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Study on the optoelectronic properties of transparent oxide semiconductor $A\text{SnO}_3$ ($A = \text{Ba, Sr, and Ca}$) epitaxial thin films

透明酸化物半導体 $A\text{SnO}_3$ ($A = \text{Ba, Sr, Ca}$)

エピタキシャル薄膜の光・電子特性に関する研究

Thesis submitted for the completion of Doctor of Philosophy

Mian Wei

Graduate School of Information Science and Technology
Hokkaido University

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<th>Description</th>
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<tbody>
<tr>
<td>ADF</td>
<td>Annular dark-field</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>CBM</td>
<td>Conduction band minimum</td>
</tr>
<tr>
<td>CRT</td>
<td>Cathode-ray-tube</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DUV</td>
<td>Deep-ultraviolet</td>
</tr>
<tr>
<td>GGA</td>
<td>Gradual gradient approximation</td>
</tr>
<tr>
<td>HAADF</td>
<td>High-angle annular dark-field</td>
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<tr>
<td>LAADF</td>
<td>Low-angle annular dark-field</td>
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<tr>
<td>LBSO</td>
<td>La-doped BaSnO$_3$</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid crystal display</td>
</tr>
<tr>
<td>LCSO</td>
<td>La-doped CaSnO$_3$</td>
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<tr>
<td>LDA</td>
<td>Local density approximation</td>
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<tr>
<td>LED</td>
<td>Light-emitting diode</td>
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<tr>
<td>LSSO</td>
<td>La-doped SrSnO$_3$</td>
</tr>
<tr>
<td>OLED</td>
<td>Organic light-emitting diode</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>RSM</td>
<td>Reciprocal space mappings</td>
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<tr>
<td>STEM</td>
<td>Scanning transmission electron microscope</td>
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<tr>
<td>TCO</td>
<td>Transparent conductive oxide</td>
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List of Acronyms

TFT Thin film transistor
TOS Transparent oxide semiconductor
UV Ultraviolet
UV-VIS Ultraviolet–visible
UV-VIS-NIR Ultraviolet-visible-near infrared
VBM Valence band maximum
XAS X-ray absorption spectroscopy
XRD X-ray diffraction
XRR X-ray reflectivity
**List of Symbols**

<table>
<thead>
<tr>
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<tr>
<td>$T$</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Absorption coefficient</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Bandgap</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$n$</td>
<td>Carrier concentration</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Conductivity</td>
</tr>
<tr>
<td>$m^*$</td>
<td>Effective mass</td>
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<tr>
<td>$F_r$</td>
<td>Fermi integral</td>
</tr>
<tr>
<td>$\mu_{FE}$</td>
<td>Field effect mobility</td>
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<tr>
<td>$\varphi_{TC}$</td>
<td>Figure-of-merit</td>
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<tr>
<td>$\mu_{Hall}$</td>
<td>Hall mobility</td>
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<tr>
<td>$D$</td>
<td>Lateral grain size</td>
</tr>
<tr>
<td>$a$</td>
<td>Lattice constant</td>
</tr>
<tr>
<td>$\Delta a$</td>
<td>Lattice mismatch</td>
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<tr>
<td>$\mu$</td>
<td>Mobility</td>
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<tr>
<td>$h$</td>
<td>Planck constant</td>
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<tr>
<td>$\xi$</td>
<td>Reduced Fermi energy</td>
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<tr>
<td>$r$</td>
<td>Scattering parameter</td>
</tr>
<tr>
<td>$S$</td>
<td>Seebeck coefficient</td>
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### List of Symbols

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<th>Symbol</th>
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<tr>
<td>( R_s )</td>
<td>Sheet resistance</td>
</tr>
<tr>
<td>( v )</td>
<td>Speed of light</td>
</tr>
<tr>
<td>( \Delta T )</td>
<td>Temperature difference</td>
</tr>
<tr>
<td>( \Delta V )</td>
<td>Thermo-electromotive force</td>
</tr>
<tr>
<td>( t )</td>
<td>Thickness</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength</td>
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Chapter 1. General Introduction

1.1 Background of this research

Traditional printing technology, which has more than 100 years of history of being the main way of disseminating knowledge and information, has been replaced by modern display technology. Nowadays, display devices such as television, laptop, and mobile phone are inseparable from people’s daily life. According to the pursuit of more colorful pixels and practicality, the display devices have gone through a long journey from cathode-ray-tube (CRT) to plasma display and liquid crystal display (LCD), then to organic light-emitting diode (OLED) [1]. Tremendous amount of research efforts and extraordinary research contributions like the blue LED, which was acknowledged with the Noble prize in 2014 awarded to a trio of Japanese scientists [2], have significantly improved display technology. And the public demand for greater performance eventually created a research discipline called optoelectronics, which refer to electrical technologies associated with controlling light.

For materials to be utilized in optoelectronic applications such as display panels, there are two essential requirements. Firstly, it needs to be transparent to at least allow the visible light to pass through, which enables switching between electrical signal to observable optical signal. In this regard, the material needs to have a relatively wide bandgap. In
addition, materials in display technology are required to exhibit high electrical properties. *i.e.*, high conductivity for reducing the power consumption and high mobility for ensuring the fast performance. In these regards, two essential class of materials in optoelectronics are transparent conductive oxides (TCOs), which is used as electrodes for the optoelectronic devices, and the transparent oxide semiconductors (TOSs), which is applied for channel materials of the transistor consisting the various applications [3].

The pioneering research work on transparent conductive materials began when military scientists started to use transparent oxides for deicing window glass for aircrafts during World War II. In 1950, the transparent semiconductor oxide $\text{In}_2\text{O}_3$ was made for the first time [4], and scientists soon realized that adding tin (Sn) in $\text{In}_2\text{O}_3$ made this material system an excellent conductor, which could be used as transparent conductive films. If Sn is doped in $\text{In}_2\text{O}_3$, Sn replaces In in the lattice and contributes an electron to the conduction band since In in $\text{In}_2\text{O}_3$ is trivalent. In addition, oxygen vacancy can be generated, and the resulting electrical transport properties of this material system can be a carrier concentration of $\sim 10^{21}$ cm$^{-3}$ and a mobility of $\sim 40$ cm$^2$ V$^{-1}$ s$^{-1}$ [5]. This mechanism provides ITO an excellent electrical conductivity $\sim 10000$ S cm$^{-1}$ [5], and commercial ITO films are widely used for the electrode for most optoelectrical devices. However, for optoelectronic devices used in ultraviolet (UV) or deep-ultraviolet (DUV) range, UV-LED for example, due to the limitation of ITO’s relatively narrow bandgap, the efficiency of the UV light transmission is relatively low. Moreover, the use of In
comes with practical cost issues due to its low abundance [6], which will limit the economic viability of using ITO in large-scale optoelectrical devices like flat panel display and solar cell. Therefore, many researchers are working on finding an alternative optoelectronic material that can potentially replace ITO.

The relationship between bandgap and conductivity can be tricky since these two physical properties are usually mutually exclusive. As an electrode is an electrical conductor used to contact nonmetallic part of a circuit, materials with high electrical conductivity are preferred. Almost all metals exhibit sufficient electrical conductivity because of the free electron gas, but these free electrons form a sea of electrons called plasma, which can effectively reflect electromagnetic waves. As such, metal exhibits excellent electrical conductivity and is opaque without a bandgap. This trade-off relationship between the bandgap and electrical transport properties is very important in optoelectronics application, and such requirements can be met with TOSs.

High carrier mobility is another essential requirement for optoelectronic applications. For flat panel displays in commercial applications like LCD, OLED, and LED, each pixel is individually controlled by thin film transistors (TFTs), and the speed of charge carriers is essential for their performance. Metaphorically speaking, the carrier mobility, which is associated with the drift speed of charge carriers, is analogous to the speed of a train. If the train speed is slow, in order to transport a certain amount of goods within a specified
General Introduction

time, multiple rails or additional carriages are required. Similarly, if the carrier mobility of the channel is high, each transistor can be made smaller, and each pixel can be made smaller to achieve higher display resolution. In order to ensure fast performance of TFTs, high carrier mobility value of their TOS channels is critical. Conventional display panels during the early era utilized Si and SiO$_2$ as the backplane and channel materials, of which the main benefits were extremely low cost and easy synthesis. However, the mobility value of amorphous-Si (a-Si) based TFTs is $< 1 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ [7]. The research efforts to find materials with better performance eventually led to the development amorphous InGaZnO$_4$ (IGZO). IGZO currently dominates the market as a channel material in the new generation of high-performance TFT to improve the resolution of display panels in large-screen OLED TVs [8] due to its many advantages. It is transparent, and the amorphous IGZO (a-IGZO) based TFT shows a mobility value around $10 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$, which is two orders of magnitude higher than that of a-Si. However, some issues still remain. For example, it still contains In, which is not abundant [6].

Widely used TCOs and TOSs are not limited to ITO (bandgap, $E_g$ 3.50–3.65 eV, $\sim 10000$ S cm$^{-1}$) [5] and a-IGZO ($E_g \sim 3$ eV, $\sim 400$ S cm$^{-1}$) [9]. For cost reduction and concerns related to preserving the environment, zinc oxide (ZnO) is considered as a candidate since it includes no rare elements. Al-doped and Ga-doped ZnO thin films show a conductivity of $\sim 5000$ S cm$^{-1}$, which is only half of that in ITO [10, 11]. Moreover, since Zn is more reactive than Sn and In under oxygen atmosphere, controlling the Zn content during
General Introduction

Synthesis is more difficult than other commercialized TOSs, limiting the use of ZnO in optoelectrical applications. As another alternative, tin oxide (SnO$_2$) based TFT shows extremely high field effect mobility ($\mu_{FE}$) $>$100 cm$^2$ V$^{-1}$ s$^{-1}$ [12, 13], which is one order of magnitude higher than that of a-IGZO. In 2016, Shin et al. reported that an extremely thin (< 4.5 nm) undoped SnO$_2$ TFT exhibited $\mu_{FE}$ of 150 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature in air [13]. However, SnO$_2$ is a well-known gas sensor material [14]. It is known that a 3–4-nm-thick depletion layer is formed at the SnO$_2$ surface [15]. Oxygen in the aerial atmosphere is adsorbed on the surface and seizes some free electrons near the surface, forming a depletion layer. The consequent sensitivity to temperature and humidity limits practical application of SnO$_2$.

There are also attempts to expand the range of transparency to Deep-UV (DUV, 200–300 nm in wavelength) for next generation optoelectronic applications [16]. One promising application area of interest is biotechnology since DNA molecules have characteristic absorption and fluorescence in DUV region [17, 18]. DUV light is also used for sterilization and cleaning, which require efficient UV-LED. Room temperature operation of DUV laser diode (271.8 nm) was developed by Zhang et al., [19] which can be utilized in integrated lithography in a large scale and high-density optical memories.

