



이학박사 학위논문

Transport properties of 2-dimensional electron gas in perovskite oxide BaSnO₃-based systems

페로브스카이트 산화물 BaSnO₃ 기반 시스템에서 2차원 전자 가스의

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물리천문학부

조 형 민

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지도 교수 차 국 린

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> 서울대학교 대학원 물리천문학부 조 형 민

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위 육	원장_	이탁희	(인)
부위	원장 _	차국린	(인)
위	원_	최석봉	<u>(인)</u>
위	원_	최현용	(인)
위	원_	진형진	(인)

Abstract

Transport properties of 2-dimensional electron gas in perovskite oxide BaSnO₃-based systems

Hyeongmin Cho

Department of Physics and Astronomy The Graduate School Seoul National University

BaSnO₃ (BSO), also known as barium stannate, is a promising material with several excellent properties that have been reported so far. The superior properties of BSO compared to other perovskite oxides include: First, BSO can be easily doped with n-type dopants (especially, La dopant) and has high carrier density $(n_{3D} \sim 10^{20} \text{ cm}^{-3})$ and high electron mobility ($\mu \sim 320 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ in single crystals and $\mu \sim 70 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ in thin films), which is the highest among other perovskite oxides at room temperature. This property is essential for achieving efficient charge transport in electronic devices, leading to improved device performance. Second, BSO possesses excellent transparency in the visible spectrum, allowing light to pass through without significant absorption or scattering. This property makes it suitable for optoelectronic devices like transparent displays, solar cells, and sensors. Third, BSO demonstrates good thermal stability, retaining its electrical and optical properties even at elevated temperatures. This stability is crucial for applications involving high-temperature operations, such as power electronics and solid oxide fuel cells. Forth, BSO demonstrates excellent chemical stability, showing resistance to

degradation in various environments. This stability is advantageous for long-term device reliability and performance, particularly in harsh conditions or corrosive atmospheres. These excellent properties of BSO make it an intriguing material for a wide range of applications, including transparent field-effect transistors, energy harvesting, optoelectronics, and high-power devices.

In this dissertation, my research is mainly focused on heterostructures between BSO and other perovskite oxides, especially LaInO₃/BaSnO₃ and LaScO₃/BaSnO₃ heterostructures, in which 2-dimensional electron gas (2DEG) was formed at each interface. With the introduction of interface polarization model based on the calculation of the self-consistent Poisson-Schrödinger simulations and the confirmation of structural modifications of the heterostructures verified with highresolution transmission electron microscope, the analysis of 2DEG at the LaInO₃/BaSnO₃ interface was reaffirmed. And, previously unreported 2DEG generated at the LaScO₃/BsSnO₃ interface was confirmed through electrical and structural characteristics analyses, comparing the results with the LaInO₃/BaSnO₃ interface. The interface polarization model was applied to the LaScO₃/BaSnO₃ system, in which the polarization exists only over 4 pseudocubic unit cells in LaScO₃ from the interface and vanishes afterward like the LaInO₃/BaSnO₃ interface. Based on the calculations of the self-consistent Poisson-Schrödinger equations, the LaScO3 thickness dependence of n_{2D} of the LaScO₃/BaSnO₃ heterointerface is consistent with this model, and furthermore, a single subband in the quantum well is predicted. Finally, field-effect transistors composed solely of perovskite oxides with high fieldeffect mobility close to 100 cm²·V⁻¹·s⁻¹ at room temperature using conductive 2DEG interface and LaScO₃ as the gate dielectric was demonstrated.

Next, the possibilities of forming different types of 2-dimensional systems based on BSO are theoretically calculated using self-consistent Poisson-Schrödinger simulations. These include 2-dimensional hole gas (2DHG) generated at the LaScO₃/BaSnO₃ interface and 2-dimensional electron gas (2DEG) generated at the SrHfO₃/BaSnO₃ interfaces. As a result of running the simulations by varying adjustments of related parameters such as energy gap, conduction band offset to BSO, deep donor level, deep donor density, dielectric constant, effective mass, and polarization, 2-dimensional charge carriers could be formed at the interfaces of these new heterostructures. The theoretical calculations by the simulations are expected to be the basis for subsequent experiments in the future.

LaInO₃/BaSnO₃ heterostructures has recently been studied as a promising platform for realizing 2DEG with excellent transport characteristics, including fieldeffect devices at room temperature, but its low-temperature behavior is still not well understood. So, detailed investigations of the low-temperature properties of 2DEG at the LaInO₃/BaSnO₃ interface were performed. Negative magnetoresistance measured in perpendicular and parallel magnetic fields and no increase in electron mobility at low-temperature from Hall measurement suggest that this system is under weak localization regimes due to the high density of disorders including defects or threading dislocations in the films. After that, fabrication of electric-double-layer transistor using ionic-liquid and application of liquid gating to BSO-based 2dimensional systems are performed to improve transport properties by modulating the carriers at low-temperature. By using ionic-liquid gating, carriers were significantly modulated to more than 1 order, indicating that the feasibility of reversible liquid gating for carrier modulation in BSO-based 2-dimensional systems. Finally, several attempts to improve the electrical properties of BSO-based systems have been introduced, and preliminarily tested using 1% La-doped BSO (BLSO). First, the film was grown using new, previously unreported LaInO₃ substrates with orthorhombic structure whose lattice constant is matched with the BLSO film. Second, a new previously unreported Sr_{1-x}Ba_xHfO₃ buffer layer whose lattice constant is matched with the BSO buffer layer was used. Last, it was checked whether the electrical properties of the BLSO film are effectively improved through adjustment of target-to-substrate spacing or subsequent high-temperature heat treatment. Then, the characteristics of previously reported BLSO films and those of BLSO films including the above trials were compared and analyzed.

Keywords: BaSnO₃, LaInO₃, LaScO₃, perovskite oxides, 2-dimensional electron gas, field-effect transistor, low-temperature measurements, ionic-liquid gating

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Chapter 2.

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Chapter 3.

Figure 3.1. Sheet conductance (σ_s) before and after the formation of the interface between polar orthorhombic perovskite LaBO₃ (B = Sc, In) and 0.3% BLSO or undoped BSO. Little conductance enhancement occurs at the interface between LaBO₃ and undoped BSO deposited on STO substrate.

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Figure 3.10. Band diagram of the LSO/un-doped BSO calculated by the P-S simulation. From the interface to about 4 Å, the Fermi level (E_F) becomes lower than the valence band level (E_V), resulting in the generation of 2-dimensional hole gas (2DHG) at the interface. The inset is a magnified image with n_{3D} near the interface.

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Figure 3.12. Band diagrams of the 30 nm SHO/150 nm un-doped BSO calculated by the P-S simulations when varying (a) ΔE_{CB} , (b) E_{DD} , and (c) N_{DD} in the SHO layer, respectively.

Chapter 4.

Figure 4.1. High-resolution X-ray diffraction (HRXRD) measurements of (a) a 150 nm step-terrace BSO film on STO substrate (by PLD), and (b) a 110 nm BSO film on MgO substrate (by MBE). Each θ -2 θ scan shows diffraction peaks corresponding to (002) of BSO film deposited by PLD or MBE. (c) Two rocking curves were measured at each (002) peak of BSO, with full width at half maximum (FWHM) of 0.06 ° (by PLD) and 0.366 ° (by MBE).

