leading to form of 2DEG in LaAlO$_3$/SrTiO$_3$ system. Some other physicists explain that when mixing occurs, secondary phase of La$_{1-x}$Sr$_x$TiO$_3$ is formed at the LaAlO$_3$/SrTiO$_3$ interface, which is close to metallic.

However, inter diffusion scenario cannot explain insulating interface of SrTiO$_3$ film on the LaAlO$_3$ substrate. This indicates that only doping effect on SrTiO3 cannot be the origin of the 2DEG. In addition, Warusawithana et al. have argued that La : Al ratio is the key factor of the formation of the 2DEG. Whether there is enough amount of inter diffusion between LaAlO$_3$ and SrTiO$_3$, 2DEG is formed only if there is excess Al in the LaAlO$_3$ films. [6] From this point of view, intermixing itself cannot explain 2DEG in LaAlO$_3$/SrTiO$_3$ system.
1.4.3. Role of oxygen vacancy

It is widely known that metal insulator transition occurs in SrTiO$_3$ even with a small amount of oxygen vacancy. Even if SrTiO$_3$ substrate itself is a band insulator with the gap of 3.2eV before growth, forming of oxygen vacancies during growth of LaAlO$_3$ film can lead to 2DEG in the LaAlO$_3$/SrTiO$_3$ system. [7]

Already in the previous work, it is confirmed that the growth conditions such as growth temperature, oxygen partial pressure greatly affect the electrical properties of the LaAlO$_3$/SrTiO$_3$ interfaces. In the case of low oxygen partial pressure and no annealing process before transport measurements, Ohtomo et al. found a large electron density, a high Hall mobility ($10^4$ cm$^2$V$^{-1}$s$^{-1}$) and a sheet resistance around $10^{-2}$ Ω/S. [2] These measurements correspond to the low oxygen partial pressure without annealing process since they are obtained by several other studies.

For high oxygen partial pressure, the density reduced significantly to $10^{13}-10^{14}$ cm$^{-2}$ in better agreement with the 0.5 e/u.c.$^2$ expected by the polarization catastrophe model. In addition, post-annealing process drops the electrical conductivity of the LaAlO$_3$/SrTiO$_3$ interface. [8]

In short, oxygen concentration, oxygen partial pressure during PLD growth, and the post-annealing process play an important role on the 2DEG and interfacial conductivity. However, because role of oxygen vacancy is based on the polarization catastrophe model, it is still a highly debated question.
1.4.4. Structural distortion

Some material scientists have suggested that the change of atomic structure at the interface leads to the metallic interface between insulating oxides, LaAlO$_3$ and SrTiO$_3$. On the other hand, Jang et al. reported that by inserting one atomic layer of rare-earth oxide into strontium titanium oxide, electronic properties of the interfaces can be insulator or conductor, depending on rare earth [(R is La, Pr, Nd, Sm, Y)]. [10]

Jang et al. found the origin of the difference in conductivity using STEM(Scanning Transmission Electron Microscopy)/EELS and first principles calculations. Using the fact that the transport properties of SrTiO$_3$/RO/SrTiO$_3$ interfaces are sensitive to charge carriers, ELNES (Ti L edge and O K edge) was investigated at the interfaces. As shown in Fig 1.3 (b), Ti L edge indicates that the Ti$^{3+}$/Ti$^{4+}$ ratio is almost the same at the interfaces. In addition, according to the O K edge spectra, there is a negligible amount of oxygen vacancy independent the type of the rare-earth. From this, that there are almost same amount of charge carriers are injected in all the samples can be inferred. Only charge transfer scenario cannot explain the origin of rare earth – dependent 2DEG in this system.

To understand the combined effects of charge injection, propagation of octahedral tilt, biaxial strain, and rare-earth electronic structure, Jang had carried out first principles calculations, including an on-site Coulomb interaction, or Hubbard U term. For the LaO-based heterostructure, the Fermi energy lies in the region of nonzero density of states whereas for the YO based heterostructure the Fermi energy lies between the split-off lower Hubbard band and the higher energy
density of states. This means that the LaO-based interface is conducting, whereas the YO-based interface is insulating. This is consistent with Jang’s experimental results. Octahedral rotations are clearly visible in the predicted structures shown in Fig. 1.6, consistent with his synchrotron measurements.