Candidate TOS materials for DUV optoelectronics include $\beta$-Ga$_2$O$_3$ ($E_g$ ~4.9 eV, ~1 S cm$^{-1}$) [20, 21], $\alpha$-Ga$_2$O$_3$ ($E_g$ ~5.3 eV, ~0.3 S cm$^{-1}$) [22], electron-doped calcium aluminate
1. General Introduction

(C12A7: $e^-$, $\sim$4 eV, $\sim$800 S cm$^{-1}$) [23-25]. $\beta$-Ga$_2$O$_3$ recently emerged to be a potential candidate for DUV optoelectronics [26, 27]. Although theoretical studies predict that carrier doping in $\beta$-Ga$_2$O$_3$ is challenging, [28] experimentalists successfully created mobile electrons using Sn or Si dopants [29, 30]. However, the resulting electrical conductivity was too low for (<30 S cm$^{-1}$) practical applications. Al doped MgZnO (AMZO) is another candidate. Undoped MgZnO (MZO) itself is a promising candidate for DUV applications due to its economic advantages [31, 32], but its UV transmittance can further be improved by adjusting the Mg content while carriers can be doped with Al, Ga or In [33, 34]. Al doped Mg$_{0.43}$Zn$_{0.57}$O (AMZO) film with a wide bandgap (cutoff wavelength of 295 nm), high carrier concentration ($\sim$1.56 $\times$ 10$^{20}$ cm$^{-3}$), high mobility (16.3 cm$^2$ V$^{-1}$ s$^{-1}$), and high conductivity (406.6 S cm$^{-1}$) has been reported by D. Zhang et al [35]. However, due to the tradeoff relationship between the optical bandgap and the electrical conductivity, DUV-TOSs exhibit low electron mobilities, and the resulting electrical conductivities are too low compared to conventional ITO electrodes.

The search for better material system is the duty of material scientists. In this regard, one promising TOS for future optoelectronic applications is the Alkaline earth elements stannate, $A$SnO$_3$. $A$SnO$_3$ has perovskite structure composed of corner-sharing SnO$_6$ octahedra with the $A$-site cations. The crystal structure of $A$SnO$_3$ is closely related to lattice parameter, which is determined by $A$-site substitution. The smaller $A$-site cation with stronger binding force of nucleus trigger the deformations in the SnO$_6$ octahedral
and further induce phase transition in $\text{A}_2\text{SnO}_3$. The valence band maximum (VBM) and conduction band minimum (CBM) of $\text{A}_2\text{SnO}_3$ is composed of O 2p and Sn 5s, respectively, and the energy location of the CBM and VBM is affected by the Sn–O bond length, enabling the A-site modulation to control all optical and electrical properties. Therefore, this system could achieve a good trade-off relationship between electrical transport properties and optical bandgap at the same time by changing the A-site ions.

La-doped $\text{A}_2\text{SnO}_3$ ($\text{A} = \text{Ba, Sr, and Ca}$) is a rapidly emerging material class for optoelectronics application, as they have both the wide bandgap and fast electrical transport properties. There has been growing interest on La-doped BaSnO$_3$ (LBSO, bandgap, $E_g \sim 3.5$ eV) with cubic perovskite structure ($a = 4.115$ Å) as a novel TOS because flux-grown LBSO single crystals exhibited a very high mobility of 320 cm$^2$ V$^{-1}$ s$^{-1}$ with a carrier concentration value of $8 \times 10^{19}$ cm$^{-3}$ at room temperature [36]. Therefore, many researchers have tried to prepare high mobility LBSO epitaxial films to date, but the observed mobility has been low compared to that of single crystals. Paik et al. obtained the highest mobility of 183 cm$^2$ V$^{-1}$ s$^{-1}$ in a LBSO film on DyScO$_3$ ($a = 3.943$ Å, $\Delta a = +4.2$ %) [37], and Raghavan et al. also achieved high mobilities of 150 cm$^2$ V$^{-1}$ s$^{-1}$ and 100 cm$^2$ V$^{-1}$ s$^{-1}$ in LBSO films deposited by high purity molecular beam epitaxy (MBE) technique on PrScO$_3$ ($a = 4.026$ Å, $\Delta a = +2.18$ %) and SrTiO$_3$, respectively [38]. Higgins et al. reported mobility values up to 81 cm$^2$ V$^{-1}$ s$^{-1}$ in LBSO films grown on TbScO$_3$ (110) ($a = 3.958$ Å, $\Delta a = +3.97$ %) by MBE [39]. A low mobility value of 10 cm$^2$
V$^{-1}$ s$^{-1}$ was also reported by Wadekar et al. in a LBSO film on SmScO$_3$ (110) ($a = 3.991$ Å, $\Delta a = +3.1$ %) [40]. The origin of this mobility suppression must be clarified to utilize the high mobility in LBSO for device applications, but it is currently under an extensive debate.

Replacing Ba in LBSO with Sr can enhance the bandgap from 3.1 eV to $> 4$ eV [41-44]. However, the substitution of Sr induces lattice distortions and reduces the electron mobility. Therefore, La-doped SrSnO$_3$ (LSSO) is not studied as extensively as LBSO. The crystal structure of SrSnO$_3$ is regarded as a pseudo-double cubic perovskite though the real lattice is orthorhombic [41]. Several researchers fabricated the epitaxial films of LSSO using vapor phase epitaxy methods. However, due to difficulties in growing high-quality LSSO films, their electron transport properties have not been extensively studied. One study reported the electrical conductivity of 5% La-doped LSSO film only to be $\sim 1000$ S cm$^{-1}$ with a low activation rate of La, which is the highest electrical conductivity reported to date [45]. However, the large bandgap enhancement observed from LSSO is worth dedicated studies due to its potential in DUV applications. The electrical conductivity of LSSO films can be improved if the solubility of La ions in the LSSO lattice is enhanced.

The trend observed from LBSO and LSSO suggests that reducing the $A$-site ion size increases the bandgap. Therefore, the optical bandgap of CaSnO$_3$ is of interest to the
optoelectronics community, but the reported values are scattered from 1.95 to 5.38 eV. [46-48] Using first principle calculations based on the density functional theory (DFT), Cherrad et al. reported a bandgap value of 2.849 eV [49], and Henriques et al. reported 1.95 eV (2.92 eV), which was estimated with gradual gradient approximation (local density approximation) (GGA (LDA)) for orthorhombic CaSnO$_3$ [50]. Zhang et al. experimentally reported ~4.44 eV from the UV-VIS absorption spectra and Raman spectroscopy, but this result contradicted their own DFT result of ~2.5 eV [51]. Mizoguchi et al. reported an optical bandgap of ~4.4 eV from CaSnO$_3$ compounds [42]. Liu et al. reported the optical bandgap of CaSnO$_3$ thin film grown on LAO. The bandgap gradually increased from 4.95 eV to 5.38 eV with decreasing film thickness, which they attributed to the quantum-size effect [48]. The electrical properties of CaSnO$_3$ has not been addressed in literature to date.
1.2 Objectives of this research

The objective of this research is to develop high-performance TOS, $A\text{SnO}_3$ by optimizing the physical properties and fabrication process. This thesis is divided into the following chapters. In chapter 1, the overall research is introduced with the background and motivation. The experimental methods including films fabrication, structural characterizations and electron transport properties are explained in chapter 2. In chapter 3-5, improving the electron transport properties and optimizing the fabrication process of LBSO and LSSO are discussed in detail. Efforts to clarify the origin of the mobility suppression in of LBSO thin films mobility have been made, and several methods have been tested, such as using an oxidate atmosphere during films growth and vacuum post-annealing to further optimize the performance. As the results, higher activation efficiency of La-dopant was achieved, and the electrical properties of LBSO and LSSO were greatly improved. In chapter 6, the research was expanded to general $A\text{SnO}_3$ system, and its optoelectronic properties were systemically clarified. The overall trade-off relationship with the substitutions of different $A$-site ions in the optoelectronic properties in this material system was demonstrated. The overall research results and recommendations for future research are summarized in chapter 7. The contributions reported in this dissertation will be of great importance in the design of the next-generation optoelectrical applications based on $A\text{SnO}_3$. 
Chapter 2. Experimental Methods

2.1 Film fabrication

In this research, epitaxial $\alpha$SnO$_3$ thin films were fabricated on various single crystal substrates using pulsed laser deposition (PLD) technique (KrF excimer laser, $\lambda$=248 nm, 10 Hz, fluence ~2 J cm$^{-2}$ pulse$^{-1}$), which is one of physical vapor deposition methods. [53] Figure 2.1 shows the schematic illustration of the PLD system. The PLD equipment largely consist of an excimer laser and a high-vacuum chamber. At the start of deposition, pulsed laser with high power will be directed to the target by mirrors to ablate the surface. This process can occur under ultra-high vacuum or the presence of background gas such as oxygen. As shown in Figure 2.2, when the laser pulse is absorbed by target, the laser energy will first be converted to electronic excitation and then into thermal excitation, resulting in plasma formation [54]. The plasma expands to the surrounding environment in the form of a plume containing many energetic target particulates at atomic level, including atoms, electrons, and ions [55]. Then they will be deposited on the substrate. Sometimes, the substrate needs to be heated to a specific temperature for growing high-quality films.

Compared to other film deposition methods, PLD can fabricate thin films with the same chemical composition as the target, which is crucial in this research for controlling the
composition in the $\text{ASnO}_3$ films. The PLD process also enables the deposition of films in a wide range of background gas compositions and pressures, which is ideal for the studying the effect of atmospheric conditions during the film deposition [50]. In order to create a higher oxidative environment and control the chemical potential of oxygen during the film growth, ozone ($\text{O}_3$) was used for film grown atmosphere in this research. $\text{O}_3$ creates a much stronger oxidation environment compared to typically used oxygen gas ($\text{O}_2$). The ozone generator is shown in Figure 2.3. The ozone generating unit in the generator converts flowing oxygen gas into a mixture of oxygen and ozone in the gap of double quartz glass tube.

\section*{2.2 Structural characterization}

High-resolution X-ray diffraction (XRD) (Figure 2.4, Cu, $\text{K}\alpha_1$, ATX-G, Rigaku Co.) measurements were used to reveal the crystal structure and other physical properties of films associated with the structure. The basic principle of XRD is expressed by the Bragg's law:

$$2d \sin \theta = n \lambda$$

As shown in Figure 2.5, the incident wave can be scattered by atoms, which reflect a small portion of the incident intensity. If the atoms are arranged symmetrically on planes with a separation $d$, these waves will be in constructive interference only at certain angles ($\theta$) when their path-length difference, $2d \sin \theta$, equals an integer multiple ($n$) of the
wavelength $\lambda$. In this case, the incident beam is deflected by an angle $2\theta$, producing a peak in the diffraction pattern [53]. X-ray reflectivity (XRR) contains the information from the thickness and density of thin films, which is based on the oscillation pattern from the interference of reflected beam at the film/substrate interface and film surface [54]. The film thicknesses were determined by analyzing Kiessing or Pendellösung fringes. In addition, it can check if the film was heteroepitaxially grown on substrates.

In order to address the structural characteristics in more detail, X-ray reciprocal space mappings (RSMs) were performed. Compared to the conventional out-of-plane XRDs, additional information like the lattice relaxation and the crystalline quality can be extracted from RSMs [55]. The lattice parameters perpendicular ($c$-axis) and parallel ($a$-axis) to the substrate surface can also be extracted from the peak position since RSM can be seen as the 2D XRD patterns of films along the in-plane and out-of-plane directions. Lastly, the lateral grain size value can be calculated from the peak width.

The surface morphology of the films was investigated using an atomic force microscope (Figure 2.6, AFM, Nanocute, Hitachi High-Tech Sci. Co.). The surface profile is collected by a sharp probe on a micro-cantilever, which is controlled precisely with a piezoelectric crystal. The conductive cantilever and AFM measure the current bias of the sample, then sense and amplify the signal between the probe and the atom on the sample surface with resolutions on the order of a few tens of nanometers.
In order to determine the atomic structure of the interface between film and substrate, the 
$\text{A}\text{SnO}_3$ films was characterized by annular dark-field (ADF) imaging in a scanning 
transmission electron microscope (STEM), of which the images are formed by collecting 
scattered electrons with an ADF detector. From high-angle annular dark-field (HAADF) 
STEM images, individual atoms can be identified. Since the HAADF-STEM image are 
formed only by incoherently scattered electrons at high angles (Rutherford scattered from 
the nucleus of the atoms), it is highly sensitive to variations in the atomic number of atoms 
in the sample (Z-contrast images). As such, atomic level defects like misfit dislocations 
can be observed. Strain contrast in the films were observed in the cross-sectional low-
angle annular dark-field (LAADF)-STEM images, which collects diffracted or 
inelastically scattered electrons at low to medium angles using the ADF detector. 
LAADF-STEM enables the acquisition of a high-resolution image with a high signal-to-
noise ratio, of which the intensity depends on the lattice strain.