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Chapter 1. Introduction

1.1. Perovskite oxide semiconductors

Oxide materials have been interested in their transparent conductive windows as well as their outstanding electrical properties. Various oxide semiconductors including SnO₂, ZnO, and In₂O₃ have been used as p-n junctions, field-effect transistors, and lasers in the UV spectrum in both academic and industrial areas [1-3]. These transparent conducting oxides, however, still have much to improve, and other types of oxide materials with higher carrier density and higher oxygen stability need to be studied. Perovskite oxides, the primary structure of ABO₃, are one of the best candidates. They can be easily doped with a higher concentration of carriers than other binary oxides (AO_x) and also possess several fascinating physical properties, such as superconductivity, ferromagnetism, ferroelectricity, and multiferroicity in YBa₂Cu₃O₇, Pb(Zr,Ti)O₃, and SrTiO₃ (STO) [4-6]. In particular, many studies have been conducted in the form of heterostructures in thin films.

1.2. BaSnO₃ properties

BaSnO₃ (BSO), also known as barium tin oxide, is a non-polar cubic perovskite oxide with a bulk lattice constant of 4.116 Å and a direct band gap of 3.1 eV [7]. This wide band gap property of BSO applies to transparent electronic devices and high-power devices. The band structure of BSO calculated from Ab initio shows that conduction bands are derived from Sn 5s orbitals, which are highly dispersive, resulting in the small effective mass of the carrier, and that the conduction band minimum is located at Γ point [8]. On the other hand, valence bands are derived from O 2p orbitals that are much less dispersive than 5s orbitals, with the valence band minimum located at R point.

1.2.1. High mobility

BSO can be easily doped with n-type dopants (especially, La dopant) [9, 10] and has high carrier density ($n_{3D} \sim 10^{20} \text{ cm}^{-3}$) and high electron mobility ($\mu \sim 320 \text{ cm}^2 \cdot \text{V}^ ^{1}$ ·s⁻¹ in single crystals and $\mu \sim 70$ cm²·V⁻¹·s⁻¹ in thin films), which is the highest among other perovskite oxides at room temperature [11-14]. La doping can be achieved up to high levels of 10^{20} cm⁻³ due to the combination of the low activation energy of La dopant and the high energy level of the donor states. And, the high room temperature mobility of BSO is attributed to its small effective mass and the single non-degenerate conduction band of 5s orbitals of Sn, whereas many perovskite oxides have triply degenerate bands of d orbitals, leading to low mobility [8,15,16]. In addition, Figure 1.1 (a) shows that the mobility of La-doped BSO (BLSO) single crystal is relatively high in the high level doping region of 10^{20} cm⁻³ compared to conventional semiconductors such as Si and GaN as well as oxide materials such as ZnO and STO [17-20]. BLSO films on STO, on the other hand, are under grain boundaries and threading dislocations caused by the large lattice mismatch between the BLSO films and the STO substrate, and nevertheless, mobility of BLSO film is still higher than that of other oxide materials [21]. So, if the lattice mismatch between the substrate and the film can be reduced by using a new substrate with a small lattice mismatch with the film or buffer layers with a complementary lattice constant as intermediate layers, the resulting threading dislocation density can be reduced, which in turn can lead to increased mobility in the BLSO film.

1.2.2. Low diffusion coefficient

Another feature of BSO compared to other perovskite oxides is that it has high oxygen stability. Figure 1.1 (b) shows the diffusion coefficient (*D*) of various perovskite oxides [1,22-26]. Perovskite oxides generally have a tendency to possess oxygen vacancy defects, which can affect their electronic and structural properties. However, BSO has a relatively high oxygen vacancy formation energy, making it less likely to form oxygen vacancies under normal conditions than other perovskite oxides. The theoretically calculated diffusion coefficient of BSO is in the order of 10^{-16} cm²·s⁻¹, which is 10^{10} times smaller than that of the well-known perovskite oxide STO [1,22,24]. In the case of STO, more oxygen vacancies are formed under similar conditions due to relatively low oxygen vacancy formation energy than that of BSO. This high oxygen stability of BSO can eliminate the effect of oxygen defects, which are considered problems with other perovskite oxides, and can interpret the electrical properties excluding the effect of oxygen diffusion when fabricating the heterostructures or devices using BSO.



Figure 1.1. (a) Mobility (μ) versus carrier density (n_{3D}) plot of La-doped BSO (BLSO) and other conventional semiconductors (Si, GaAs, and GaN) and oxide materials (ZnO and STO). (b) Diffusion coefficient (*D*) versus the reciprocal of absolute temperature (1/T) plot of various perovskite oxides.

1.2.3. 2-dimensional electron gas

For decades, the study of 2-dimensional electron gas systems has been conducted in various material systems due to their high electron mobility transistor (HEMT) fabrication possibilities, as well as their intriguing quantum phenomena. There are well-known conventional 2DEG heterostructures, such as AlGaAs/GaAs [27-29], AlGaN/GaN [30-33], and MgZnO/ZnO [34-37], with high 2-dimensional carrier density (n_{2D}) and mobility at each interface. There are well-known 2DEG heterostructures such as AlGaAs/GaAs, AlGaN/GaN, and MgZnO/ZnO, where n_{2D} is reported to be about 1013 cm⁻² at AlGaN/GaN, MgZnO/ZnO interfaces and to be about 1011 cm-2 at AlGaAs/GaAs interface, and the mobility has increased to hundreds of thousands as the fabrication process progresses. And in recent years, many studies have been conducted as perovskite oxide interfaces have been found to have n_{2D} larger than conventional 2DEG heterostructures, higher than 10^{13} cm⁻². The research of 2DEG at the perovskite oxide interfaces started with the polar LaAlO₃/non-polar SrTiO₃ (LAO/STO) interface. This interface has a high carrier density of about 3×10^{14} cm⁻² at the interface [38], as well as interesting physical phenomena such as superconducting [39], ferromagnetic [40], and Rashba spin-orbit coupling [41-43]. However, the origin of this high carrier density is still controversial due to the oxygen instability of STO, and its application as a semiconductor device is very insufficient due to its very low mobility at room temperature. In contrast, our report shows that LaInO₃/BaSnO₃ (LIO/BSO) interface, an alternative polar/nonpolar perovskite oxide interface, can produce stable 2DEG even at high temperatures, and using this stable 2DEG to fabricate all-perovskite HEMT operating at room temperature [44-51]. Figure 1.2 (b) shows the sheet conductance enhancement at the



Figure 1.2. (a) A 3-dimensional view of the LaInO₃/BaSnO₃ (LIO/BSO) interface. (b) Sheet conductance (σ_s) before and after LaInO₃ deposition as a function of the La concentration of the BaSnO₃ films.

LIO/BSO interface. Prior to LIO deposition, the BSO film by itself remains insulating ($\sigma_s > 10^{10} \Omega$) until La concentration of 0.3%. The conductance enhancement was measured after LIO deposition, and the sheet conductance was increased to more than 10⁴, meaning that 2DEG is generated at the interface at room temperature.

1.2.4. Field-effect transistor

Field-effect transistors (FETs) can be fabricated by using the BLSO as a channel layer and various oxide materials as gate oxides, which is also due to the oxygen stability of BSO. Table 1.1. shows the field-effect mobility (μ_{FE}) and on/off ratio when using various gate oxides. It can be confirmed that the FETs work well not only when using Al₂O₃ [52] and HfO₂ [53], which are often used in industry, but also

Interface	$\mu_{FE}~(cm^2~V^{-1}~s^{-1})$	Ion/Ioff
Al ₂ O ₃ /BLSO	17.8	10 ⁵
HfO ₂ /BLSO	24.9	10^{6}
BHO/BLSO	52.4	10 ⁶
LIO/BLSO	90	10^{7}
LSO/BLSO	98.7	10^{6}

when using the perovskite oxides BaHfO₃ (BHO) [54], LaInO₃ (LIO) [55], and LaScO₃ (LSO) [56].

Table 1.1. Field-effect transistors (FETs) fabricated by using the BLSO as a channel layer and various oxide materials as gate oxides.