However, those arguments are based on assumptions such as atomically abrupt interfaces. As mentioned in the previous section, atomically abrupt interface in oxide heterostructures cannot exist. Furthermore, as shown in Fig 1.3 (a), interface of SrTiO$_3$/LaO/SrTiO$_3$ does not seem to atomically abrupt. From this point of view, only strain effect and octahedral tilt cannot be the key factor of the difference of conductivities at the interfaces.
Fig 1.5. (a) Aberration – corrected High Angle Annular Dark Field (HAADF) image of a 10-uc SrTiO$_3$/1-ML LaO film grown on SrTiO$_3$. The rectangular box represents the region of EELS line scans. (b) EELS spectra of Ti-L$_{2,3}$, L$_{3}$ and O-K edges obtained from line scans across the interface shown in (a). The spacing along the line scan between consecutive EELS spectra is 2.8 Å. The spectra at the LaO layer are highlighted by thicker lines. For the spectra for Ti L$_2$ and L$_3$ edges, peak broadening and less pronounced peak splitting at the interface are clearly observed. (c) HAADF images of 10-uc SrTiO$_3$/1-ML LaO/SrTiO$_3$ and 10-uc SrTiO$_3$/1-ML SmO/SrTiO$_3$ heterostructures. Both samples show no obvious defects or dislocations, indicating coherent interfaces. (d) Selected area Ti-L$_{2,3}$ EELS spectra obtained at the interfaces for 10-uc SrTiO$_3$/1-ML LaO/SrTiO$_3$ and 10-uc SrTiO$_3$/1-ML SmO/SrTiO$_3$ heterostructures. The arrow is a guide for comparison.
Fig 1.6 Density of states and structural relaxation of 3.5-uc SrTiO$_3$/1-ML LaO ((a) and (c)) periodic superlattice and 3.5-uc SrTiO$_3$/1-ML YO periodic superlattice ((b) and (d)) obtained from DFT calculations. Positive density of states is for spin up and negative is for spin down. The dashed line indicates the position of the Fermi level. The results indicate conducting behavior for the 3.5-uc SrTiO$_3$/1-ML LaO periodic superlattice and insulating behavior for the 3.5-uc SrTiO$_3$/1-ML YO periodic superlattice.
1.4. Motivation

There is not any widely-accepted theory related to origin of 2DEG although this has been a lot of interest for more than a decade. This is because LaAlO$_3$/SrTiO$_3$ structure has been grown on various conditions, leading to form a wide range of atomic and electronic structure at the LaAlO$_3$/SrTiO$_3$ interfaces. On the other hand, in 2013, Moon et al. reported the relationship between 2DEG and interfacial composition. [11] Moon et al. insisted that interfacial conductivity can be varied from insulator to metal depend on Sr content of Sr$_x$Ca$_{1-x}$TiO$_3$ films. As seen in Fig 1.6, as the Sr composition in Sr$_x$Ca$_{1-x}$TiO$_3$ increased, the conductivity of the system increased by 6 orders of magnitude. This experimental data has nothing to do with electrical properties of SrTiO$_3$, CaTiO$_3$ and Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ as shown in Table 1.1. Moon et al suggested that the origin of this big difference in transport properties is mainly the difference of the TiO$_6$ octahedral tilt angle of SrTiO$_3$, CaTiO$_3$ and Sr$_{0.5}$Ca$_{0.5}$TiO$_3$. As shown in Fig 1.5, phase contrast image was also acquired in Moon’s work. In Fig 1.5 (d), (1-21) peak with a small intensity indicates that the CaTiO$_3$ film has an orthorhombic crystal structure and possesses octahedral tilting. The same result was shown in the case of the Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ film.

However, only measuring octahedral tilt angle of Sr$_x$Ca$_{1-x}$TiO$_3$ films cannot explain the relationship between atomic structure and 2DEG on the interfaces. Even if there is directional relationship between octahedral rotation angle and electrical properties of perovskite oxides as mentioned in the previous study [11], only differences in octahedral tilt angle cannot explain the differences in electronic structures at the interfaces. This is because first, electrical properties at the ‘interface’ does not have direct relationship with atomic structure of ‘thin films’.
Even if non-negligible amount of octahedral rotation is observed at the Sr\textsubscript{x}Ca\textsubscript{1-x}TiO\textsubscript{3} films, atomic structure of interfaces can be different from that of the perovskite films in bulk. Second, as mentioned in the previous section, atomically abrupt interfaces cannot exist. Such an intermixing at the interfaces can modify electronic states of transition metal ions, which may not mainly depend on octahedral rotations. Thus, our approach was different from what Moon et al. had suggested. [11]