2.3 Electron transport properties

The electron transport properties, such as Hall mobility ($\mu_{\text{Hall}}$), carrier concentration ($n$), 
and electrical conductivity ($\sigma$) of the $\text{A}\text{SnO}_3$ films were measured using the conventional 
DC four-probe method with the van der Pauw electrode configuration. In-Ga alloy was 
used as the contact electrode. In order to measure the Seebeck coefficient ($S$) of the films,
two Peltier devices were used to provide a temperature difference between source and drain electrodes, and the thermo-electromotive force ($\Delta V$) and temperature difference ($\Delta T$) were monitored simultaneously (Figure 2.7). The $S$ values were obtained from the slope of the $\Delta V$-$\Delta T$ plots.

### 2.4 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS, Figure 2.8) is a widely used technique for determining the local electronic state of the atoms in a substance. As the X-ray goes through the sample, its intensity attenuates, which is closely related to the structure and composition of the sample. Since the attenuation comes from the sample’s absorption and scattering of X-rays, but the effect of absorption is much greater than that of scattering. The X-ray absorption is related to the atomic number and valence, which can be used for the composition as well as the valence state of the material constituents. In order to investigate the chemical state of the $\text{A} \text{SnO}_3$ films, XAS is performed around the Sn M4,5 edge of LBSO film.

### 2.5 Optical properties

The optical bandgap of the films was calculated using the optical transmission and reflectance measured by the ultraviolet-visible-near infrared (UV-VIS-NIR) spectrometer (Figure 2.9). A beam is separably divided into its constituent wavelengths by a prism,
and each monochromatic (single wavelength) beam is divided into two beams of equal intensity by the half mirror device. One beam (sample beam) passes through the sample to be tested, and the other beam (reference beam) passes through only the substrate. The electronic detector measures the intensity of the beams and compares them to yield the optical properties of the films.
Figure 2.1 Schematic illustration of PLD system.
Figure 2.2 Plasma created by pulsed laser during the deposition of SrSnO₃ films.
Figure 2.3 Ozone generator.
Figure 2.4 High-resolution XRD.
Figure 2.5 Schematic illustration of Bragg’s law.
Figure 2.6 AFM.
Figure 2.7 Four-probe electron transport property and thermopower measurements.
2. Experimental Methods

Figure 2.8 Schematic diagram of XAS measurements.
Figure 2.9 UV-VIS-NIR spectrometer.
Chapter 3. Large Thickness Dependence of the Carrier Mobility in a Transparent Oxide Semiconductor, La-doped BaSnO$_3$

3.1 Objective of this chapter

LBSO single crystals exhibit an extraordinarily high mobility of 320 cm$^2$ V$^{-1}$ s$^{-1}$ ($n \approx 8 \times 10^{19}$ cm$^{-3}$) at room temperature [36], which is even comparable to classical semiconductors. Such high mobility is originated from its small carrier effective mass ($m^*$ = 0.40 $m_e$ [56]) and long carrier relaxation time [57]. For this reason, many researchers attempted to prepare LBSO epitaxial films on various substrate, but the resulting electron mobility values vary in the range of 10–183 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature. These studies attributed the origin of the low mobility to the misfit/threading dislocations, which are generated from a large lattice mismatch ($\Delta a$) at the film/substrate interface (i.e., $\Delta a = +5.4$ % for LBSO/SrTiO$_3$ interface) [58-61]. In order to minimize $\Delta a$, various forms of buffer layers, even including BaSnO$_3$, were implemented, but the resulting mobilities were still lower than 100 cm$^2$ V$^{-1}$ s$^{-1}$. These contradict the misfit/threading dislocations scenario since there was almost no lattice mismatch between the substrate and the film, especially for BaSnO$_3$ substrates.

Several studies suggest that cation off-stoichiometry or cation mixing can introduce
charge point defects and dislocations [62-64], which may act as scattering sources and thus suppress the mobility. Due to the existence of many possibilities, the origin of the limited electron mobility in LBSO thin films has not been clearly explained to date, and a fundamental study on other simple factors such as the film thickness is required to understand this phenomenon. Therefore, in this chapter, the structural and electrical features of epitaxial LBSO films with various thicknesses (14–1040 nm), which were grown on (001) perovskite SrTiO$_3$ ($\Delta a = +5.4 \%$) and non-perovskite (001) MgO ($\Delta a = -2.3 \%$), were analyzed.

This chapter demonstrates that the carrier mobility of the LBSO films strongly depends on the thickness whereas it is unrelated to the lattice mismatch. Despite the large observed differences in lattice parameters, lateral grain size, density of threading dislocations, surface morphology, and density of misfit dislocations, the mobility increased very similarly with the thickness on both substrates and saturated at $\sim100$ cm$^2$ V$^{-1}$ s$^{-1}$ while approaching to the nominal carrier concentration (= [2% La$^{3+}$]), clearly indicating that the behavior of mobility depends on the film thickness.

3.2 Experimental

Epitaxial 2% LBSO films with thicknesses varying from 14 nm to 1.04 $\mu$m were heteroepitaxially grown on (001) SrTiO$_3$ and (001) MgO single crystal substrates using
PLD. The temperatures during the film growth were 700 °C for SrTiO$_3$ substrates and 750 °C for MgO substrates while the oxygen pressure was kept at 10 Pa. In case of SrTiO$_3$ substrates, the LBSO films were annealed at 1200 °C in the air to obtain atomically smooth surfaces [56, 65].

### 3.3 Results and Discussion

High-resolution XRD measurements revealed that the LBSO films were heteroepitaxially grown on (001) SrTiO$_3$ substrates and (001) MgO substrates with a cube-on-cube epitaxial relationship. For very thick films, Pendelloesung fringes were used to determine the thickness. Figure 3.1 shows the observed stepped and terraced surface on the film grown on (001) SrTiO$_3$ substrate, whereas very tiny grains were observed from the film grown on (001) MgO substrate. The AFM images show that the films grown on SrTiO$_3$ and MgO have very different surface morphologies.

Figure 3.2 shows the X-ray RSMs performed around the asymmetric 103 diffraction spot of BaSnO$_3$ with the 103 diffraction spot of SrTiO$_3$ and the 204 diffraction spot of MgO, respectively. While the $q_x/2\pi$ peak position of BaSnO$_3$ and the substrate are different from each other, they are both located nearby the red dotted line (cubic), indicating that incoherent epitaxial growth occurred in both cases. In order to determine the lateral grain size ($D$), the cross-sectional peak intensity as a function of $q_x/2\pi$ was plotted. In the case
of SrTiO$_3$ substrate, an integral width of 0.0306 nm$^{-1}$ was obtained for the 14-nm-thick film whereas that of 0.0127 nm$^{-1}$ was obtained for the 1040-nm-thick film. In the case of MgO substrate, an integral width of 0.1085 nm$^{-1}$ was obtained for the 44-nm-thick film whereas that of 0.0557 nm$^{-1}$ was obtained for the 1000-nm-thick film.

**Figure 3.3 (a)** shows the calculated average lattice parameters, $(a^2\cdot c)^{1/3}$ of the LBSO films grown on SrTiO$_3$ and MgO substrates, where $a$ and $c$ are the in-plane and the out-of-plane lattice parameters, respectively. The $(a^2\cdot c)^{1/3}$ values of the films on SrTiO$_3$ and MgO substrates initially showed opposite behaviors; $(a^2\cdot c)^{1/3}$ of the films on MgO was larger than the bulk value whereas that of the films on SrTiO$_3$ was smaller than the bulk value, which are probably attributed to the differences in the lattice mismatch. On both substrates, the $(a^2\cdot c)^{1/3}$ values were nearly similar when the thickness was greater than 300 nm. The lateral grain size ($D = \text{integral width in } q_x/2\pi \text{ direction of the RSM}^{-1}$) of the LBSO films grown on SrTiO$_3$ and MgO substrates were calculated, which are shown in **Figure 3.3 (b)**. The lateral grain sizes were quite different as the LBSO films on SrTiO$_3$ exhibited a maximum grain size of $\sim 85$ nm whereas the grains in the LBSO films on MgO were 20 nm or less.

**Figure 3.4** shows the cross-sectional HAADF-STEM images of the 1.04-µm-thick LBSO/SrTiO$_3$ and 1-µm-thick LBSO/MgO films. In case of LBSO/SrTiO$_3$, mismatch dislocations (indicated by arrows) are observed periodically at the interface. The spacing
of the mismatch dislocation was about 7.3 nm, which agrees with the $\Delta a = +5.3 \%$. On the other hand, in case of LBSO/MgO, mismatch dislocations were not periodically spaced. Highly dense threading dislocations were observed in the cross-sectional LAADF-STEM images of the films as shown in Figure 3.5. The average distance between two threading dislocations was $\sim$100 nm on SrTiO$_3$ substrate and $\sim$30 nm on MgO substrate, reflecting the lateral grain sizes obtained from the RSMs ($\sim$85 nm for SrTiO$_3$ substrate and $\sim$20 nm for MgO substrate). Thus, the densities of the threading dislocations are $1.4 \times 10^{10}$ cm$^{-2}$ for the film on SrTiO$_3$ substrate and $2.5 \times 10^{11}$ cm$^{-2}$ for the film on MgO substrate. These results show that there are several structural differences between the LBSO films on SrTiO$_3$ and MgO substrates, including surface morphology, lattice parameter, lateral grain size, density of threading dislocations, and density of misfit dislocations.

Figure 3.6 summarizes the electron transport properties of the LBSO films grown on SrTiO$_3$ and MgO substrates at room temperature. As far as the overall tendencies are concerned, no clear difference was observed from LBSO films deposited on SrTiO$_3$ and MgO substrates. The value of $n$ increased with increasing thickness and approached the nominal carrier concentration ($= [2\% \text{ La}^{3+}]$). Approximately, 88 % La$^{3+}$ dopants were activated and produced conducting electrons for films thicker than 350 nm. Similarly, as shown in Figure 3.6 (b) the magnitude of $S$, which decreases with increasing $n$, gradually decreased with the thickness, which is consistent with Figure 3.6 (a). All values of $S$ were
negative, indicating the LBSO films are \( n \)-type semiconductors [66]. In addition, \( \mu_{\text{Hall}} \) increased gradually with thickness and became constant for films thicker than 350 nm. The highest mobility values were 97.7 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for 1040 nm thick LBSO/SrTiO\(_3\) and 99.2 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for 450 nm thick LBSO/MgO. The thickness dependence of \( \mu_{\text{Hall}} \) and \( n \) in the LBSO films were similar on both the SrTiO\(_3\) and MgO substrates. In addition, since \( \mu_{\text{Hall}} \) and \( n \) of LBSO films thicker than 350 nm do not show a significant dependence on the substrates, the contributions from the structural differences between LBSO/SrTiO\(_3\) and LBSO/MgO on the mobility are likely small.