Figure 1.3. (a) Schematic of the structure of the field-effect transistor using 0.2% BLSO as a channel layer and LaScO₃ (LSO) as a gate oxide. (b) Transfer characteristics of the device with the source-drain current (I_{DS}) represented by a red line, the leakage current (I_{GS}) represented by a red dashed line, and the calculated field-effect mobility (μ_{FE}) represented by the blue circles at room temperature.

Figure 1.3 (a) schematically shows the structure of the FET using 0.2% BLSO as a channel layer and LSO as a gate oxide. And, transfer characteristics of the device with the source-drain current (I_{DS}) represented by a red line, the leakage current (I_{GS}) represented by a red dashed line, and the calculated μ_{FE} represented by the blue circles are shown in Figure 1.3 (b). In particular, when using LIO or LSO as gate dielectrics, the maximum μ_{FE} is close to 100 cm²·V⁻¹·s⁻¹, which are also known as the highest μ_{FE} among FETs composed of all-perovskite oxides at room temperature [56]. It has recently been reported that 2DEG is formed not only at the LIO/BSO interface but also at the LSO/BSO interface. Therefore, the origin of the device's high performance can be attributed to the high conductivity of the channel from the formation of the 2DEG at the LIO/BLSO and LSO/BLSO interfaces, as well as the excellent gate dielectric properties of LIO and LSO which are chemically stable at high temperatures with high dielectric constant.

In this dissertation, my research based on BSO is largely divided into 4 chapters. First, I will focus on the 2-dimensional systems formed between BSO and other perovskite oxides, especially LIO/BSO interface and LSO/BSO interface. Second, the possibilities of forming different types of 2-dimensional systems based on BSO will be theoretically calculated using self-consistent Poisson-Schrödinger simulations. Third, low-temperature measurements and ionic-liquid gating of BSObased 2-dimensional systems will be performed and analyzed. Finally, several attempts will be introduced to improve the electrical properties of BLSO such as substrate change, buffer layer change, target-to-substrate spacing change, and heat treatment.

Chapter 2. 2-dimensional systems formed with BaSnO₃ – I. Basic

2.1. Introduction

The investigation of the 2-dimensional electron gas (2DEG) at the interface between perovskite oxides has been a subject of considerable interest for more than two decades, particularly at the polar LaAlO₃/non-polar SrTiO₃ (LAO/STO) interface. This interface has shown various intriguing physical phenomena, including superconductivity [39], ferromagnetism [40], and Rashba spin-orbit coupling [41-43]. These discoveries have generated considerable interest in SrTiO₃-based LaBO₃/SrTiO₃ polar interfaces with different 3d cations at the B-site, but none have surpassed the limitations of SrTiO₃-based interfaces, particularly their unstable oxygen stoichiometry. Several scenarios have been discussed for the principle that the 2DEG is generated at the interface, but have not yet been integrated. The polar catastrophe model, which is also known as the charge transfer model, is the most commonly accepted theory to explain the electronic reconstruction over the heterostructures [57]. Although this model can explain many of the observed physical phenomena related to the 2DEG, it can't explain some experimental results such as the insulating properties of the p-type interface [58], or the 2DEG density about 1 order lower than that calculated in this model. Other scenarios have also been reported, such as oxygen vacancies in the STO layer [59], La inter-diffusion from the LAO layer [60], and strain-induced lattice distortion at the interface [61], to elucidate the origin of the 2DEG. Meanwhile, recent reports first published by our laboratory have demonstrated that novel polar/non-polar perovskite interface, LaInO₃/BaSnO₃ (LIO/BSO), can generate 2DEG, and this interface is advantageous because it remains stable even at high temperatures [44-51]. Several experiments have shown that the origin of conductance enhancement at the LIO/BSO interface is neither from formation of oxygen vacancies in the BSO layer nor from La interdiffusion of the LIO layer. In addition, no conductance enhancement was observed at the BaHfO₃/BaSnO₃ (BHO/BSO) and SrZrO₃/BaSnO₃ (SZO/BSO) interfaces, in which BHO and SZO are non-polar perovskite with band gaps of 5.8 eV and 5.6 eV, respectively. Considering 2DEG is generated at the interface with LIO which has a smaller band gap and conduction band offset (ΔE_{CB}) than those of BHO and SZO, the polar nature of LIO and the resulting polar interface are critical factors in forming a conductive interface [44]. In this chapter, experimental and theoretical combined approaches were used to study the conductance enhancement in 2-dimensional systems formed with BSO. First, through the introduction of "interface polarization model" based on the calculation of the self-consistent Poisson-Schrödinger (P-S) simulations, and the confirmation of structural modifications of the heterostructures verified with a high-resolution transmission electron microscope, the analysis of 2DEG at the LIO/BSO interface was checked again [46]. Next, previously unreported 2DEG generated at the LaScO₃/BsSnO₃ (LSO/BSO) interface was confirmed through electrical and structural characteristics analyses, and was compared with that generated at the LIO/BSO interface, and finally all-perovskite high mobility field-effect transistor (FET) with best performance at room temperature was fabricated [56]. In all experiments, samples were grown by pulsed laser deposition using a KrF excimer laser ($\lambda \approx 248$ nm; Coherent) with following conditions: the temperature of 750 °C, the oxygen pressure of 100 mTorr, the targetto-substrate distance in the range of 45 - 55 mm, and the energy fluence in the range

of 1.3 - 1.5 J/cm² during all deposition. All targets were provided by Toshima Manufacturing Co. in Japan. To measure electrical transport properties such as sheet resistance (R_s), carrier density (n_{3D}), and electron mobility (μ), the Van der Pauw method and Hall measurement were conducted at room temperature. All of the above electrical properties were measured by using a Keithley 4200 SCS.

2.2. 2-dimensional electron gas at the LaInO₃/BaSnO₃ interface



Figure 2.1. (a) Polar orthorhombic perovskite (*Pnma*) LaInO₃ structure, and (b) non-polar cubic perovskite BaSnO₃ structure. Both figures were generated using VESTA software.

As shown in Figure 2.2, LaInO₃ (LIO) is a polar orthorhombic perovskite (*Pnma*) of a GdFeO₃-type with a band gap of 5.0 eV [55,62]. Its pseudocubic lattice constants (a_{pc}), calculated from the three lattice constants (a = 5.722 Å, b = 5.94 Å, and c = 8.215 Å) in the orthorhombic structure, is 4.117 Å, which almost matches with $a_{BSO} = 4.116$ Å [7,63,64]. Given the lattice constant of BSO, the growth of LIO on BSO is epitaxial coherent. When depositing an LIO layer on a BLSO layer on both STO and MgO substrates [44,45], conductance enhancement more than 10⁴ times were observed at room temperature, and using this LIO/BLSO heterostructures, high



Figure 2.2. (a) A 3-dimensional view of the LaInO₃/Ba_{0.997}La_{0.003}SnO₃ (LIO/BLSO(0.3%)) interface. (b) Changes of sheet conductance (σ_s) and sheet carrier density (n_{2D}) at the LaInO₃/Ba_{0.997}La_{0.003}SnO₃ interface as a function of the LIO thickness.