Above all, there is not any report about experimental study about the electronic structures of interfaces, which directly affect the electrical properties at the LaAlO\textsubscript{3}/CaTiO\textsubscript{3} or LaAlO\textsubscript{3}/SrTiO\textsubscript{3} interfaces. Not only observing atomic structures of the LaAlO\textsubscript{3}/Sr\textsubscript{x}Ca\textsubscript{1-x}TiO\textsubscript{3} interfaces but also interfacial electronic structure driven by chemical or bonding states at the interfaces should be included in our research. The change of the electronic structures at the interfaces, whether they are driven by chemical reaction or strain effect can explain the origin of the difference of interfacial electrical conductivity. This is how our research is motivated.
Fig 1.7 (a) HRTEM image of a LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ structure. The inset is the FFT patterns from the CaTiO$_3$ layer. HRTEM images of (b) LaAlO$_3$/CaTiO$_3$ and (c) CaTiO$_3$/SrTiO$_3$ interfaces showing the sharp interface indicated by red arrows. (d) SAED pattern of the LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ structure. (e) Phase contrast TEM images and (f) SAED pattern of a LaAlO$_3$/Sr$_{0.5}$Ca$_{0.5}$TiO$_3$/SrTiO$_3$ structure. (12-1) weak spot was detected in the pattern.
Fig 1.8 (a) Typical I-V curves of LaAlO$_3$ (5 nm)/Sr$_x$Ca$_{1-x}$TiO$_3$ (10 nm)/SrTiO$_3$ structures. For comparison, I-V curves of LaAlO$_3$/SrTiO$_3$ and bulk SrTiO$_3$ are presented. (b) Current at 5V and sheet conductance of the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$/SrTiO$_3$ structures as a function of atomic composition of Sr. As the composition of Sr increased, sheet conductance increased by 6 orders of magnitude.
Fig 1.9 Schematic illustration of TiO$_6$ octahedron in cubic (a) SrTiO$_3$ and orthorhombic (b) CaTiO$_3$. Octahedral rotations in CaTiO$_3$ are highlighted by the Ti-O-Ti angle much lower than 180 degrees. This is because ionic radius of Ca is smaller than Sr, leading to lower the tolerance factor, ‘t’.
<table>
<thead>
<tr>
<th>Compound</th>
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</tr>
</thead>
<tbody>
<tr>
<td>CaTiO$_3$</td>
<td>$6.04 \times 10^{-10}$</td>
</tr>
<tr>
<td>Sr$<em>{0.5}$Ca$</em>{0.5}$TiO$_3$</td>
<td>$1.68 \times 10^{-6}$</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>$10^6$</td>
</tr>
</tbody>
</table>

**Table 1.1** List of conductivity of CaTiO$_3$, Sr$_{0.5}$Ca$_{0.5}$TiO$_3$ and SrTiO$_3$ at the room temperature
1.5. **Goal of this work**

In this research, the relationship between electronic and atomic structures were inspected in the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$/SrTiO$_3$ heterostructures. (x = 0, 1.0). This research contains not only observation of atomic and electronic structures of LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ interfaces depending on Sr:Ca atomic ratio, but also investigation of the relationships between them. Our main question on this research is ‘How inter diffusion between LaAlO$_3$ and Sr$_x$Ca$_{1-x}$TiO$_3$ affect interfacial conductivity?’ and ‘Can octahedral tilt in Sr$_x$Ca$_{1-x}$TiO$_3$ affect electrical property of interfaces?’ Our research is divided into two parts.

First, this work is proposed to compare electronic structure of the interfaces between LaAlO$_3$ and Sr$_x$Ca$_{1-x}$TiO$_3$ films. Using core-loss EELS (ELNES), the differences in Ti L edge and O K edge were observed. Interpretation of the EELS spectra can determine whether the new chemical states are formed at the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ interfaces.

The second part of this thesis is focused on direct observation of the atomic structures of the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ interfaces. Using Cs corrected STEM, we directly observed the atomic structure of the interfaces. Of course, roughness of the oxide interfaces are strongly dependent on the growth conditions. However, the existence of interfacial bonding state is independent of growth condition considering the noticeable difference in electronic properties of interlayer Sr$_x$Ca$_{1-x}$TiO$_3$ films.

The research is not focused on interface itself but the relationship between
atomic structures and electronic structures at the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$ interfaces.
Chapter 2. Experimental Method