The electron mobility in LBSO films rapidly increased with the thickness. However, the maximum mobility (~100 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) was still low compared to the bulk values (~320 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). In order to further investigate the suppression of electronic transport properties, XAS was performed around the Sn M\(_{4,5}\) edge of a 500-nm-thick LBSO film on SrTiO\(_3\) substrate in Pohang accelerator laboratory as shown in Figure 3.7. Several peak structures (A–F) were clearly observed in the XAS spectra. The peaks labelled as B–F are well matched with BaSnO\(_3\). However, there is an additional peak from 2\(^+\) valence state of Sn (SnO, peak A). Since Sn\(^{2+}\) ions in LBSO films should play as electron acceptors as well as ionized impurities, they may be related to the suppression of \( \mu_{\text{Hall}} \) and \( n \) in the films (compared to bulk values).

Figure 3.8 shows the measured the temperature dependence of the electron transport
3. Large Thickness Dependence of the Carrier Mobility in a Transparent Oxide Semiconductor, La-doped BaSnO$_3$

properties of the LBSO films grown on (001) SrTiO$_3$ substrates. Metallic behavior was observed in all the films as shown in Figure 3.8 (a), indicating that the Fermi energy is located above the conduction band edge and the films behave as degenerate semiconductors [61]. The values of $n$ for all films shown in Figure 3.8 (b) were almost temperature independent and similar for films thicker than 350 nm. $\mu_{\text{Hall}}$ increased with decreasing temperature, and the change was more significant for thicker films. The highest $\mu_{\text{Hall}}$ of 163 cm$^2$ V$^{-1}$ s$^{-1}$ was observed in 1040 nm thick LBSO film at 8 K (Figure 3.8 (c)). $|S|$ almost linearly decreased with decreasing temperature (Figure 3.8 (d)), which is typical for degenerate semiconductors [66].

3.4 Conclusions

This chapter demonstrated that the electron transport properties of the LBSO films grown on (001) SrTiO$_3$ and (001) MgO substrates show strong thickness dependence in the range of 14 nm to 1040 nm. Although the LBSO/SrTiO$_3$ and LBSO/MgO exhibited several drastic structural differences, these discrepancies did not play a major role in the carrier mobility as no clear structure-originated difference was observed in the electron transport properties. $\mu_{\text{Hall}}$ and $n$ increased with increasing LBSO film thickness. On both SrTiO$_3$ and MgO substrates, the maximum $\mu_{\text{Hall}}$ observed was $\sim$100 cm$^2$ V$^{-1}$ s$^{-1}$. While the origin of the strong thickness dependence of $\mu_{\text{Hall}}$ remains unclear, the presence of 2+ valence state of Sn in the XAS spectrum of a 500 nm thick LBSO film offers on insight. Since
Sn$^{2+}$ ions should be electron acceptors as well as ionized impurities, they may increase the scattering cross section of the electrons and contribute to the mobility suppression. These results can provide a guideline for the thickness optimization of high-mobility LBSO films grown on other substrates and further insights on the development of LBSO-based electronic devices.
Figure 3.1 Topographic AFM images of the LBSO films grown on (a) (001) SrTiO$_3$ and (b) (001) MgO substrates.
Figure 3.2 Crystallographic characterization of the LBSO epitaxial films grown on (001) SrTiO$_3$ and (001) MgO substrates. X-ray reciprocal space mapping around 103 LBSO on (a) (001) SrTiO$_3$ substrates (14-nm-thick and 1040-nm-thick films) and (b) (001) MgO substrates (44-nm-thick and 1000-nm-thick films). The red dotted lines show cubic symmetry. Cross-sectional intensity profiles of 103 LBSO peak on (c) (001) SrTiO$_3$ substrates (from (a)) and (d) (001) MgO substrates (from (b)).
3. Large Thickness Dependence of the Carrier Mobility in a Transparent Oxide Semiconductor, La-doped BaSnO$_3$

![Figure 3.3](image)

Figure 3.3 Thickness dependence of the crystal quality of the LBSO epitaxial films grown on (001) SrTiO$_3$ and (001) MgO substrates. (a) Average lattice parameters $(a^2c)^{1/3}$ and (b) lateral grain size ($D$) of the LBSO films grown on SrTiO$_3$ (white) and MgO (red).
Figure 3.4 Cross-sectional HAADF-STEM images for the LBSO films grown on (a) (001) SrTiO$_3$ and (b) (001) MgO substrates. Periodically spaced dislocations are seen on SrTiO$_3$ substrates while dislocations on MgO substrates are randomly located.
Figure 3.5 Cross-sectional LAADF-STEM images for the LBSO films grown on (a) (001) SrTiO$_3$ and (b) (001) MgO substrates. Threading dislocations are indicated with lines on the top surface of the LBSO films.
Figure 3.6 Thickness dependent electron transport properties of the LBSO films on SrTiO$_3$ and MgO substrates: (a) carrier concentrations, (b) thermopower, and (c) Hall mobility.
Figure 3.7 XAS around the Sn M$_{4,5}$ edge of a 500-nm-thick LBSO film on SrTiO$_3$ substrate. Additional Sn$^{2+}$ can be observed in LBSO (left, A).
Figure 3.8 Temperature dependence of electron transport properties of LBSO epitaxial films grown on (001) SrTiO$_3$ substrate. (a) conductivity, (b) carrier concentration, (c) Hall mobility, (d) thermopower.
Chapter 4. Buffer Layer-Less Fabrication of High-Mobility Transparent Oxide Semiconductor, La-doped BaSnO₃

4.1 Objective of this chapter

Although the previous chapter showed that threading dislocations are not the main source of mobility suppression in LBSO films, many reports approach the mobility suppression and the charge carrier propagation hindrance from reducing threading dislocations or grain boundaries. Therefore, the most common method for enhancing the mobility of LBSO films is inserting thick undoped BaSnO₃ buffer layers between doped BaSnO₃ film and substrate to reduce the density of threading dislocations. For example, A. Prakash et al. optimized the thickness of buffer and LBSO layer and found that the ideal buffer layer thickness was 124 nm [67]; Shin et al. used buffer layer thickness of 150 nm whereas Shiogai et al. used 200 nm [60, 68]. Although these studies observed improved electron mobilities in LBSO films, the buffer layer insertion does not fully compensate the extra deposition step in the film fabrication process since the mobility values are still significantly low compared to that of bulk single crystals. This can be an issue for practical device applications because one-step fabrication processes are much more preferred in mass productions.
In the previous chapter, it was observed that the electron mobility of epitaxial LBSO films was strongly suppressed for films thinner than 50 nm. The mobilities increased with increasing thickness and eventually saturated at 90–100 cm² V⁻¹ s⁻¹ (~200 nm on (001) MgO substrate and ~400 nm on (001) SrTiO₃ substrate). This implies that the initial several hundred nanometers in LBSO films play as buffer layers. Furthermore, the XAS spectrum of an LBSO film exhibited 2⁺ Sn valence states, which should not be detected from stoichiometric LBSO and suggest the presence of oxygen vacancies. Since the thickness dependence shows that the buffer region does not contribute much to the electron transport, the buffer region thickness needs to be reduced to achieve high mobility values without inserting additional buffer layers (Figure 4.1).

In this chapter, the results from the previous chapter was employed to design a one-step fabrication process for high-mobility LBSO films without inserting buffer layers. According to the existence of Sn²⁺ from the previous chapter, the driving hypothesis of this chapter regarded oxygen vacancies as the main lattice defects in the mobility suppressed buffer region (several hundred nanometers), which can be reduced by depositing the film under highly oxidative atmosphere (Figure 4.1). To reduce the formation of Sn²⁺ ions and oxygen vacancies in LBSO films [69], O₃ was injected during the film growth, which creates a much stronger oxidation environment compared to typically used O₂. The LBSO films grown in ozone (O₃-LBSO) indeed exhibited higher electron mobilities compared to the LBSO films deposited in oxygen (O₂-LBSO) without
inserting any buffer layer, especially for films thinner than 150 nm.

4.2 Experimental

2 %-La-doped LBSO epitaxial films were grown on (001) surface of SrTiO$_3$ substrates under O$_3$ and O$_2$ atmospheres using PLD technique. The substrate temperature was kept at 700 °C during the film growth, whereas the chamber pressures were 17 Pa for O$_3$-LBSO and 10 Pa for O$_2$-LBSO, respectively. In case of O$_2$-LBSO, only oxygen gas was injected in the chamber while the partial pressure of O$_3$ was set to 10% by an ozone generator for the synthesis of O$_3$-LBSO films. The films were annealed at 1200 °C in air to obtain the atomically smooth surfaces [56], and the thicknesses of the films varied from 11 nm to 450 nm.

4.3 Results and Discussion

All LBSO films were heteroepitaxially grown on the (001) SrTiO$_3$ substrates, which were confirmed by the XRD measurements. As shown in the Figure 4.2, stepped and terraced surfaces were observed in both O$_3$-LBSO and O$_2$-LBSO films. In order to clarify the structural differences in the LBSO films grown under O$_3$ and O$_2$ atmospheres in detail, the X-ray RSMs of the films were measured as shown in the Figure 4.3-6, respectively. In both cases, an asymmetric 103 diffraction spot of BaSnO$_3$ was observed around the 103 diffraction spot of SrTiO$_3$. Using these RSMs, both in-plane ($a$-) and cross-plane ($c$-)
lattice parameters were extracted as shown in Figure 4.7 (a). Due to the large lattice mismatch between LBSO and SrTiO$_3$ (−5 %), the lattice parameter $a$ was much smaller than the bulk value (0.4116 nm) whereas $c$ was larger than the bulk value at the beginning of the film growth (Figure 4.7 (a)). The $a/(c)$ increased/(decreased) with increasing the film thickness and approached the bulk value (0.4116 nm). It should be noted that the O$_3$-LBSO showed larger differences from the bulk at the beginning of the film growth.

The average lattice parameter $(a^2 \cdot c)^{1/3}$ calculated from the RSMs is shown in Figure 4.7 (b), which represents the bulk strain in the films. Although the $(a^2 \cdot c)^{1/3}$ of the O$_2$-LBSO films did not reach the bulk value, that of the O$_3$-LBSO increased drastically with the thickness and almost reached the bulk value. These results suggest that the lattice relaxation of the LBSO films occurred more quickly in the O$_3$ atmosphere. However, the lateral grain size ($D$) of films from both atmosphere showed similar tendencies (Figure 4.7 (c)): at the beginning of the film growth, the $D$ of the LBSO films were ~30 nm, which increased with thickness and saturated when the thickness exceeded ~150 nm.

In order to further clarify the lattice strains, the microstructure of the films was observed using LAADF-STEM as shown in Figure 4.8. While columnar structures were seen in both the O$_3$-LBSO [Figure 4.8 (a)] and the O$_2$-LBSO films [Figure 4.8 (b)], the density of the bright columns in the O$_2$-LBSO film is higher. Since the contrast in LAADF image is sensitive to the strain field (i.e., bulk strain), these results suggest that lattice strain was
be reduced under ozone atmosphere, which is in agrees with the RSM results.

The room temperature electron transport properties of the O$_3$-LBSO and O$_2$-LBSO films against the film thicknesses are summarized in Figure 4.9. The $n$ in the LBSO films increased with the thickness and approached the nominal $n_{nom}$, which is defined by the atomic concentration of the La-dopants ($\equiv$[2\%\,-La$^{3+}$] = 2.87 × 10$^{20}$ cm$^{-3}$). It should be noted that the $n$ of O$_3$-LBSO films exhibited a much faster increase compared to O$_2$-LBSO films. For example, the $n$ of ~100-nm-thick O$_3$-LBSO film is 87 % of the $n_{nom}$ while that $n$ of the O$_2$-LBSO film with the same thickness was only 46 % of the $n_{nom}$ (Figure 4.9 (a)).