mobility FET ($\mu_{FE} \sim 60 \text{ cm}^2 \cdot V^{-1} \cdot s^{-1}$) with a large on/off current ratio ($I_{on}/I_{off} \sim 10^9$) were demonstrated. To further identify the mechanism of the 2DEG formation, the conductance variation of LaInO₃/Ba_{0.997}La_{0.003}SnO₃ (LIO/BLSO(0.3%)) as a function of LIO thickness on 0.3% BLSO ($N_d = 4.3 \times 10^{19} \text{ cm}^{-3}$) was investigated [46]. In Figure 2.2 (a), a 3-dimensional view of the LIO/BLSO(0.3%) interface was shown, and this was fabricated according to the following steps. A 150 nm un-doped BSO buffer layer was grown on the entire area of the 5 mm×5 mm TiO₂-terminated STO substrate. Next, a 12 nm 0.3% BLSO channel layer was deposited using a 3 mm×3 mm square-patterned Si stencil mask. Subsequently, 60 nm 4% BLSO contact layers were deposited using another type of Si stencil mask on the four corners of the channel layer, which can serve as good metallic contact layers as highly degenerately doped [7,21]. Last, LIO layers were deposited using the same 3 mm×3 mm mask, which covers the entire channel layer. Figure 2.2 (b) shows the variation of σ_s and n_{2D} during unit cell by unit cell deposition of the LIO layer on the 0.3% BLSO

channel layer. A significant increase in σ_s was observed from the first unit cell deposition of LIO. The level of σ_s rises steadily until it reaches its peak when the thickness of LIO is 4 unit cells. Beyond this point, the LIO layer becomes thicker, resulting in a gradual decrease in σ_s until reaching 100 nm. Furthermore, n_{2D} follows a similar pattern, with an increase in n_{2D} until an LIO thickness of 4 unit cells, followed by a slow decline. This augmentation of σ_s and n_{2D} with an increase in the LIO thickness has been replicated in numerous LIO/BLSO heterostructures samples. Compared to the well-known LAO/STO 2DEG [38,65,66], the critical thickness at which the conductance begins to increase after 4 unit cells of LAO deposition doesn't exist for the LIO/BLSO interface. This suggests that polar catastrophe model commonly used to describe polar LAO/non-polar STO system may not be applicable to polar LIO/non-polar BLSO systems. Therefore, a new model was needed to explain the change in electrical properties of this particular LIO/BLSO interface, and analysis was initiated using Poisson-Schrödinger formalism, which is used in a consistent manner in semiconductor heterostructres.

2.2.1. Analysis using Poisson-Schrödinger simulations

The Poisson-Schrödinger formalism is a method of determining both the charge distribution and the band bending throughout a semiconductor heterostructures in a consistent manner. It establishes the potential landscape relative to the Fermi level (E_F) , which helps to calculate n_{3D} and n_{2D} as well as the confinement length. To accomplish this, self-consistent 1-D Poisson-Schrödinger (P-S) band calculator developed by Snider was utilized [67]. From this solver, the calculation of n_{2D} was performed to find an adequate model to explain the LIO/BLSO interface. The

Poisson-Schrödinger simulations (P–S simulations) computes the 1-dimensional Poisson and Schrödinger equations self-consistently in an iterative manner.

$$-\frac{\hbar^2}{2}\frac{d}{dx}\left(\frac{1}{m^*(x)}\frac{d}{dx}\right)\psi_k(x) + V(x)\psi_k(x) = E_k\psi(x)$$
(2.1)

$$V(x) = -q\phi(x) + \Delta E_C(x)$$
^(2.2)

$$-\frac{d}{dx}\left(\varepsilon_{s}(x)\frac{d}{dx}\right)\phi(x) = \frac{q(p(x) - n(x) + N_{D}^{+}(x) - N_{A}^{-}(x))}{\varepsilon_{0}}$$
(2.3)

$$n(x) = \sum_{k=1}^{m} \psi_k^*(x) \psi_k(x) n_k$$
(2.4)

$$n_{k} = \frac{m^{*}}{\pi\hbar^{2}} \int_{E_{k}}^{\infty} \frac{1}{1 + \exp{\frac{E - E_{F}}{k_{B}T}}} dE$$
(2.5)

First, we use a trial potential in the Schrödinger equation of eq (2.1) to obtain the eigenfunctions and energy eigenvalues. Then, we put these eigenfunctions and energy eigenvalues into the Poisson equation of eq (2.3) and get a corrected potential as a solution. Last, we take this modified potential back into the Schrödinger equation of eq (2.1) and repeat this process until the solution again satisfies both equations. From such P-S simulations, the band bending, the charge distribution, and the subband characteristics in the given semiconductor heterostructures can be



Figure 2.3. General flow diagram of the self-consistent Poisson-Schrödinger (P-S) band calculator developed by Snider *et al* [67].

obtained. A schematic diagram of the described simulation flow is summarized in Figure 2.3. In most of the simulations conducted in this chapter, the surfaces and the interfaces with substrates were subjected to an ohmic boundary condition, in which all E_F are in the middle of the band gaps. Additionally, all simulations included undoped BSO buffer layer over 100 nm from the substrate. The results showed that the interface between the layers led to charge transfer and band bending, but as the layers passed through the buffer layer and approached the substrate, the bands reverted to their original, flat bulk values. Therefore, it is reasonable to assume that the interface with the substrate is charge-neutral because any charge transfer that could violate the charge neutrality condition is located far from the interface with substrate. However, the validity of charge neutrality at the surface is uncertain. In the structures studied in this chapter, LIO is present at the surface, which is in contact with air. It may not be appropriate to use ohmic boundary conditions when there is no charge reservoir like metal present at the surface. The important input material parameters of BSO

Material	$E_{\rm g}$ (eV)	$\Delta E_{\rm CB}$ to BSO (eV)	к	m _e */m _e	E _D (eV)	E _A (eV)
BaSnO ₃	3.1	_	20	0.42	-0.63	1.55
LaInO ₃	5.0	1.6	38	0.46	2.5	_

Table 2.1. Material parameters used for BaSnO₃ and LaInO₃ in P-S simulations. and LIO for this simulation are energy gap (E_g), conduction band offset to BSO (ΔE_{CB}), dielectric constant (κ), effective mass (m_e^*), and polarization (P), and so on [7,46,55,68,69]. These values are summarized in Table 2.1. In those, donor ionization energy of BSO (E_D) is set to be -0.63 eV to ensure full ionization of Ladonors based on the experimental result that 4% BLSO has the E_F above the conduction band by 0.55 eV [54]. All values except P were used as the values obtained through the experimental results. Since it is not possible to directly measure P experimentally, various simulations were performed by substituting various values for P. The results from the P-S simulations of the LIO/BLSO(0.3%) heterostructures are shown in Figure 2.4. If there is a uniform polarization that extends infinitely in a



Figure 2.4. (a) Calculated n_{2D} as a function of the LIO thickness using different uniform polarization ($P_{uniform}$) values inside the LIO bulk. When $P_{uniform}$ is equal to 50 µC/cm², n_{2D} approaches the value of 3×10^{14} cm⁻² based on the "charge discontinuity" model, which is observed under the condition that the LIO thickness is large. (b) Interface polarization values used for P-S simulations of the LaInO₃/Ba_{0.997}La_{0.003}SnO₃ (LIO/BLSO(0.3%)) interface. The polarization exists over 4 pseudocubic LIO unit cells from the interface and disappears after them. (c) Comparison of n_{2D} by experiments (red circles) with those by simulations (sky blue dotted lines) at room temperature. The deep donor density (N_{DD}) in the LIO is set to 2×10^{20} cm⁻³ in the middle of the band gap.