2.1 TEM sample preparation

TEM analysis requires an enough thin specimen that electron beam can transmit through it. When the specimen is not thin enough, multiple scattering events can occur, leading to artifacts in the diffraction and inelastic scattering information. Electron transparent specimen can be accomplished by mechanical polishing and Ar ion milling. This procedure is depicted for a cross sectional TEM sample of an epitaxial film in Fig. 3.1. A SrTiO$_3$ substrate with the same film is glued to the surface of the film using M Bond 610 and placed on a hot plate at 195°C for at least 3 hours. The sandwich is then sectioned into 1.5mm slices by a diamond cutting saw. The cross section surface is then mounted with crystal wax to a multiprep polisher pyrex holder and polished using a series of progressively finer diamond lapping film under water flow (9, 6, 3, 1μm), usually ending with 0.5μm with the lubricant. The sample is then flipped, remounted, and polished until the overall specimen thickness becomes less than 10 μm. The specimen is then soaked in acetone until the sample falls free. A molybdenum slot grid is then glued to the 2nd polished surface and allowed to dry for at least 3-4 hours under the IR lamp. The specimen with Mo slot grid is Argon ion milled in a Gatan precision ion polishing system (PIPS). The sample is ion milled from both the top and bottom surfaces with the ion beam oriented normal to the interface. The angle and energy of the ion guns is progressively reduced from an initial setting of ±6° and 3.5 keV ultimately to a ±5° and 500 eV surface cleaning step. To minimize the heating effect and surface damage on the specimen, liquid nitrogen was poured into the
PIPS system. The paired SrTiO$_3$ is milled preferentially and the process is stopped when the SrTiO$_3$ just barely covers the film. The finished sample usually appears as in Fig. 2.1
Fig 2.1 Schematic diagram of the TEM sample preparation using polishing and precision ion milling (a) Thin film specimen is glued to another. (b) After curing, the whole specimen was sectioned. (c) Sectioned specimen is polished until its thickness gets under 10μm. (d) After the thinned specimen is separated from the pyrex holder, it is glued to molybdenum slot grid. (f) Top view of the specimen with the Mo grid. Finally, the specimen was thinned using PIPS system.
2.2 Film characterization

2.2.1. Sheet resistance measurement

As performed in the previous work, sheet resistance of the heterostructures was measured using indium ohmic contacts on the diagonal corners of the square samples.

2.2.2. Atomic Force Microscopy (AFM)

After conductivity of the heterostructures was measured, AFM images were acquired. From AFM image, we could confirm the surface profile of the thin films.

2.3 TEM characterization

To investigate the relationship between atomic, electronic structure and electrical properties of the interfaces, several modes of TEM will be used. Especially, advanced analytical technique such as Cs corrected HAADF STEM and EELS will be taken advantage of.

2.3.1 HRTEM imaging

Using phase contrast high resolution imaging, crystal structure of Sr$_x$Ca$_{1-x}$TiO$_3$ films were investigated. Then, uniformity of the Sr$_x$Ca$_{1-x}$TiO$_3$ on the SrTiO$_3$ substrate can be confirmed. HRTEM images were obtained with a 200-kV field-emission TEM instrument (JEOL JEM-2100F).
2.3.2 Cs – corrected HAADF / ABF STEM imaging

To investigate atomic structure of the interfaces, Cs-corrected high resolution STEM images were obtained with Cs-probe corrected TEM instrument (JEOL JEM ARM 200F). STEM imaging with spherical aberration (Cs) corrector provides more clear images with spatial resolution of 80pm. Thus Cs corrected HR-STEM imaging enables not only identifying elements but also finding atomic positions in high accuracy.

Images are obtained in HAADF and ABF STEM modes simultaneously. Especially, in this research, aberration – corrected high resolution STEM images were obtained.

In HAADF STEM mode, scattered electrons in high angle (Fig 2.1) is collected to the detector, leading to formation of the images. Because detected electrons in high angle are Rutherford-scattered, intensity of the HAADF STEM image is approximately proportional to the square of the atomic number. In this sense, HAADF STEM imaging is beneficial to observe heavy elements such La, Pr, Sm, Ir but this mode cannot find the position of light elements such as Li, Be, N, O.

On the other hand, ABF imaging is advantageous to identify the light elements. In our work, using ABF imaging technique, B-O-B bonding angle can be measured in ABO₃ perovskite oxides.
Fig 2.2 Schematic illustration of STEM. Depending on the electron scattering angle, HAADF, ADF, BF and LAADF STEM image can be obtained. [12]
2.3.3 EELS

When a specimen in TEM has an interaction with a beam of electrons, elastic / inelastic scattering of electrons occur. In case of elastic scattering, kinetic energy of the electrons are preserved whereas electrons loss their energy and kinetic paths are randomly modified when electrons are under inelastic scattering. The amount and the electron distribution of energy loss can be measured via a spectrometer. Analyzing this data is called EELS. Inelastic scattering of electrons come in various forms such as plasmon and phonon excitations, transition of energy states, inner shell ionizations.

EELS can be taken advantage of various quantitative analysis such as thickness measurement of the specimen, stoichiometric analysis, valence measurement of transition metal ions, etc. EELS can be divided two parts, low loss spectra and core-loss spectra. Core loss spectra reflects transition states of electrons in the specimen when electrons are interacted with it. In our work, Ti L edge and O K edge spectrums were acquired. In particular, Ti L edge spectra contains information of valence of Ti cations. As shown in Fig 2.1, EELS spectrum of Ti$^{3+}$ and Ti$^{4+}$ are definitely different. Using this as reference, the valence state of Ti at the interfaces were investigated.