Similar trends were observed in the $\mu_{Hall}$ and $\sigma$ of the LBSO films (i.e., faster increase with thickness in O$_3$-LBSO); the $\mu_{Hall}$ of ~100-nm-thick O$_3$-LBSO film was 103 cm$^2$ V$^{-1}$ s$^{-1}$, which is almost two times higher than 57 cm$^2$ V$^{-1}$ s$^{-1}$ for the O$_2$-LBSO film with the same thickness. The effect of the O$_3$ atmosphere can be clearly seen as O$_3$-LBSO films always exhibited significantly higher $\mu_{Hall}$ values compared to O$_2$-LBSO films at the same thickness (Figure 4.9 (b) and (c)). The highest $\mu_{Hall}$ value (115 cm$^2$ V$^{-1}$ s$^{-1}$) was observed in the 452-nm-thick O$_3$-LBSO film. In addition, the thermopower ($-S$) of the LBSO films decreased with increasing thickness (Figure 4.9 (d)), and the $S$ declination rate of O$_3$-LBSO films was much higher than that of O$_2$-LBSO films (Figure 4.9 (d)). Since $|S|$ decreases with $n$ [70], the observed $-S$ reduction is consistent with the thickness.
dependence of \( n \) (Figure 4.9 (a)). These results show that LBSO films grown under O\(_3\) atmosphere exhibit improved electron transport properties.

To validate the initial hypothesis on the role of oxygen deficiencies on the formation of Sn\(^{2+}\) states [69], XAS was performed around the Sn \( M_{4,5} \) edge of \( \sim 100 \)-nm-thick LBSO films on SrTiO\(_3\) substrate. Surface sensitive electron yield mode was used (the penetration depth of X-ray \( \sim 10 \) nm). The XAS spectra of the LBSO films are shown in Figure 4.10. In both films, four absorption peaks from stoichiometric Sn\(^{4+}\) ions were observed (Figure 4.10 (a)), which agree with other studies [39, 71, 72]. Interestingly, just as intended, Sn\(^{2+}\) peak at \( \sim 488 \) eV disappeared in the O\(_3\)-LBSO film and can only be seen from the XAS of O\(_2\)-LBSO film (Figure 4.10 (a)) [71, 73, 74]. The thicknesses of the O\(_2\)-LBSO and O\(_3\)-LBSO films were 107 nm and 125 nm, respectively. Despite the similar thickness values, the \( \mu_{\text{Hall}} \) of the O\(_2\)-LBSO film (57 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \)) was much lower compared to that of the O\(_3\)-LBSO film (103 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \)). This result suggests that the existence of the Sn\(^{2+}\) ion can indeed be related to the mobility suppression of LBSO films.

In the stoichiometric composition of BaSnO\(_3\), the stable valence state of Sn is 4+. If the two extra electrons from an oxygen vacancy form Sn\(^{2+}\) ion, the Sn\(^{2+}\) ions may degrade the carrier generation efficiency of La\(^{3+}\) ions and scatter electrons. Therefore, it is plausible for oxygen deficiencies to reduce the transport properties of electrons in LBSO.
In fact, MBE-grown LBSO films with high mobility were fabricated using highly oxidative atmosphere [37, 38, 67]. Thus, in the context of this chapter, it can be suspected that low mobility and low carrier concentration in LBSO films observed in other studies are related to the non-oxidative atmosphere. The mobility dependence on the thickness suggest that these defects are concentrated at the film/substrate interface. However, it should be noted that the formation of Sn$^{2+}$ states and oxygen vacancies in LBSO needs to be studied much more thoroughly to clarify their exact location in the film.

### 4.4 Conclusions

In this chapter, the electron mobility of LBSO films was successfully improved without inverting buffer layers by using highly oxidative atmosphere (O$_3$) during the film growth. The lattice relaxation of the O$_3$-LBSO films occurred when the film thickness was thinner than the O$_2$-LBSO films. Despite being smaller than single crystal values, the highest electron mobility observed here ($115 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is among the highest in LBSO films on SrTiO$_3$ substrates and similar to LBSO films with buffer layers. The XAS results showed that the Sn$^{2+}$ concentration in the LBSO films was successfully reduced by creating an oxidative atmosphere during the film growth with the injection of O$_3$. 
Figure 4.1 Hypothesis: Schematic illustration of LBSO films. (a) LBSO film grown under less oxidative atmosphere. Since the buffer layer is not fully oxidized, several hundred nanometer thick oxygen deficient buffer layer is initially grown on the substrate. After the lattice relaxation, high mobility LBSO film growth occurs. (b) LBSO film grown under enough oxidative atmosphere. A fully oxidized buffer layer is initially formed on the substrate. The lattice relaxation occurs in the thinner film, after that, high mobility LBSO film growth occurs. It is suspected that the buffer layer thickness should be very high to achieve the high mobility for low oxidative atmosphere since the buffer contains oxygen deficiency. On the other hand, buffer layer thickness highly reduced by using enough oxidative atmosphere to acquiring high mobility, which will be useful for practical application.
Figure 4.2 Topographic AFM images of the LBSO films grown on (001) SrTiO$_3$ under oxygen (left) and ozone (right) atmosphere.
Figure 4.3 Crystallographic characterizations of the O$_3$-LBSO films grown on (001) SrTiO$_3$ substrates. (a) RSMs of asymmetric (103) diffraction of O$_3$-LBSO films. The symmetry axis of a cubic lattice is indicated by a red line. (103) BaSnO$_3$ diffraction peak approaches the red line, which suggests that lattice strain due to the film/substrate mismatch is gradually decreasing; (b) the cross-sectional intensity plot along the in-plane axis in reciprocal space ($q_x/2\pi$); (c) thickness dependence of the lateral grain sizes; (d) thickness dependent lattice parameter along the in-plane direction (blue), out-of-plane direction (red), and the average lattice parameter (green). All these values approach the lattice parameter of bulk LBSO (black dashed line) with increasing film thickness.
4. Buffer Layer-Less Fabrication of High-Mobility Transparent Oxide Semiconductor, La-doped BaSnO$_3$

Figure 4.4 RSMs of O$_3$-LBSO films grown on (001) SrTiO$_3$ substrate around the (103) Bragg diffraction. The thicknesses of the films were (a) 11 nm, (b) 21 nm, (c) 28 nm, (d) 48 nm, (e) 85 nm, (f) 125 nm and (g) 452 nm.
**Figure 4.5 Crystallographic characterizations of the O$_2$-LBSO films grown on (001) SrTiO$_3$ substrates.** (a) RSMs of asymmetric (103) reflection of O$_3$-LBSO films. The symmetry axis of a cubic lattice is indicated by a red line. (103) BaSnO$_3$ diffraction peak approaches the red line, which suggests that lattice strain due to the film/substrate mismatch is gradually decreasing; (b) the cross-sectional intensity plot along the in-plane axis in reciprocal space ($q_x/2\pi$); (c) thickness dependence of the lateral grain sizes; (d) thickness dependent lattice parameter along the in-plane direction (blue), out-of-plane direction (red), and the average lattice parameter (green). All these values approach the lattice parameter of bulk LBSO (black dashed line) with increasing film thickness. The crystallographic characteristics of O$_2$-LBSO films were very similar with those of O$_3$-LBSO films.
Figure 4.6 RSMs of O$_2$-LBSO films grown on (001) SrTiO$_3$ substrates around the (103) Bragg diffraction. The thicknesses of the films were (a) 14 nm, (b) 21 nm, (c) 54 nm, (d) 107 nm, (e) 163 nm, (f) 234 nm, (g) 367 nm, and (h) 457 nm.
Figure 4.7 Lattice characteristics of the LBSO films at room temperature. Thickness dependences of (a) lattice parameters, $a$ and $c$, (b) average lattice parameter $(a^2 \cdot c)^{1/3}$, and lateral grain size for the resultant LBSO films grown under ozone (filled symbols) and oxygen (open symbols) atmospheres. Average lattice parameter of the O$_3$-LBSO increased dramatically with the thickness and almost reached the bulk value (0.4116 nm).
Figure 4.8 Cross-sectional LAADF-STEM images of the LBSO films. Columnar structure is seen in both (a) the O$_3$-LBSO and (b) the O$_2$-LBSO films. The strain contrast in O$_3$-LBSO is lower.
4. Buffer Layer-Less Fabrication of High-Mobility Transparent Oxide Semiconductor, La-doped BaSnO$_3$

Figure 4.9 Electron transport properties of the LBSO films. The O$_3$-LBSO (red) and the O$_2$-LBSO films: (a) conductivity, (b) carrier concentration, (c) Hall mobility, and (d) thermopower.
Figure 4.10 XAS spectra of the LBSO films. (a, b) Schematic cross-sectional structure and (c, d) XAS spectra at around the Sn $M_{4,5}$ edge of the LBSO films. Sn$^{2+}$ peak is not observed in the O$_3$-LBSO film.
Chapter 5. High Electrical Conducting Deep-Ultraviolet-Transparent Oxide Semiconductor, La-doped SrSnO$_3$

5.1 Objective of this chapter

Despite the excellent electron transport properties, applications of LBSO is limited to visible range, and optoelectronic engineers search for transparency in other ranges too. DUV (200–300 nm in wavelength) TOSs have attracted attention as transparent electrodes for DUV optoelectronic devices such as DUV light emitting diode and DUV detector for biological applications because most DNA show their absorption peaking around 260 nm in wavelength [75]. Among several DUV-TOSs, LSSO ($E_g$ ~4.6 eV) is one of the most promising materials since LSSO can be grown heteroepitaxially on the single crystalline substrates such as MgO [76], SrTiO$_3$ [77], and KTaO$_3$ [78]. Further, the electrical conductivity of LSSO films (~1000 S cm$^{-1}$) [45] is larger than other well-known DUV-TOSs such as $\beta$-Ga$_2$O$_3$ (~1 S cm$^{-1}$) [20, 21], $\alpha$-Ga$_2$O$_3$ (~0.3 S cm$^{-1}$) [22], electron-doped calcium aluminate (C12A7, ~800 S cm$^{-1}$) [23-25], and recently developed Al: Mg$_{0.43}$Zn$_{0.57}$O (~400 S cm$^{-1}$) [35]. However, the electrical conductivity of LSSO films is still much lower than that of commercially available transparent conducting oxide ITO.

The crystal structure of SrSnO$_3$ is regarded as pseudo-double-cubic perovskite ($a =$
0.8068 nm) [79] although the real lattice is orthorhombic [80]. Several researchers fabricated the epitaxial films of LSSO by using vapor phase epitaxy method such as PLD and MBE. However, due to difficulties in growing high-quality conductive LSSO films, their electron transport properties have not been extensively studied compared to the optical properties and electronic structures. Baba et al. reported that the electrical conductivity of 5% La-doped LSSO film on lattice matched NdScO₃ substrate was ~1000 S cm⁻¹ [45], which is the highest electrical conductivity to date. However, the carrier concentration was only 2.5 × 10²⁰ cm⁻³, which was only ~1/3 of La concentration, [La].

To improve the electrical conductivity of LSSO films, the activation of La dopants in the LSSO lattice needs to be enhanced.