direction perpendicular to an ideal boundary, any polarization discontinuity (ΔP) across that boundary will lead to a surface charge density of $n_{2D} = \Delta P/e$. Figure 2.4 (a) shows Calculated n_{2D} as a function of the LIO thickness using different uniform polarization ($P_{uniform}$) values inside the LIO bulk. When $P_{uniform}$ is equal to 50 µC/cm², n_{2D} approaches the value of 3×10^{14} cm⁻² based on the "charge discontinuity" model, which is observed under the condition that the LIO thickness is large [57]. However, it is evident that none of the uniform polarization values replicate the experimental n_{2D} data in Figure 2.2 (b) across the entire LIO thickness range. To match the first data point at 8 Å of LIO, a significant polarization value of 65 μ C/cm² is necessary. Nevertheless, to align with the n_{2D} values for greater LIO thickness, a substantially lower polarization value is required. As a result, after the initial two unit cells of LIO, a non-uniform polarization with a sharp decrease in high polarization was considered. The peak of n_{2D} for 4 unit cells LIO layer, as seen in Figure 2.2 (b), we hypothesize an interface polarization in LIO that vanishes after 4 unit cells. The optimal fit to the experimental data as a function of LIO film thickness was accomplished by establishing the polarization in the first two pseudocubic unit cells 65 μ C/cm², the third unit cell 25 μ C/cm², and the fourth and final unit cell 10 μ C/cm², as presented in Figure 2.4 (b). we named this vanishing polarization the "interface polarization" model where the 2DEG-inducing polarization in the polar orthorhombic LIO exists only near the interface with non-polar cubic BSO [46,70]. Applying this model, we described the variation of the n_{2D} , in which the n_{2D} increases for the first 4 unit cells of LIO, reversely decreases for a few nm of LIO, and then approaches a constant value for thicker LIO. Furthermore, no critical thickness of LIO in forming 2DEG can also be explained by this model. At the same time, these polarization values are primarily dependent on the conduction band offset to BSO (ΔE_{CB}). For the currently set the interface polarization values ($65/65/25/10 \ \mu C/cm^2$), it acts like a 1.5 eV of $\Delta E_{\rm CB}$ (Then, total $\Delta E_{\rm CB}$ is equal to 3.1 eV), and if the experimental $\Delta E_{\rm CB}$ is to be 2.0 eV instead of 1.6 eV, setting polarization to be 50 μ C/cm² in the first two unit cells effectively acts like a 1.1 eV of ΔE_{CB} , producing almost the same n_{2D} [51,71]. In other words, n_{2D} is determined by combining the values of the interface polarization and the effect of ΔE_{CB} . As can be seen in Figure 2.4 (c), the calculated n_{2D} with introducing interface polarization is well matched to the experimental n_{2D} at room

temperature even until the thickness of the LIO reaches 100 nm, in which the deep donor density (N_{DD}) in the LIO is set to 2×10²⁰ cm⁻³ in the middle of the band gap. The decreasing n_{2D} beyond 4 unit cells of LIO is due to the reversing potential starting at the end of the interface polarization. In order to screen such potential, positive charges will be needed, hence the introduction of the deep donors. These deep donors can provide the positive charges for screening when they are excited when the E_F is lower than the deep donor state level near the interface. Once the screening is finished by such deep donors, the band bending stops. In this case, N_{DD} = 2×10²⁰ cm⁻³ in the middle of the band gap of LIO can fit our experimental n_{2D} very well. These deep donor states can very well be the oxygen vacancy states in the LIO film, which can be ionized to be positively charged when the E_F is lower than the



Figure 2.5. Band diagram of the LaInO₃/Ba_{0.997}La_{0.003}SnO₃ (LIO/BLSO(0.3%)) calculated by the P-S simulations. The sample structure in the simulations is the same as Figure 2.2 when the LIO thickness is 100 nm, and the N_{DD} value in Figure 2.4 was applied.
oxygen vacancy state level. the N_{DD} of 2×10^{20} cm⁻³ in LIO corresponds to LaInO_{2.993}. Next, the band diagram of LIO/BLSO(0.3%) calculated by P-S simulations with interface polarization is shown in Figure 2.5. The sample structure in the simulations is the same as Figure 2.2 when the LIO thickness is 100 nm, and the N_{DD} value in Figure 2.4 was applied. The bands in the LIO layer are being tilted by the interface polarization, resulting in an overall downward tilt of the bands at the LIO/BLSO interface. Then, it creates a quantum well of about 2 nm in the BLSO layer near the interface. This confinement length of 2 nm is consistent with the results of thermopower measurements or capacitance-voltage (C–V) measurements of the LIO/BSO heterostructures recently reported by other groups [15,50,51]. So far, we have well explained the particular trend of n_{2D} at the LIO/BLSO interface using P-S simulations by stages, which include novel interface polarization model. The next issue is, what is the origin of this polarization that exists only in a few unit cells near the interface. We were trying to find the reason through structural analysis of the heterostructures.

2.2.2. Origin of polarization at the interface

Figure 2.6 (a) shows cross-sectional high-resolution transmission electron microscope (HRTEM) image of the LIO/BSO interface together with inset with the black frame [46]. The specimen for HRTEM measurements were prepared by tripod polishing and Ar ion milling at liquid nitrogen temperature using Gatan PIPS at reduced ion beam energies between $0.2 \sim 4$ keV. Examining the HRTEM pattern



Figure 2.6. (a) Cross-sectional high-resolution transmission electron microscope (HRTEM) image of the LIO/BSO interface. (b) An enlarged view of the LIO unit cells with a stick-and-ball-model of the orthorhombic structure of the LIO, showing octahedral tilting. Green, purple, and red balls represent La, In and O atomic columns, respectively. The image contains the tilt angle of the out-of-plane (t_{oop}) and in-plane (t_{ip}) oxygen octahedra axis, and the lattice constant of the out-of-plane ($2d_{oop}$). (c) Line profiles across the LIO/BSO interface of the laterally averaged values of $|t_{oop}|$, $|t_{ip}|$, $2d_{oop}$, and the intensity of oxygen atomic columns.

more closely, both as a whole and at individual atomic columns, indicates that despite the atomic number differences between LIO and BSO being minor, it is still possible to differentiate between them. And, the HRTEM patterns reveals that the LIO film grow epitaxially well on the BSO film. An enlarged view of the LIO unit cells with a stick-and-ball-model of the orthorhombic structure of the LIO are schematically indicated in Figure 2.6 (b), showing octahedral tilting. In this image, Green, purple, and red balls represent La, In and O atomic columns, respectively. The image also contains the tilt angle of the out-of-plane (t_{oop}) and in-plane (t_{ip}) oxygen octahedra axis, and the lattice constant of the out-of-plane (2_{doop}) . Line profiles across the LIO/BSO interface of the laterally averaged values of $|t_{oop}|$, $|t_{ip}|$, 2_{doop} , and the intensity of oxygen atomic columns are represented in Figure 2.6 (c), in which the BSO layer extends from layer 1 to layer 8 along the growth direction, and the LIO from layer 9 to layer 16. Then, the precise analysis of line profiles leads to the following conclusions: The gradual increase in the octahedra tilt from BSO layer to LIO layer takes place over a distance of 3 pseudocubic perovskite layers (from layer 7 to layer 10). This can be seen in the red and blue graphs in the line profiles. At the same time, for these 3 layers at the LIO/BSO interface where the octahedra tilt is suppressed, the 2_{doop} increases by more than 1.5%, as indicated by the orange graph in the line profiles. This indicates that the lattice constant of LIO at the interface was shifted by about 0.13 Å with respect to that of BSO, even though the difference in the pseudocubic lattice parameters of BSO and LIO is less than 0.01 Å, which corresponds to about 0.2%. It was recently reported that 2DEG formation due to the gradual suppression of the octahedral tilt and the resulting polar effect was also observed at the LAO/STO interface [61,73,74]. Hence, it is possible to assume that interface polarization of the orthorhombic perovskite near the interface can be produced by suppression of the octahedral tilt by coherent epitaxial growth on the cubic perovskite. Unfortunately, exact quantitative correlations between the structural modifications of the interface in the orthorhombic/cubic heterostructures and the resulting interface polarization have not yet been established in this work. Therefore, I tried to fabricate BSO-based novel orthorhombic/cubic systems other than the LIO/BSO heterostructures to further validate interface polarization model due to the coherent epitaxial growth of orthorhombic perovskite on cubic BSO.