On the other hand, O K edge at the interfaces were also investigated. By analyzing O K edge, we can qualitative determine the amount of oxygen vacancy and the bonding state at the interfaces.
Fig 2.3 Core loss spectra acquired from the reference sample Ti$^{3+}$ from LaTiO$_3$ and Ti$^{4+}$ from SrTiO$_3$ with the same specimen thickness and same experimental conditions. [10]
Chapter 3. Results and Discussions

3.1 Reproducibility of the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$/SrTiO$_3$ system

3.1.1 Conductivity measurement

To check the reproducibility of the LaAlO$_3$/Sr$_x$Ca$_{1-x}$TiO$_3$/SrTiO$_3$ system, we measured the electrical resistance using the same method as performed in the previous work. We also compared our data with what Moon had measured. As shown in Table 3.1, there is a difference in the resistivity by 1~2 orders of magnitude. However, in case of LaAlO$_3$/CaTiO$_3$/SrTiO$_3$, sheet resistance could not be measured because the value is over the limit of the resistance-measuring device so we could not measure the electrical property of this structure in precise. Still, as already shown in Moon’s work, metal insulator transition depending on composition of Sr has been confirmed. The difference between our experiment and previous work would be discussed in the section 3.1.4.
<table>
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<th>reference</th>
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<td>LaAlO$_3$/SrTiO$_3$</td>
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<td>$10^4$</td>
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</tbody>
</table>

3.1.2 AFM image

Fig 3.1 corresponds to surface profile image of the LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ and LaAlO$_3$/SrTiO$_3$ system. In Fig 3.1 (a), step and terrace profile was observed. This indicates that CaTiO$_3$ and LaAlO$_3$ film were deposited in high quality without several amount of misfit dislocations.

On the other hand, in Fig 3.1 (b), step and terrace pattern was not clearly observed. However, considering that measured roughness is less than 1nm, we concluded that 1~2 unit cells of roughness exists on the LaAlO$_3$ surface. This result is not seem to be directly related to crystalline quality of the samples.
Fig 3.1. AFM images of (a) LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ and (b) LaAlO$_3$/SrTiO$_3$ structures.
3.1.4 HRTEM (Phase contrast) imaging

Although quality of thin films are verified using characterization tools such as XRD and AFM, these techniques cannot identify dislocations, point defects, grain boundaries in the films and interfaces between films and SrTiO$_3$ substrates. However, HRTEM imaging enables us identify point and planar defects in the oxide heterostructures and give feedbacks on optimizing growth condition of thin films. In addition, the quality of TEM specimens were identified.

3.1.4.1 LaAlO$_3$/CaTiO$_3$/SrTiO$_3$

Fig 3.2 refers to a cross-sectional HRTEM image of a LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ structure. It is evident that CaTiO$_3$ film is poly crystal and grain boundaries are distributed in the periodic arrangement. This indicates that the strain was relaxed when the CaTiO$_3$ film was deposited on SrTiO$_3$ substrate. However, the stripe pattern is observed in the Region 2. Even if CaTiO$_3$ has an orthorhombic crystal symmetry, experimental image of the film is similar to that of SrTiO$_3$ substrate. To demonstrate this, we performed HRTEM simulation using JEMS program. As shown in Fig 3.4, HR image of stoichiometric CaTiO$_3$ film does not have a stripe pattern. This indicates that in the Region 2, ion vacancy is ordered like brownmillerite phase. We additionally investigated grain distribution of CaTiO$_3$ film to grasp how CaTiO$_3$ film was deposited. The result is shown in Table 3.2. Each grain was almost uniformly formed in the CaTiO$_3$ film.

It is generally accepted that defects such as grain boundaries, dislocations in the films can be the source of higher resistivity of the complex oxide heterostructures
compared to oxide system without any defects. Thus, observed defects in the CaTiO₃ film can be the cause of increased sheet resistance compared to that of the previous report. [9]

3.1.4.2 LaAlO₃/SrTiO₃

Growth of SrTiO₃ film on SrTiO₃ substrate had not been on optimized condition so our work could not follow the previous work in precise. Instead, LaAlO₃ film was directly deposited on SrTiO₃ substrate. As shown in Fig 3.2 (d), LaAlO₃ film was grown with high crystalline quality. In addition, there is no misfit dislocations in the LaAlO₃ film and LaAlO₃/SrTiO₃ interface seemed to be sharp. We could not find the cause of the difference in the sheet conductance compared to the previous work. [9]
Fig 3.3 Projection of CaTiO$_3$ atomic unit cell on the (a) [100]$_p$ and (b) [001]$_p$ zone axis using ball and stick model. In the case of (a), out of phase octahedral tilt can be observed whereas in phase octahedral tilt is observed in the case of (b). This is because the Glazer notation of CaTiO$_3$ is $a^-$ $a^+$ $c^+$. 
<table>
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<th>Average (nm)</th>
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</thead>
<tbody>
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<td>22.000±4.777</td>
</tr>
<tr>
<td>$[001]_p$</td>
<td>8</td>
<td>15.833±4.238</td>
</tr>
<tr>
<td>$[100]_p + [001]_p$</td>
<td>10</td>
<td>13.671±1.764</td>
</tr>
</tbody>
</table>