In this chapter, in order to enhance the activation of La dopants, the LSSO films were annealed at 790 °C in vacuum (<10⁻² Pa). In case of LBSO films, annealing in oxygen reducing atmospheres enhance the lateral grain size. Therefore, it can be suspected that the point defect formation during the annealing in vacuum would induce grain growth and increase the activation of La dopants in LSSO films. After annealing, grain growth was indeed observed in LSSO films from ~10 nm to ~28 nm, and the electron transport properties of the annealed LSSO films were significantly improved. This chapter reports highly conducting (>3000 S cm⁻¹) LSSO thin films fabricated by PLD on MgO ($E_g \sim 7.8$ eV) [81] substrate followed by a simple annealing in vacuum.
5.2 Experimental

La$_x$Sr$_{1-x}$SnO$_3$ ($x = 0.005, 0.02, 0.03$ and $0.05$) epitaxial films were fabricated on (001) MgO ($a = 0.4212$ nm) single crystal substrates using PLD technique. During the film growth, substrate temperature and oxygen pressure inside the chamber were kept at 790 °C and 20 Pa, respectively. Conducting LSSO film was not obtained when the oxygen pressure was lower than 20 Pa, indicating that oxygen vacancies do not play as the electron donor, similar to LBSO. After the film growth, the substrate heater was immediately turned off, and the sample was cooled down to room temperature. The resultant film was annealed in vacuum at 790 °C for 30 mins.

5.3 Results and Discussion

The lateral grain sizes can be observed from the RSM of the resultant LSSO film ($x = 0.03$, as grown) measured around 204 diffraction spot of LSSO (Figure 5.1 (a)). Broad diffraction spot of 204 LSSO is seen peaking at ($q_x/2\pi, q_z/2\pi$) = (−4.97 nm$^{-1}$, 9.88 nm$^{-1}$) together with the 204 diffraction spot of MgO at (−4.75 nm$^{-1}$, 9.50 nm$^{-1}$), indicating that incoherent epitaxial growth occurred. The lateral grain size was ~12 nm, which was calculated by Scherrer's equation and the cross sectional diffraction pattern along $q_x/2\pi$ direction.

In order to increase the lateral grain size, the LSSO films were annealed at 790 °C in
5. High Electrical Conducting Deep-Ultraviolet-Transparent Oxide Semiconductor, La-doped SrSnO$_3$

vacuum ($<$10$^{-2}$ Pa) for 30 min and cooled down to room temperature. After the vacuum annealing, the 204 diffraction spot intensity increased as shown in Figure 5.1 (b), and the lateral grain size was successfully increased up to 28 nm. Similar increase in the diffraction spot intensity was observed in all cases ($x = 0.005$, 0.02 and 0.05) as shown in Figure 5.6. Using the 204 diffraction spots, the average lattice parameters, $(a^2\cdot c)^{1/3}$ of the LSSO films were determined before and after annealing (Figure 5.1 (c)). The annealed films showed more relaxation, which is likely attributed to the grain growth. Note that this annealing condition is the optimized condition among air, 1 Pa oxygen, and vacuum ($<$10$^{-2}$ Pa). Significant grain growth was observed when the LSSO film was annealed in vacuum. This is consistent with the observation of accelerated dislocation movement due to oxygen vacancy-assisted recovery in ionic crystals [82]. According to previous studies on stannate films, extra charge carriers from oxygen vacancies are compensated by the formation of charge accepting $A$-site vacancies [83]. Therefore, any carrier concentration changes that may result from the vacuum annealing are likely attributed to the activation of La dopants. In addition, no conducting LSSO film was obtained when undoped SrSnO$_3$ film was annealed in vacuum, which means that oxygen vacancy does not significantly affect carrier generation.

In order to further confirm the grain growth due to the vacuum annealing, the microstructures of the LSSO films were observed using LAADF-STEM. While columnar structures were observed for both the as-deposited (Figure 5.2 (a)) and annealed LSSO
films (Figure 5.2 (b)), the width of the columns for the annealed LSSO film was significantly greater. This indicates that the vacuum annealing indeed induces grain growth, which is in excellent agreement with the RSM results. It should be noted that incoherent interfaces with misfit dislocations was observed at the interface between the LSSO film and MgO substrate in both cases as shown in Figure 5.2 (c) and Figure 5.2 (d), indicating that the interface structures were not affected by the vacuum annealing.

Figure 5.3 summarizes the electron transport properties of the resultant LSSO films at room temperature. Both carrier concentration and Hall mobility gradually increased with [La] until [La] = 3% and decreased at [La] = 5%, probably due to the low solubility limit of La in SrSnO$_3$ lattice, which is similar to LBSO. Significant enhancements in the electron transport properties were observed in the vacuum annealed LSSO films. Compared to the as grown LSSO films, the annealed LSSO films showed greater $\sigma$ (Figure 5.3 (a)), $n$ (Figure 5.3 (b)), and $\mu_{\text{Hall}}$ (Figure 5.3 (d)) at room temperature while the largest enhancement was observed in 5% La doped LSSO film. The absolute value of $S$ for LSSO films decreased after annealing (Figure 5.3 (e)). This is consistent with the fact that carrier concentration increased after annealing. The activation rate of La ion (Figure 5.3 (e)), which was calculated as $n \cdot [\text{La}]^{-1}$ assuming La$^{3+}$ ions solely generate carrier electrons, increased after the vacuum annealing. Thus, the increased $\sigma$ and $\mu_{\text{Hall}}$ of annealed films are probably attributed to the improved efficiency of the carrier activation from the La dopant and the grain growth. In other words, carrier electrons are more
efficiency provided in the annealed films. The highest $\sigma$ and $\mu_{\text{Hall}}$ were observed from annealed 3%-La doped LSSO films, of which the activation of La ion and lateral grain size showed the largest value.

The experimental $m^*$ value of the LSSO epitaxial films was also clarified by the relationship of $S$ and $n$ of resultant films at room temperature (Figure 5.4 (a)). Since $n$ and $S$ values both are only sensitive to the density of states and Fermi level, the $m^*$ was calculated using the following equations [84].

\begin{equation}
S = -\frac{k_B}{e} \left( \frac{(r + 2)F_{r+1}(\xi)}{(r + 1)F_r(\xi)} - \xi \right)
\end{equation}

where $k_B$, $\xi$, $r$, and $F_r$ are the Boltzmann constant, reduced Fermi energy, scattering parameter of relaxation time, and Fermi integral, respectively. The $r$ value was assumed to be 0.5 (acoustic phonon scattering) because the temperature dependence of Hall mobility showed that phonon scattering is dominant at room temperature. $F_r$ and $n$ are given by,

\begin{equation}
F_r(\xi) = \int_{0}^{\infty} \frac{x^r}{1 + e^{x-\xi}} dx
\end{equation}

\begin{equation}
n_{-} = 4\pi \left( \frac{2m^*k_B T}{\hbar^2} \right)^{3/2} F_{3/2}(\xi)
\end{equation}

where $\hbar$ and $T$ are the Planck constant and absolute temperature, respectively. Most of the $S - n$ plots ($n > 10^{20}$ cm$^{-3}$) are located on the line obtained from $m^* = 0.23 m_0$, similar to that of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{SnO}_3$, though two points ($n < 10^{20}$ cm$^{-3}$) are located on the lower side,
probably due to the contribution of the tail state around the CBM.

**Figure 5.4 (b)** summarizes the $\mu_{\text{Hall}}$ of the LSSO epitaxial films as a function of $n$ at room temperature. The values reported by Wang et al. and Baba et al. are also plotted for comparison [85, 45]. The $\mu_{\text{Hall}}$ increased with increasing $n$. The highest $\mu_{\text{Hall}}$ and electrical conductivity were observed from 3% La-doped LSSO film. The $\mu_{\text{Hall}}$ reached 55.8 cm$^2$ V$^{-1}$ s$^{-1}$ at a $n$ of $3.26 \times 10^{20}$ cm$^{-3}$, which a record high value reported from LSSO films. Moreover, an electrical conductivity exceeding 3000 S cm$^{-1}$ was achieved in the annealed 3% La-doped LSSO film, which is much higher than that of many other DUV transparent conducting oxides.

Finally, the optical transmission and reflection spectra of the vacuum annealed 3% La-doped LSSO film (thickness: 112 nm) grown on double side polished (001) MgO substrate are shown in the inset of **Figure 5.5**. The optical transmission in the deep UV region was kept ~70% at 300 nm and exceeded 25% at 260 nm, which is the absorption peak wavelength of most DNAs. Although SrSnO$_3$ has an indirect bandgap [86], the bandgap was estimated by assuming a direct bandgap for simplicity; $(\alpha \cdot h \cdot \nu)^2$–photon energy plot was used to estimate the bandgap of the LSSO film (**Figure 5.5**), where $\alpha$ is the absorption coefficient and $\nu$ is speed of light. The bandgap obtained was ~4.6 eV, agreeing well with the reported values. The $\alpha$ at 260 nm in wavelength was calculated to be $8.3 \times 10^4$ cm$^{-1}$; the penetration depth of 260 nm light in LSSO is ~120 nm, which is
the origin of low transmission (25%) in the 260 nm light through the 112 nm LSSO film. Thus, most of the 260 nm light can transmit through LSSO film when the thickness is thinner. From these results, it can be concluded that present LSSO film, which exhibited high electrical conductivity of \( \sim 3000 \text{ S cm}^{-1} \) and deep UV transparency, would be useful as the transparent electrode for developing DUV-transparent optoelectronic devices for biological applications. The figure-of-merit \( \varphi_{TC} = \frac{T^{10}}{R_s} \) (\(T\) is transmission and \(R_s\) is the sheet resistance) [87] of the present LSSO film is \( 14.5 \times 10^{-3} \Omega^{-1} \), which is four orders magnitude higher than that of \( \beta-\text{Ga}_2\text{O}_3 \) (\( \varphi_{TC} = 7.8 \times 10^{-7} \Omega^{-1} \)) at 300 nm.

### 5.4 Conclusions

In this chapter, highly conducting (>3000 S cm\(^{-1}\)) LSSO thin films with an optical bandgap of \( \sim 4.6 \text{ eV} \) were fabricated. From the XRD and the STEM analyses, it was found that lateral grain growth occurred during the vacuum annealing, which improved the activation rate of La ion, leading to significant improvements in the carrier concentration (\( 3.26 \times 10^{20} \text{ cm}^{-3} \)) and Hall mobility (55.8 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). The optical transmission at 300 nm was \( \sim 70 \% \) and that at 260 nm exceeded 25 %. The present DUV-TOS would be useful as the transparent electrode in DUV-transparent optoelectronic devices, especially for biological applications.
Figure 5.1 Lateral grain growth of the LSSO films by vacuum annealing. (a, b) RSMs around 204 LSSO diffraction spot of (a) as grown and (b) annealed films. The cross-sectional diffraction patterns along $q_x/2\pi$ direction are shown at the bottom of each RSM. (c) Changes in (upper) the average lattice parameter and (lower) lateral grain size of the as-deposited LSSO films (white) and annealed LSSO films (red) as a function of La concentration in the target materials. The vacuum annealing substantially increased the lateral grain size.
Figure 5.2 Cross-sectional LAADF-STEM images for the LSSO films. (a, c) as grown and (b, d) annealed LSSO films. The lateral grain growth of annealed LSSO films is clearly visualized. Incoherent interfaces with misfit dislocations are seen at the interface between the LSSO film and MgO substrate in both cases. The interfaces are not affected by the vacuum annealing.
Figure 5.3 Electron transport properties of the resultant LSSO thin films as a function of La content (%) at room temperature. (a) Electrical conductivity ($\sigma$), enhancement of $\sigma$ for the vacuum annealed LSSO films increased with the La content. (b) Carrier concentration ($n$). $n$ of LSSO film increased after annealing in vacuum. (c) Thermopower ($-S$). The absolute value of thermopower ($S$) decreased after annealing. (d) Hall mobility ($\mu_{\text{Hall}}$). The $\mu_{\text{Hall}}$ of the annealed LSSO films was largely enhanced at 5% La$^{3+}$. (e) Activation rate of La ion. After vacuum annealing, La ion became more active.
Figure 5.4 (a) Thermopower ($-S$) and (b) Hall mobility ($\mu_{\text{Hall}}$) of resultant LSSO films as a function of carrier concentration ($n$) at room temperature. The carrier effective mass ($m^*$) values of LSSO is 0.23 $m_0$, which is clarified by the thermopower measurements. By the thermal annealing in vacuum, electrical conductivity exceed 3000 S cm$^{-1}$ in LSSO film was achieved in addition to the mobility reached value as high as 55.8 cm$^2$ V$^{-1}$ s$^{-1}$ at a carrier concentration of $3.26 \times 10^{20}$ cm$^{-3}$. The values reported by Wang et al. (blue square) and Baba et al. (orange circle) are also plotted for comparison.
Figure 5.5 Optical bandgap of the resultant 3% La-doped LSSO thin film. The $E_g$ was ~4.6 eV, which was obtained from the linear relationship of $(\alpha h\nu)^2$ – photon energy with assuming a direct bandgap. The absorption coefficient $\alpha$ was obtained from the transmission and reflection data shown in the inset.
FIG. 5.6 RSM near 204 diffraction spot of the LSSO films. (a-d) as-deposited film, (e-h) vacuum annealed at 790 °C for 30 min (< 10^{-2} Pa).
Chapter 6. Tuning of the Optoelectronic Properties for Transparent Oxide Semiconductor $\text{A}\text{SnO}_3$ by Modulating the Size of $A$-ions