2.3. 2-dimensional electron gas at the LaScO₃/BaSnO₃ interface

Material	Three lattice constants (Orthorhombic structure)	Orthorhombicity √2(b-a)/c	Pseudocubic lattice constant
LaGaO ₃	5.4922, 5.5245, 7.7740 Å	0.59 %	(pseudocubic) 3.891 Å
LaScO ₃	5.6800, 5.7911, 8.0950 Å	1.94 %	(pseudocubic) 4.053 Å
LaInO ₃	5.7229, 5.9404, 8.2158 Å	3.74 %	(pseudocubic) 4.117 Å
LaLuO ₃	5.8090, 6.0000, 8.3470 Å	3.24 %	(pseudocubic) 4.174 Å

Table 2.2. Lattice constants and orthorhombicity of polar orthorhombic perovskite $LaBO_3$ (B = Ga, Sc, In, and Lu).

Based on the experimental results of 2DEG at the LIO/BSO interface, it can be deduced that i.) polar interface and ii.) orthorhombic/cubic interface are required for 2DEG formation. A candidate group of materials for LaBO₃ that satisfies the above two conditions is shown in Table 2.2. In addition to $LaInO_3$ (LIO) [55,63,64], LaGaO₃ (LGO) [75-77], LaScO₃ (LSO) [78-80], and LaLuO₃ (LLO) [81-83] are all polar orthorhombic perovskites and have a similar pseudocubic lattice constant to BSO. With the same structure as the sample structure in chapter 2.2, 10 nm thick $LaBO_3$ (B = Ga, Sc, and Lu) was deposited on 0.3% BLSO, respectively, to check whether 2DEG was formed at each interface, and the results are summarized in Figure 2.7 (a); Conductance enhancement occurred at the interface between LSO and 0.3% BLSO, but no conductance enhancement occurred at the LGO/BLSO(0.3%) and LLO/BLSO(0.3%) interface. This means that the growth of polar perovskites on BSO which satisfy both conditions (polar interface and orthorhombic/cubic interface) is not sufficient conditions for 2DEG formation: iii.) In-plane lattice constant of polar orthorhombic perovskite, which is pinned with that of BSO due to the coherent epitaxial strain, is also critical to create 2DEG at the interface. In fact, according to a recently reported study of the BSO-based heterostructures, when a polar orthorhombic perovskite with a lattice constant similar to BSO grows coherently on the BSO, the in-plane lattice constant of the orthorhombic perovskite is pinned with



Figure 2.7. (a) Sheet conductance (σ_s) before and after the formation of the interface between polar orthorhombic perovskite LaBO₃ (B = Ga, Sc, In, and Lu) and 0.3% BLSO. (b) In-plane lattice constant of the LaBO₃ (B = Ga, Sc, In, and Lu) deposited on 0.3% BLSO film as a function of oxygen partial pressure during the deposition process. Only the in-plane lattice constants of LIO and LSO are nearly pinned with that of BSO.

that of the BSO due to coherent epitaxial strain, which induces inversion symmetry breaking near the orthorhombic/cubic interface, allowing the interfacial polar perovskite to possess polarization. In contrast, when a polar orthorhombic perovskite with relatively large lattice mismatch with BSO grows on the BSO, the in-plane lattice of the orthorhombic perovskite can't be pinned with that of the BSO, resulting in structural relaxation by forming new dislocations right from the interface [84]. These dislocations interfere with coherent epitaxial strain near the interface, which in turn greatly reduces the interfacial polarization at the polar interface. LIO corresponds to the former case, while LGO and LLO correspond to the latter case. Experimental results similar to those described above are shown in Figure 2.7 (b); Through HRXRD measurements, the in-plane lattice constants of each LaBO₃ (B = Sc, In, and Lu) in various heterostructures as a function of oxygen partial pressure during the deposition process were obtained. Interestingly, for LSO/BLSO(0.3%) heterostructures, the in-plane lattice of LSO is pinned to that of BSO only when the oxygen partial pressure is 100 mTorr during the deposition process, and only this heterostructures show conductance enhancement at the interface. On the other hand, there was no conductance enhancement for LSO/BLSO(0.3%) heterostructures deposited at 10 mTorr, in which the in-plane lattice of LSO is not pinned to that of BSO. In order to verify the validity that the coherent epitaxial strain plays an important role for the interface polarization and the resulting formation of the 2DEG state at the polar interface, the studies of unreported heterostructures between polar orthorhombic perovskite and BSO are needed, and I focused on the LSO/BLSO heterostructures.





Figure 2.8. (a) Polar orthorhombic perovskite (*Pnma*) LaScO₃ (LSO) structure which is generated using VESTA software. (b, c) A 3-dimensional view and a top view of the 21 (7×3) mesa-like capacitors with 4% BLSO contact layers. The area of the top electrode is about 5.31×10^{-4} cm⁻², and the appearance of the breakdown can be seen in the top view image.

As shown in Figure 2.8 (a), LaScO₃ (LSO) is a polar orthorhombic perovskite (*Pnma*) of a GdFeO₃-type with a band gap of 5.8 eV [85-88]. Its pseudocubic lattice constants (a_{pc}), calculated from the three lattice constants (a = 5.492 Å, b = 5.525 Å, and c = 8.095 Å) in the orthorhombic structure, is 4.053 Å [78-80]. Generally, rareearth scandates (ReScO₃, with Re = La, Y, Pr, Nd, Gd, Dy, Lu, etc.) are known to be chemically stable at high temperatures and have a high dielectric constant (κ), and thus have a large potential to be used in field-effect transistor applications [78]. Prior to the formation of LSO/BLSO heterostructures, the property of LSO as an excellent dielectric with high- κ was attempted to be identified. First, 21 (7×3) mesa-like capacitors with a 165 nm LSO layer sandwiched between 4% BLSO contacts with an area of 5.31×10^{-4} cm² were fabricated. A 3-dimensional view and a top view of the capacitors are detailed in Figure 2.8 (b, c). Figure 2.9 (a) shows the results of the capacitance (C_p) and dissipation factor (tan δ) when an AC voltage of the root-mean-square 30 mV with a frequency variation from 10^3 to 10^5 Hz was applied to obtain the admittance and the phase shift, from which the parallel C_p and tan δ were derived from the following relation.

$$|Y| = \omega C_p \sqrt{1 + \tan^2 \delta} \tag{2.6}$$

 C_p remains almost constant over the given frequency range, and tan δ , which is composed of all the resistive sources in our 2-point measurement, remains below 0.2, excluding the high-frequency region. Then, κ of the LSO capacitors is calculated from the obtained C_p to be about 28 on average, which is almost similar with those of the previously reported LSO films grown on a SiO₂ ($\kappa \sim 22$) [89], a SrRuO₃/SrTiO₃ substrate ($\kappa \sim 26$) [87], and a LaAlO₃ substrate ($\kappa \sim 32$) [78], respectively. Subsequently, a DC voltage was applied to measure the leakage current in the capacitors to estimate the breakdown field. In Figure 2.9 (b), it can be confirmed that a sudden and irreversible increase of the current density (J) took place at 3.29 MV·cm⁻¹, which is defined as the breakdown field (E_{BD}). Although E_{BD} usually improves as the growth is further optimized, from the initial κ and E_{BD} measurements of the LSO dielectric capacitors, the maximum modulated carrier density $n_{max} =$ 5.2×10^{13} cm⁻² can be deduced from the definition ($n_{max} = (\kappa \epsilon_0 E_{BD})/e$) where ϵ_0 and e are the permittivity of the vacuum and the elementary charge, respectively. To further estimate band alignment between LSO and BSO, the leakage current density before the dielectric breakdown was analyzed using the Fowler-Nordheim (F-N) tunneling process [90].