**Table 3.2** Distribution, size of the two type of grains in the polycrystalline CaTiO$_3$ film.

**Fig 3.4** Simulated HR image of stoichiometric CaTiO$_3$ on the $[100]_p$ zone axis. Stripe pattern is not observed in the simulated image.
3.2 Atomic-scale observation of the LaAlO\textsubscript{3}/Sr\textsubscript{x}Ca\textsubscript{1-x}TiO\textsubscript{3}/SrTiO\textsubscript{3} interfaces

After the quality of LaAlO\textsubscript{3}/Sr\textsubscript{x}Ca\textsubscript{1-x}TiO\textsubscript{3}/SrTiO\textsubscript{3} structures and TEM specimens were confirmed, atomic structure of the LaAlO\textsubscript{3}/Sr\textsubscript{x}Ca\textsubscript{1-x}TiO\textsubscript{3} interfaces were investigated. Using spherical aberration – corrected high resolution STEM imaging, atomic structure of the interfaces were identified. Particularly, ABF STEM imaging enabled us to measure bonding angle between Ti, O, and Ti atomic columns at the interfaces. To measure octahedral tilt angle in precise, Peak Pairs Analysis (PPA) method was used in this work.

3.2.1 HADDF STEM

3.2.1.1 LaAlO\textsubscript{3}/CaTiO\textsubscript{3}/SrTiO\textsubscript{3}

Fig 3.4 refers to the HAADF STEM image of the LaAlO\textsubscript{3}/CaTiO\textsubscript{3}/SrTiO\textsubscript{3} structure. Each atomic column of the component is marked as circles. The image shows that the interface is atomically sharp without any inter diffusion across the interfaces. We also analyzed the CaTiO\textsubscript{3} part of the HAADF STEM image. As shown in the Fig 3.6, the observed CaTiO\textsubscript{3} part is correspond to the CaTiO\textsubscript{3} [100]p projection. Because TiO\textsubscript{6} octahedrons were rotated out of phase, when ABF STEM image is acquired in the same region, oxygen atomic columns would be averaged out so octahedral tilt angle is cannot be observed.

3.2.1.2 LaAlO\textsubscript{3}/SrTiO\textsubscript{3}

Fig 3.5 refers to the Z-contrast STEM image of the LaAlO\textsubscript{3}/SrTiO\textsubscript{3} structure. The image indicates that the interface is atomically sharp. However, as shown in Fig 3.4
(b), the intensity of the A site does not changes abruptly, which indicates there is several amount of inter diffusion (in about 4 unit cells) However, HAADF STEM imaging can hardly detect the position of O columns so we could not measure octahedral tilt angle in the HAADF mode. Then, ABF STEM imaging technique was used. ABF STEM images were simultaneously acquired.
**Fig 3.5** Cs corrected high resolution HAADF STEM image of (a) LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ and (b) LaAlO$_3$/SrTiO$_3$ structures. Interfaces are atomically sharp in both.
Fig 3.6 (a) HAADF STEM image of the CaTiO$_3$ film. (b) [100]$_p$ projection of the CaTiO$_3$ film. Image (a) is observed in this projection. (c) Simulated HAADF image of the CaTiO$_3$ film. This well matches with the experimental image.
3.2.2 ABF STEM imaging

3.2.2.1. LaAlO$_3$/CaTiO$_3$/SrTiO$_3$

As shown in Fig 3.3, even if several amount of octahedral rotation exists, we should observe CaTiO$_3$ film on particular zone axis. If CaTiO$_3$ image is obtained on the [100]$_p$ or [010]$_p$ zone axis, oxygen atomic columns would be averaged out. This is because on the [100]$_p$ and [010]$_p$ zone axis, TiO$_6$ octahedrons are rotated out of phase. Oxygen signals are averaged out so the amount of octahedral rotation cannot be measured. Instead, we found the region where the projection of CaTiO$_3$ on the [001]$_p$ zone axis is observed and then, ABF image was acquired. To measure Ti-O-Ti bonding angle in precise, we conducted peak pairs analysis to find atomic position of Ti and O.