6.1 Objective of this chapter

Optimizing the tradeoff relationship between optical bandgap and electrical conductivity is essential in DUV optoelectronic applications. In this regard, La-doped $\text{A}\text{SnO}_3$ films are interesting due to their wide bandgap and high electrical properties. As shown in previous chapters, LBSO thin films show high mobility value of 115–183 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature [37]. When a smaller Sr atom is substituted in the $A$-site, SrSnO$_3$ show $E_g$ of $\sim$4.6 eV allowing SrSnO$_3$-based TFT to transmit DUV light with a wavelength of 260 nm by more than 50%, which has great potential in DNA-sensing. Following this trend, if Ca, an even smaller alkaline element, occupies the $A$-site (CaSnO$_3$), further widening of the $E_g$ value can be expected. However, the reported theoretical and experimental bandgap values of CaSnO$_3$ scattered from 1.95 to 5.38 eV [46-48].

$\text{A}\text{SnO}_3$ has perovskite structure composed of corner-sharing SnO$_6$ octahedra with the $A$-site cation. The crystal structure of $\text{A}\text{SnO}_3$ is closely related to lattice parameter which determined by $A$-site substitution. The smaller $A$-site cation with stronger binding force of nucleus trigger deformations in the SnO$_6$ octahedral and further induce phase transition
in $\text{ASnO}_3$ [88]. As shown in Figure 6.1, $\text{BaSnO}_3$ ($a = 4.116 \text{ Å}$) is cubic crystal structure with the space group $Pm\bar{3}m$. $\text{SrSnO}_3$ ($a_{pc} = 4.037 \text{ Å}$) and $\text{CaSnO}_3$ ($a_{pc} = 3.954 \text{ Å}$) are pseudo cubic crystal structure with the space group $Pnma$, both distorted by an octahedra tilting. Thus, the lattice parameter of $\text{ASnO}_3$ can be modulated from 3.954 to 4.116 Å by substituting the $A$-site. Although this system can be considered as an excellent solution to find balanced optoelectronic properties, the effect of $A$-site substitution on the optoelectronic properties of $\text{ASnO}_3$ has not been clarified in detail due to the lack of a systematic study.

This chapter investigates the optoelectronic properties of $\text{ASnO}_3$ in forms of solid solution systems. With increasing average ionic radius of the $A$-site ion, the lattice parameter almost linearly increased from 3.95 to 4.14 Å while the optical bandgap decreased from $\sim 4.6$ to $\sim 3.6$ eV. With increasing lattice parameter, the electrical conductivity gradually increased from $\sim 10^0$ to $\sim 10^3$ S cm$^{-1}$ due to a gradual increase in both the carrier concentration and mobility. The electron transport properties of Ca-rich side solid solution films are greatly suppressed due to the large octahedral phase deformation, and La-doped $\text{CaSnO}_3$ (LCSO) showed an insulating behavior. On the other hand, LSSO exhibited a great balance between bandgap and electrical performance, which makes it a suitable $\text{ASnO}_3$ system for advanced optoelectronic applications.
6.2 Experimental

3% La-doped ASnO$_3$ solid solution epitaxial films were fabricated on (001) LaAlO$_3$ ($a = 3.821$ Å) single crystal substrates by PLD. 3% La-doped ASnO$_3$ single phase ceramics were used as the PLD targets. During the film growth, the substrate temperature and oxygen pressure inside the chamber were kept at 750 °C and 20 Pa, respectively. In order to relax the lattice strain caused by the mismatch between film and substrate, the thickness of all films was chosen to be ~200 nm. The X-ray RSMs were recorded to clarify the change of the lateral (in-plane) coherence length ($D$) evaluated from the diffraction spots using Scherrer equation. A spectrophotometer (solidspec-3700, Shimazu Co.) was used to collect ultraviolet-visible (UV-vis) diffuse reflectance data in 200–1700 nm wavelength range. The optical bandgap ($E_{\text{g opt}}$) was calculated using the Tauc plot, $(\alpha h\nu)^2 = C (h\nu - E_{\text{g}})$.

6.3 Results and Discussion

According to the XRD results, all the resultant films were heteroepitaxially grown on (001) LaAlO$_3$ substrate. The RSM of the resultant films was used to extract the lattice parameters perpendicular to the substrate surface ($c$-axis) and along the substrate surface ($a$-axis). In order to directly compare the lattice parameter of the films, the average values of $(a\cdot c)^{1/3}$ was used. Figure 6.2 shows change in the $(a\cdot c)^{1/3}$ with $A$-site ion substitution. Almost linear increase of lattice parameter was observed as a function of $x$ in
6. Tuning of the Optoelectronic Properties for Transparent Oxide Semiconductor $A\text{SnO}_3$
by Modulating the Size of $A$-ions

$\text{Ca}_{1-x}\text{Sr}_x\text{SnO}_3$, $\text{Sr}_{1-x}\text{Ba}_x\text{SnO}_3$, and $\text{Ba}_{1-x}\text{Ca}_x\text{SnO}_3$, confirming that ionic radii of the $A$-site ion dominate the lattice parameter. The lateral coherence length ($D$) of the $A\text{SnO}_3$ films was also calculated. Although the average lattice parameters of the $A\text{SnO}_3$ films are different from each other, the $D$ values are in the range of 20–30 nm, and there is no clear tendency observed with respect to the lattice parameter.

The optical transmission and reflection spectra of the resultant films were measured to calculate the absorption coefficient $\alpha$ as $\alpha = -[\ln (T + R) \cdot t^{-1}]$, where $T$, $R$, and $t$ are transmission, reflection, and thickness, respectively. Figure 6.3 shows the $E_{\text{g opt}}$ of the resultant films as a function of average lattice parameter, which gradually decreased from 4.64 eV ($\text{CaSnO}_3$) to 3.59 eV ($\text{BaSnO}_3$) with increasing the lattice parameter. By adjusting the composition of the solid solution, the $E_{\text{g}}$ of $A\text{SnO}_3$ can easily be modulated. This is attributed to the interaction between O 2p and Sn 5s orbitals, which consist the VBM and CBM of $A\text{SnO}_3$ respectively. The location of the CBM and VBM are affected by the Sn–O bond length. When the distance between two adjacent Sn$^{4+}$ and O$^{2-}$ becomes shorter, the energy splitting between the antibonding state (=CBM) and bonding state (VBM) becomes greater. Therefore, the optical bandgap decreased with increasing the lattice parameter.

Figure 6.4 summarizes room temperature electron transport properties of the La-doped $\text{Ca}_{1-x}\text{Sr}_x\text{SnO}_3$, $\text{Sr}_{1-x}\text{Ba}_x\text{SnO}_3$, and $\text{Ca}_{1-x}\text{Ba}_x\text{SnO}_3$ solid solution films as a function of the
average lattice parameter. The $\sigma$ increases more than three orders of magnitude from ~0.5 to 2240 S cm$^{-1}$ with increasing the average lattice parameter. This is due to gradual increases in both $n$ and $\mu_{\text{Hall}}$, which increase gradually with the average lattice parameter. The observed $n$ values are smaller than that of the nominal value, especially in regions of smaller lattice parameters. The absolute values of $S$ gradually decrease with lattice parameter, which is consistent with the fact that $n$ increases with lattice parameter. The increasing tendency of $n$ with lattice parameter is most likely due to the reduction of the bandgap with the lattice parameter increase. Suppression of $\mu_{\text{Hall}}$ fundamentally occurs due to two reasons. One is an increase in the carrier effective mass, and the other is the reduction of relaxation time, which strongly depends on the crystalline quality of the material. For example, with the presence of boundaries, carrier transport is suppressed at the boundary when the carrier concentration is low. According to the relationship between $S$ and log $n$, the carrier effective mass of the films were in the range from 0.2 to 0.3 $m_0$. Therefore, the $A$-site substitution does not strongly affect the carrier effective mass of the films. Thus, the small $\mu_{\text{Hall}}$ value at small lattice parameter side is mainly attributed to the reduction of carrier relaxation time.

In order to further investigate the tendency observed from the electron transport properties, temperature dependence of electrical resistivity of the films was measured (Figure 6.5 (a)). In La-doped Ca$_{1-x}$Sr$_x$SnO$_3$ and Sr$_{1-x}$Ba$_x$SnO$_3$ films, when lattice parameter is shorter than 3.97 Å, the ASnO$_3$ films showed an insulating behavior. On the other hand, when
lattice parameter is longer than 4.01 Å, the films showed a metallic behavior. The activation energy ($E_a$) of the electrical conductivity around room temperature is shown in Figure 6.5 (b). The $E_a$ gradually decreased from +22 meV to −14 meV with increasing the average lattice parameter. These results clearly indicate that the optoelectronic properties of $A$SnO$_3$ can be tuned by modulating the average $A$-site ionic radius.

Larger $A$-site ion substitutions result in the decrease of the bandgap and the mobility edge; the carrier generation efficiency increases when the bandgap decreases. The carrier relaxation time increases when the mobility edge decreases. Thus, the electrical conductivity increases when larger ion is substituted in the $A$-site.

6.4 Conclusions

This chapter systematically investigated the optoelectronic properties of $A$SnO$_3$ epitaxial films on (001) LaAlO$_3$ substrates and demonstrated that ionic radius of $A$-site ion can be used to modulate the optoelectronic properties of $A$SnO$_3$. The lattice parameter can be controlled almost linearly from 3.95 to 4.14 Å with increasing the average ionic radius of the $A$-site ion from 1.34 ($Ca^{2+}$) to 1.61 Å ($Ba^{2+}$) while the optical bandgap gradually decreased from ~4.6 to ~3.6 eV with a small positive bowing. The electrical conductivity gradually increased from ~$10^0$ to ~$10^3$ S cm$^{-1}$ due to a gradual increase in both the carrier concentration and mobility when the lattice parameter increased. The present results are
of significant importance for designing $A$SnO$_3$ material system in future transparent electronic devices.
Table 6.1 Electrical and optical properties of the La-doped $A\text{SnO}_3$ ($A = \text{Ca}, \text{Sr}, \text{Ba}$) films.