$$J \propto E^2 exp \left(\frac{-4\sqrt{2m_{LSO}^*}\phi^{\frac{3}{2}}}{3e\hbar E} \right)$$
 (2.7)

J, E, m_{LSO}^* , and Φ are the current density, the electric field, the effective mass of conduction electrons in LSO, and the barrier height between the LSO and 4% BLSO, respectively. Here Φ is derived from the following relation $\Phi = E_{CB,LSO} - E_{F,BLSO}$ where $E_{CB,LSO}$ and $E_{F,BLSO}$ are the energy level of the conduction band minimum (CBM) of LSO and the Fermi level of 4% BLSO, respectively. In order to calculate Φ from the above equation, the ln(J/E²) versus E⁻¹ graph was shown in the inset of Figure 2.9 (b). The barrier height can be calculated using linear fitting of the slope of the graph in the high electric field ranging from 2 to 3 MV·cm⁻¹, resulting in $\Phi = 0.65$ eV. The energy level of the CBM of BSO ($E_{CB,BSO}$) should be calculated to determine the band alignment between LSO and BSO. And, $E_{F,BLSO} - E_{CB,BSO}$ was previously reported to be 0.55 eV [54]. Using this result and Φ obtained from above, the ΔE_{CB} between $E_{CB,LSO}$ and $E_{CB,BSO}$ is finally calculated to be about 1.2 eV, which is an underestimate value since other transport processes often exist before the breakdown. The determined the conduction band offset between LSO and BSO

 (ΔE_{CB}) is derived from the experimental results in Figure 2.9 (a) and (b) is shown in Figure 2.9 (c). This large ΔE_{CB} can be a critical role in forming 2DEG state at the LSO/BSO interface.



Figure 2.9. The dielectric characteristics of LSO dielectric. (a) The capacitance and dissipation factor of the 165 nm LSO dielectric between 4% BLSO contacts were measured with respect to the applied frequencies of AC voltage. Dielectric constant (κ) was calculated from the measured capacitance. (b) In the plot of leakage current density (log J) versus electric field (E) for the LSO dielectric, E_{Breakdown} is determined from the rapidly increasing J. In the inset, the ln(J/E²) versus E⁻¹ graph is plotted for analysis which is called the Fowler-Nordheim (F-N) tunneling process in the LSO dielectric. (c) In the band alignment, the conduction band offset between LSO and BSO (ΔE_{CB}) is derived from the experimental results in (a) and (b).

2.3.2. Electrical characteristics of heterostructures

Next, to measure the electrical characteristics of the LSO/BLSO interface such as sheet conductance (σ_s), sheet carrier density (n_{2D}), and electron mobility (μ), LSO/BLSO heterostructures with the same structure in the previously reported LIO/BLSO heterostructures (in chapter 2.2) were fabricated [44]. A 3-dimensional 26



Figure 2.10. (a, b) A 3-dimensional view and a top view of the LaScO₃/Ba_{1-x}La_xSnO₃ (LSO/BLSO) interface. (c) σ_s before and after LSO deposition as a function of the La concentration of the BLSO layer (crimson color), and comparison with those of LIO deposition (sky blue color). (d) n_{2D} and μ generated at the LSO/BLSO interface (crimson empty squares) and LIO/BLSO interface (sky blue empty squares). schematic and a top view of the samples are shown in Figure 2.10 (a, b). Variation

of the σ_s before and after the LSO deposition as a function of the doping rate of the BLSO channel layer. The crimson data points are the experimental results of the LSO/BLSO samples, shown against the background of sky blue data points for the results of the LIO/BLSO samples from our previous reports. In the trend of the graph, the conductance enhancement of the LSO/BLSO interface is almost the same as that of the LIO/BLSO interface. Prior to LSO deposition, the BLSO layer by itself remains insulating ($R_s > 10^{10} \Omega$) until La concentration of 0.3%. This is due to the large density of the deep acceptors ($N_{DA,STO} = 6 \times 10^{19} \text{ cm}^{-3}$) in the BLSO films on STO substrates, including the high density of threading dislocations (TDs), which are needed to be compensated by the La donors in the film. Because of the large deep acceptor density in BSO, no conductance enhancement occurs in the LSO/un-doped BSO interface, as in the LIO/un-doped interface. For the LIO/BLSO interface deposited on MgO substrate, however, the conductance increases by about a factor

of 10⁵ at the LIO/un-doped interface due to the relatively smaller deep acceptor density ($N_{DA,MgO} = 4 \times 10^{19}$ cm⁻³) of the BSO films on the MgO substrate [14]. So, if the LSO/BLSO heterostructures are made on the MgO substrate, it can be predicted that there will be conductance enhancement at the LSO/un-doped BSO interface. To rule out the possibility of conduction enhancement from oxygen vacancies of the BLSO layer which can be generated during the deposition process, LSO/BLSO(0.3%) sample was annealed in the O₂ environment at 400 °C for 5 hours, and the increased σ_s by forming an interface with 100 nm LSO is rarely changed after annealing in O_2 atmosphere, indicating that the effects of the oxygen vacancies on the LSO/BLSO interface are almost negligible, unlike the LaAlO₃/SrTiO₃ (LAO/STO) interface where oxygen annealing changes its electrical properties [91,92]. The following Figure 2.10 (d) shows n_{2D} and μ generated at the LSO/BLSO interface, which are also compared to those generated at the LIO/BLSO interface. Here, μ increases with increasing n_{2D} , consistent with the previously reported carrier behavior in BLSO films, in which μ is limited by charged impurity scattering, such as TDs [7,11,13,21]. The difference in n_{2D} between the two types of interfaces is very small, but μ at the LSO/BLSO interface seems a little smaller, and the reason for relatively low μ will be discussed in the structural analysis section (in chapter 2.3.3) to see if μ of the LSO/BLSO interface is related with the strain difference between the interfaces of the LSO/BSO and LIO/BSO. Next, the changes of σ_s , n_{2D} , and μ were measured while laying down LSO layer unit cell by unit cell on 0.3% BLSO layer, and the results are shown in Figure 2.11 (a). The thickness dependence of the LSO/BLSO(0.3%) interface also shows a similar thickness variation as that of the LIO/BLSO(0.3%) interface [46]. Even if only 1 unit cell of the LSO is deposited on



Figure 2.11. (a) Changes of σ_s , n_{2D} , and μ generated at the LaScO₃/Ba_{0.997}La_{0.003}SnO₃ (LSO/BLSO(0.3%)) and LaInO₃/Ba_{0.997}La_{0.003}SnO₃ (LIO/BLSO(0.3%)) interfaces as a function of the LSO (crimson color) and LIO (sky blue color) thickness. (b) Interface polarization values used for P-S simulations of the LSO/BLSO(0.3%) and LIO/BLSO(0.3%) interfaces. The polarization exists over 4 pseudocubic LSO and LIO unit cells from the interface and disappears after them. (c) Comparison of n_{2D} by experiments (circles) with those by simulation (dotted lines). The deep donor density (N_{DD}) in the LSO bulk is set to 2.5×10^{20} cm⁻³.

the 0.3% BLSO layer, a rapid increase of σ_s can be confirmed. σ_s and n_{2D} continue

to increase until 4 unit cells of LSO are deposited, and then begin to gradually decrease as 5 more unit cells are deposited. n_{2D} remains almost unchanged from 6 more unit cells until hundreds of unit cells are deposited. In order to understand LSO/BLSO interfaces more quantitatively, the previously reported "interface polarization" model was applied, which successfully described the conductance behavior for the LIO/BLSO(0.3%) interface in chapter 2.2. For this, the self-consistent Poisson-Schrödinger (P-S) band calculator developed by G. Snider was

Material	$E_{\rm g}$ (eV)	$\frac{\Delta E_{\rm CB}}{\rm BSO} (\rm eV)$	к	m _e */m _e	E _D (eV)	E _A (eV)
LaScO ₃	5.8	1.2	28	0.3 ~ 0.4	2.5	_

Table 2.3. Material parameters used for LaScO₃ in P-S simulations.