As shown in Fig 3.5, considerable amount of octahedral rotation was observed in the CaTiO$_3$ film far from the LaAlO$_3$/CaTiO$_3$ interface. Due to the tensile strain on the CaTiO$_3$ film, the TiO$_6$ octahedral tilt angle was increased compared to bulk. To analyze it quantitatively, we measured Ti-O-Ti angle position by position. We averaged all the angles in the same line of the position as denoted in the Fig 3.6 (b) which indicates that the octahedral tilt angle of CaTiO$_3$ near the interface is larger than that of CaTiO$_3$ far from the interface. Because the CaTiO$_3$ film is biaxially tensile strained, the whole Ti-O-Ti bond angle is smaller than that of bulk.
3.2.2.2 LaAlO$_3$/SrTiO$_3$

Fig 3.5 (b) refers to the high resolution ABF STEM image of the LaAlO$_3$/SrTiO$_3$ structure. As shown in the Fig, there is a negligible TiO$_6$ octahedral tilt at the LaAlO$_3$/SrTiO$_3$ interface. The result of PPA also showed the same as directly shown in the image. This result is self-consistent considering that the Ti-O-Ti bonding angle is exactly 180 degrees even if the SrTiO$_3$ substrate near the interface is compressively strained.
Fig 3.7 Aberration corrected high resolution ABF STEM image of (a) LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ and (b) LaAlO$_3$/SrTiO$_3$ structures. Octahedral tilt has been observed in the CaTiO$_3$ film whereas there is not any octahedral rotation in the SrTiO$_3$ substrate in the LaAlO$_3$/SrTiO$_3$ structure. Each atomic columns are marked as colored circles.
Fig 3.8 (a) High Resolution ABF STEM image of the LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ structure. Ti-O-Ti angle had been measured by averaging all of the angles in the same line. The number of the lines are denoted in the image. (b) Average angle distribution of the CaTiO$_3$ film. Error bars are correspond to standard deviation.
3.3 Investigation of the electronic structures at the interfaces (EELS)

After observing the atomic arrangement of the interfaces, electronic structures were obtained using monochromated EELS. EELS spectra were obtained from FEI Titan 80-300.

3.3.1. LaAlO$_3$/CaTiO$_3$/SrTiO$_3$

To identify the change in chemical states at the interface, we first acquired Ti L edge spectra from the CaTiO$_3$ film and the LaAlO$_3$/CaTiO$_3$ interface. There is not a significant change in Ti L edge at the LaAlO$_3$/CaTiO$_3$ interface as shown in Fig 3.9. We also measured the peak position of L$_3$, L$_2$ edge and calculated L$_3$/L$_2$ ratio in the case of the SrTiO$_3$ substrate and the LaAlO$_3$/SrTiO$_3$ interface. The white line ratio (L$_3$/L$_2$ ratio) is hardly decreased from the CaTiO$_3$ film to the LaAlO$_3$/CaTiO$_3$ interface (See Table 3.4). However, we can see that Ti$^{3+}$ was observed in the whole CaTiO$_3$ film. The ratio of Ti$^{3+}$ is roughly confirmed by comparing Ti L edge of CaTiO$_3$ with that in the SrTiO$_3$ substrate in the LaAlO$_3$/SrTiO$_3$ system. This is due to non-stoichiometric growth of CaTiO$_3$, which leads to valence shift of Ti ions to compensate ordered defects.

The Ti L edge spectra at the interface in this work is similar to what the previous work have expected. Although considerable amount of Ti$^{3+}$ is detected at the LaAlO$_3$/CaTiO$_3$ interface and CaTiO$_3$ is not grown in the stoichiometric condition, the interface is still an insulator. In this sense, regardless of the amount of Ti$^{3+}$ at the interface, octahedral rotation plays a crucial role determining interfacial
conductivity.

### 3.3.2. LaAlO$_3$/SrTiO$_3$

Compared to Ti L edge spectra in the SrTiO$_3$ substrate, there is a significant change in Ti L edge at the LaAlO$_3$/SrTiO$_3$ interface as shown in Fig 3.9. There is less orbital splitting of Ti L edge at the interface. [11] This result is contrast to the case of LaAlO$_3$/CaTiO$_3$ where no significant change in Ti L edge spectra is observed.

We also calculated L$_3$/L$_2$ ratio in the case of the SrTiO$_3$ substrate and the LaAlO$_3$/SrTiO$_3$ interface. As expected, the white line ratio (L$_3$/L$_2$ ratio) is considerably decreased from SrTiO$_3$ substrate to the LaAlO$_3$/SrTiO$_3$ interface (See Table 3.2).

The significant change in Ti L edge at the interface can be interpreted as the transition in the valence of Ti ions. [10] Comparing with Ti L edge from SrTiO$_3$ (Ti$^{4+}$) and Ti L edge from LaTiO$_3$ as shown in Fig 2.3, we can argue that substantial proportion of Ti ions were under the reduction. Or, Ti L edge spectra at the interface can be considered as the linear combination of EELS spectra of Ti$^{4+}$ (from SrTiO$_3$) and Ti$^{3+}$ (from LaTiO$_3$). Already, in the previous studies, change of Ti valence at the LaAlO$_3$/SrTiO$_3$ interfaces had been detected. Most of the previous work interpreted this change(s) as the way of avoiding polarization catastrophe, called interfacial electronic reconstruction.