<table>
<thead>
<tr>
<th>$A$-site ion</th>
<th>$n$ ($10^{19}$ cm$^{-3}$)</th>
<th>$\mu_{\text{Hall}}$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
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<td>$-$</td>
<td>$-$</td>
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</tr>
<tr>
<td>Sr$^{2+}$</td>
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<td>51</td>
<td>1900</td>
<td>4.43</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>22</td>
<td>64</td>
<td>2235</td>
<td>3.59</td>
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</tbody>
</table>
6. Tuning of the Optoelectronic Properties for Transparent Oxide Semiconductor $A\text{SnO}_3$
by Modulating the Size of $A$-ions

Figure 6.1 Schematic crystal structure of (a) $\text{BaSnO}_3$ (b) $\text{SrSnO}_3$ and (c) $\text{CaSnO}_3$.

Crystal structures were obtained from the Rietveld refinement of the powder XRD patterns. $A\text{SnO}_3$ is consisted of layers of $\text{SnO}_6$ octahedra separated by $A$ atoms. $\text{BaSnO}_3$ ($a = 4.116 \text{ Å}$) is cubic crystal structure with the space group $Pm-3m$, $\text{SrSnO}_3$ ($a_{pc} = 4.037 \text{ Å}$) and $\text{CaSnO}_3$ ($a_{pc} = 3.954 \text{ Å}$) are orthorhombic crystal structure with the space group $Pnma$. The Shannon’s ionic radius of $\text{Ca}^{2+}$ is 1.34 Å, $\text{Sr}^{2+}$ is 1.44 Å, and $\text{Ba}^{2+}$ is 1.61 Å, respectively, when the coordination number is 12.
6. Tuning of the Optoelectronic Properties for Transparent Oxide Semiconductor $\text{A}\text{SnO}_3$
by Modulating the Size of $\text{A}$-ions

**Figure 6.2** Crystallographic analyses of the $\text{A}\text{SnO}_3$ films grown on (001) LaAlO$_3$ substrates. (a–c) RSMs of La-doped (a) CaSnO$_3$, (b) SrSnO$_3$, and (c) BaSnO$_3$. Red × symbol indicates the peak position of the diffraction spot of 103 $\text{A}\text{SnO}_3$. (d) Relationship between average lattice parameter and average ionic radius of $\text{A}$-site ion in $\text{A}\text{SnO}_3$. Solid line indicates the fitted curve. (e) Lateral coherence length of the $\text{A}\text{SnO}_3$ films plotted as a function of average ionic radius of $\text{A}$-site ion. The lateral coherence length is ranging around 20–30 nm and independent from the average ionic radius.
Figure 6.3 Optical properties of the ASnO$_3$ films. (a) Optical transmission spectra of the ASnO$_3$ films. The film thickness was $\sim$100 nm. The inset shows the magnified spectra around DUV region. (b) $(\alpha h\nu)^2$−$h\nu$ plots. (c) Optical bandgap ($E_g$) plotted as a function of average lattice parameter. $E_g$ gradually decreases with increasing lattice parameter. The $E_g$ of the La-doped CaSnO$_3$, SrSnO$_3$, and BaSnO$_3$ films are 4.64, 4.43, and 3.59 eV, respectively.
Figure 6.4 Room temperature electron transport properties of the La-doped Ca$_{1-x}$Sr$_x$SnO$_3$, Sr$_{1-x}$Ba$_x$SnO$_3$ and Ca$_{1-x}$Ba$_x$SnO$_3$ solid solution films as a function of average lattice parameter. (a) Electrical conductivity ($\sigma$). (b) Carrier concentration ($n$). (c) Hall mobility ($\mu_{\text{Hall}}$). (d) Thermopower ($S$). The solid lines are the guide-to-eyes. The dotted line in (b) indicates $n$ when doped La is fully activated. Both $n$ and $\mu_{\text{Hall}}$ gradually increase with increasing the lattice parameter. Therefore, $\sigma$ increases with lattice parameter. The increasing tendency of $n$ is confirmed by the decreasing tendency of $-S$. 
Figure 6.5 Activation energy of the electrical conductivity. (a) Temperature dependence of the electrical resistivity of the $\text{ASnO}_3$ films with various lattice parameters. (b) Activation energy of the electrical conductivity ($E_a$), which was calculated using the Arrhenius plot.
Chapter 7. Summary and Recommendations for Future Work

The given doctoral research addressed the fundamental optoelectronic properties of perovskite $A SnO_3$ system. The potential of this material system was examined in various optoelectronic applications including high-speed TFTs (LBSO), DUV-transparent biosensors (LSSO), and wide-bandgap semiconductors (LCSO).

Chapter 3 reported that the carrier mobility of LBSO films on (001) SrTiO$_3$ and (001) MgO substrates strongly depends on the thickness without any noticeable effects from the film/substrate lattice mismatch ($+5.4\%$ for SrTiO$_3$, $-2.3\%$ for MgO). The films on SrTiO$_3$ and MgO substrates exhibited large structural differences including the threading dislocation densities. However, the mobility dependences on the film thickness in both cases were almost the same, saturating at $\sim100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ while the charge carrier densities approached the nominal carrier concentration ($=[2 \% \text{ La}^{3+}]$). This clearly indicates that the carrier mobility in LBSO films strongly depends on the thickness. Previous studies mostly focused on eliminating threading dislocations for improving the mobility of LBSO films, but this chapter showed that other factors also have to be considered thoroughly.

The presence of Sn$^{2+}$ states in LBSO films lead to a hypothesis: the mobility of LBSO
films near the film/substrate interface is suppressed due to oxygen deficiency, which forms a buffered region. Therefore, in chapter 4, the buffered region in LBSO films with low electron mobility was eliminated by growing the films under highly oxidative ozone (O₃) atmospheres. The O₃ environments relaxed the LBSO lattice and reduced the formation of Sn²⁺ states, which are known to suppress the electron mobility in LBSO. The resultant O₃-LBSO films showed improved mobility values up to 115 cm² V⁻¹ s⁻¹, which is among the highest in LBSO films on SrTiO₃ substrates and comparable to LBSO films with buffer layers.

Investigation of the optoelectronic properties of ASnO₃ extended to LSSO, which is known as one of DUV-TCOs with an energy bandgap of ~4.6 eV. As such, LSSO has an excellent potential as a DUV-transparent electrode. However, the reported electrical conductivities of LSSO films are below 1000 S cm⁻¹, most likely due to the low activation solubility of La dopant in the LSSO lattice. Therefore, chapter 5 demonstrated that highly conducting (>3000 S cm⁻¹) LSSO thin films with an energy bandgap of ~4.6 eV can be fabricated by PLD on MgO substrate if a simple post annealing in vacuum is implemented. From the XRD and the STEM analyses, it was found that lateral grain growth occurred during the annealing, which improved the activation rate of La ion, leading to a significant improvement of carrier concentration (3.26 × 10²⁰ cm⁻³) and Hall mobility (55.8 cm² V⁻¹ s⁻¹). This showed that LSSO would be useful as a DUV-transparent electrode for advanced optoelectronic devices.
Chapter 6 showed that the optoelectronic properties of $A\text{SnO}_3$ can be tuned systematically by changing the average size of $A$-site ions. According to the structural characteristics, the optical absorption spectra, and the electron transport properties of the $A\text{SnO}_3$ films, the lattice parameter almost increased linearly from 3.95 to 4.14 Å with increasing the average ionic radii of the $A$-site ion from 1.34 ($\text{Ca}^{2+}$) to 1.61 Å ($\text{Ba}^{2+}$). The optical bandgap gradually decreased from $\sim$4.6 to $\sim$3.6 eV with a small positive bowing. The electrical conductivity gradually increased from $\sim$10$^0$ to $\sim$10$^3$ S cm$^{-1}$ due to gradual increase of both carrier concentration and mobility with increasing the lattice parameter. This chapter systematically demonstrated the overall trade-off relationship between the optical bandgap and the electrical transport properties in $A\text{SnO}_3$.

This doctoral research addressed all essential optoelectronic properties of $A\text{SnO}_3$ perovskites in both fundamental science and engineering perspectives. The fundamental characteristics of perovskite stannates associated with the optoelectronic properties found in this doctoral research will be of significant value in their utilizations in future device applications.

While this doctoral research addressed the all important optoelectronic properties of $A\text{SnO}_3$ perovskite systems, the commercialization of devices always down to the economic and technical viability. For example, high-quality epitaxial $A\text{SnO}_3$ films grow
7. Summary and Recommendations for Future Work

requires single-crystal substrates and high fabrication temperatures. In this regard, technologies associated with cost reduction such as film transfer [89-92] can be considered in future. Since the given research showed that post-treating process is an effective tool for enhancing the functional properties of $\text{ASnO}_3$ films, utilizing a low-cost fabrication tool that allows large-area deposition (i.e., sputtering, chemical vapor deposition) can be of value for examining the feasibility of mass production. The versatility in the optoelectronic properties of $\text{ASnO}_3$ system can also be considered in other functional applications. For example, since the electrical properties of LBSO strongly depends on the oxygen deficiency (chapter 4), electrochemical redox process [93] can be implemented in LBSO films for memory application. Further investigations in the fundamental transport characteristics will also be important. For instance, the interface between $\text{ASnO}_3$ films and substrates needs to be examined in more details with an emphasis on the electron transport mechanism to reduce the film thicknesses in devices. Dopants other than La can also be of interest in research community, especially for CaSnO$_3$ since no conducting CaSnO$_3$ film was reported to date.
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Acknowledgments

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*Girls, be ambitious!*

Mian Wei

Sapporo

2021.8
List of Publications

Papers related to this thesis:


Other papers:


List of Publications

contributed to this work) \( \text{IF} = 7.295, \text{TC} = 1 \text{WoS} \)
List of Presentations


List of Presentations

3rd Workshop on Functional Materials Science, Sapporo, Japan, December 18th-20th, 2019. (Poster)


[9] Mian Wei, Anup V. Sanchela, Bin Feng, Yuichi Ikuhara, Hai Jun Cho, and Hiromichi Ohta, “New Deep-Ultraviolet Transparent Oxide Semiconductor, La-doped SrSnO\(_3\)”, TOEO-11, Nara, Japan, October 7-9, 2019 Best Poster Award (Gold)

9月18日-21日。


List of Presentations

海道支部/第 14 回日本光学会北海道支部合同学术讲演会, Hokkaido University, 6-7 Jan. 2018 (Domestic) **Encouragement Award**
List of Awards

[1] Best Poster Award (Gold) at 11th International Symposium on Transparent Oxide and Related Materials for Electronics and Optics (TOEO-11) (October 9th, 2019). “New Deep-Ultraviolet Transparent Oxide Semiconductor, La-doped SrSnO$_3$”, Mian Wei, Anup Sanchela, Bin Feng, Yuichi Ikuhara, Hai Jun Cho, and Hiromichi Ohta


[3] Encouragement Award for Presentation in Hokkaido Branch of the Japan Society of Applied Physics, Mian Wei, Anup V. Sanchela, Bin Feng, Joonhyuk Lee, Gowoon Kim, Hyoungjeen Jeen, Yuichi Ikuhara, Hiromichi Ohta, “Origin of mobility suppression in La-doped BaSnO$_3$ films”, The 53rd JSAP Hokkaido Branch Meeting, Hokkaido University, Sapporo, Japan, 6-7 January, 2018