On the other hand, there is not a significant change in O K edge from SrTiO$_3$ substrate to the interface. There is a negligible amount of oxygen vacancy at the interface. This indicates that Ti$^{3+}$ at the interface is not come from oxygen vacancies. Instead, shift of valence state if Ti ion is due to the formation of
interfacial chemical states.

However, as mentioned in the previous section, there is not significant change in Ti ion valence at the interface in the case of the LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ system but because CaTiO$_3$ is grown on nonstoichiometric condition, nearly half portion of Ti$^{3+}$ ions were detected. However, considering conductivity measurement data, the emergence of Ti$^{3+}$ does not directly affect the formation of 2DEG.
Fig 3.9 (a) HAADF STEM image, (b) Ti L edge and (c) O K edge of the LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ structure. (d) HAADF STEM image, (e) Ti L edge and (f) O K edge of the LaAlO$_3$/SrTiO$_3$ structure.
Fig 3.10. Ti L edge at the (a) LaAlO$_3$/CaTiO$_3$ and (b) LaAlO$_3$/SrTiO$_3$ interface. Both interfaces contain Ti$^{3+}$ ions. Ratio of Ti$^{3+}$ at the LaAlO$_3$/CaTiO$_3$ interface is higher than that of LaAlO$_3$/SrTiO$_3$ interface because CaTiO$_3$ is grown in non-stoichiometric condition. Ti$^{3+}$ was observed not only at the interface but whole the CaTiO$_3$ film.
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<th>Position</th>
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<th>(L_3/L_2) ratio ((\text{LaAlO}_3/\text{SrTiO}_3))</th>
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<tr>
<td>10</td>
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</table>

**Table 3.3** Peak position of \(L_2\), \(L_3\) (in eV) and \(L_3/L_2\) intensity ratio in the \(\text{LaAlO}_3/\text{CaTiO}_3/\text{SrTiO}_3\) and \(\text{LaAlO}_3/\text{SrTiO}_3\) structure. Each positions are marked in the HAADF STEM image as shown in Fig 3.9.
Chapter 4. Summary and Conclusions

In this work, atomic, electronic structures and bonding states at the LaAlO$_3$/CaTiO$_3$ and LaAlO$_3$/SrTiO$_3$ interfaces and the relationship between them were investigated. In the previous work, microscopic studies related to 2DEG is focused on the LaAlO$_3$/SrTiO$_3$ interfaces but there is no established theory to explain 2DEG in the LaAlO$_3$/SrTiO$_3$ structure. Recently, there were attempts to discover 2DEG in the other oxide interfaces but the origin of 2DEG in the other system has not been studied using TEM and EELS.

Using Cs corrected STEM and monochromated EELS, we studied LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ and LaAlO$_3$/SrTiO$_3$ system. This research is in an extension of Moon’s work. This is the first trial to compare electronic structures of the LaAlO$_3$/CaTiO$_3$ and LaAlO$_3$/SrTiO$_3$ interfaces using EELS. Our experiment showed the same tendency in electrical property as Moon has already reported. [7] However, in the case of the LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ structure, the deviation from the previous work is come from periodic arrangement of grain boundaries in the CaTiO$_3$ film.

Using HAADF and ABF STEM imaging, we directly observed the interfacial atomic structure. Both LaAlO$_3$/CaTiO$_3$ and LaAlO$_3$/SrTiO$_3$ interfaces are relatively atomically abrupt. In addition, as expected, considerable amount of octahedral tilt was observed in the CaTiO$_3$ film whereas Ti-O-Ti angle is near 180 degrees at the LaAlO$_3$/SrTiO$_3$ interface.

Using EELS, we identified the electronic structure of the interfaces. In particular,
we compared Ti L edge spectra in the LaAlO$_3$/CaTiO$_3$/SrTiO$_3$ and LaAlO$_3$/SrTiO$_3$ system. Unlike Jang’s work, there is a significant difference in the Ti L edge spectra between in the case of the LaAlO$_3$/CaTiO$_3$ and LaAlO$_3$/SrTiO$_3$ interface. We can conclude that regardless of the stoichiometry of the CaTiO$_3$ films and amount of Ti$^{3+}$ ions at the interface, TiO$_6$ octahedral tilt plays a crucial role determining interfacial conductivity. However, in our research, LaAlO$_3$/Sr$_{0.5}$Ca$_{0.5}$TiO$_3$/SrTiO$_3$ structure has not been investigated. This will be studied in the future work.
Chapter 5. References


초 록


주요어: 이차원 전자 가스, 구면 수차보정 투과전자현미경, 꼭면체 틀어짐 각도, 페로브스카이트 산화물

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