			Surface		
	LSO V	90 nm	$P = 0 \ \mu C \cdot cm^{-2}$	$N_{\rm DD}$ = 2.5 × 10 ²⁰ cm ⁻³	
	LSO IV	8.4 nm	$P = 0 \ \mu C \cdot cm^{-2}$	$N_{\rm DD} = 2.5 \times 10^{20} {\rm cm}^{-3}$	
	LSO III	0.4 nm	P = 10 µC · cm ⁻²	$N_{\rm DD} = 2.5 \times 10^{20} {\rm cm}^{-3}$	
	LSO II	0.4 nm	P = 23 µC ⋅ cm ⁻²	$N_{\rm DD} = 2.5 \times 10^{20} {\rm cm}^{-3}$	
_	LSO I	0.8 nm	$P = 61.5 \ \mu C \cdot cm^2$	$N_{\rm DD} = 2.5 \times 10^{20} {\rm cm}^{-3}$	
	0.3% BLSO	12 nm	$N_{\rm d} = 4.3 \times 10^{19} {\rm cm}^{-3}$	$N_{\rm DA}$ = 6 × 10 ¹⁹ cm ⁻³	2DEG (2 1111)
	BSO I	30 nm	$N_{\rm d} = 0 {\rm ~cm}^{-3}$	$N_{\rm DA}$ = 6 × 10 ¹⁹ cm ⁻³	
	BSO II	120 nm	$N_{\rm d} = 0 {\rm ~cm}^{-3}$	$N_{\rm DA} = 0 {\rm ~cm}^{-3}$	

STO	ר כו	ihet	rata

Figure 2.12. Parameters in the P-S simulations applying the "interface polarization" model. The structure is 100 nm LSO/12 nm 0.3% BLSO/150 nm BSO on STO substrate.

used again [67]. The important input material parameters for this simulations are summarized in Table 2.1 and Table 2.3, and the LSO/BLSO(0.3%) heterostructures used in the simulations are shown in Figure 2.12 [7,46,55,68,69,87]. Based on the experimental results in Figure 2.11 (a), where the n_{2D} increases while the deposition of 4 unit cells, we assumed the interface polarization in LSO that exists only in 4 unit cells near the interface and disappears after that. In the case of the LIO/BLSO(0.3%) interface that also showed the maximum n_{2D} at 4 unit cell of LIO, interface polarization values of $65/65/25/10 \ \mu\text{C/cm}^2$ over the LIO 4 unit cells were found to fit with the experimental n_{2D} . Considering this, several P-S simulations for the best fit with the experimental n_{2D} were performed, and the interface polarization values were concluded to be $61.5/61.5/23/10 \ \mu\text{C/cm}^2$ in the LSO, as shown in Figure 2.11 (b). Subsequently, the decreasing n_{2D} beyond 4 unit cells of LSO is from the reversing potential starting at the end of the interface polarization. In order to screen such potential, positive charges should be needed, hence the introduction of the deep donors. These deep donors can provide the positive charges for screening when the $E_{\rm F}$ is lower than the deep donor state level near the interface. Once the screening is finished by such deep donors, the band bending stops. The deep donor density (N_{DD}) was set to be 2.5×10^{20} cm⁻³ at the level of 2.5 eV below its conduction band minimum in the LSO, in which it fits best with our experimental n_{2D} . These deep donor states can be the oxygen vacancy states in LSO or LIO, which can be ionized to be positively charged when the $E_{\rm F}$ is lower than the oxygen vacancy state level; the $N_{\rm DD}$ of 2.5×10^{20} cm⁻³ in the LSO corresponds to LaScO_{2.991}. Also, judging from the O₂ environment annealing results, the deep donor states in LSO seem stable and intrinsic, same as in the LIO/BLSO cases. Next, the calculated band diagram of the LSO/BLSO(0.3%) heterostructures when the LaScO₃ thickness is 100 nm is shown in Figure 2.13. From this band diagram, it can be seen that the interface polarization, along with the conduction band offset, largely tilts the bands of the LSO at the interface. Although the interface polarization values and the conduction band offset to BSO of LSO are smaller than those of LIO, the relatively lower κ of LaScO₃ ($\kappa \sim$ 28) [55] than that of LIO ($\kappa \sim 38$) [56] makes band bending on the LSO side easier



Figure 2.13. Band diagram of the LSO/BLSO(0.3%) calculated by the P-S simulation. Around 10 to 30 Å, the Fermi level (E_F) becomes lower than deep donor level (E_{DD}) where E_{DD} is ionized. The free electrons emitted from the ionized E_{DD} move toward the 0.3% BLSO and create a quantum well. The inset is a magnified image near the interface with n_{3D} and a single occupied subband (E_1). than for LIO, resulting in the same 2DEG density as in the case of the

LIO/BLSO(0.3%) interface. Taking a closer look, in the region around 10 to 30 Å, the E_F becomes lower than deep donor states (E_{DD}), so that the E_{DD} are ionized. Then, the resulting free electrons released from the ionized E_{DD} move toward the 0.3% BLSO layer, creating a confined 2DEG quantum well with about 2 nm width near the interface. This confinement length of about 2 nm is consistent with the results of thermopower measurements or in-line electron holography measurements of the LSO/BSO heterostructures recently reported by other groups [15,51,72]. The carrier transfer mechanism of the LSO/BLSO(0.3%) interface is similar to that of conventional modulation-doped semiconductor heterojunctions. For example, in the

case of the AlGaAs/GaAs heterostructures, Si is intentionally doped into the AlGaAs layer around 50 to 150 Å away from the interface, where Si donor level is located at 0.1 eV below the conduction band of AlGaAs. When this Si-doped AlGaAs makes heterojunctions with GaAs, Si dopants in the AlGaAs layer are jonized by band bending, and the resulting free electrons move to the GaAs layer [27-29]. In the same way, the deep donors present in the LSO layer play a similar role to the Si dopants present in the AlGaAs layer. In the inset of Figure 2.13, n_{3D} in the quantum wells are shown with a single occupied subband (E_1) . Such single subband occupation differs from the LAO/STO interface with multiple subbands [93]. Calculations using $E_{\rm F}$ – E_1 (~ 0.1 eV), and the 2D density of states (2D DOS), m_e^{*}/ π h², of about 2×10¹⁴ cm⁻ 2 eV⁻¹ in BSO predict that LSO/BLSO(0.3%) can accommodate the n_{2D} of about 2 × 10^{13} cm⁻², which is quite consistent with our experimental values. These nondegenerate quantum states at the LSO/BLSO(0.3%) interface can make it easier to observe quantum phenomena such as the Shubnikov-de Haas oscillation [94] or Ouantum Hall effect [95] in 2DEG systems, when the low-temperature mobility improves by reducing the scattering by defects such as TDs.

2.3.3. Structural analysis of heterostructures

After the electrical properties of the interface, the structural properties were then analyzed starting with a spherical aberration-corrected scanning transmission electron microscope (Cs-STEM), using a JEM-ARM200F (JEOL Ltd, Japan) equipped with a cold field emission gun (Cold FEG) operating at an electron acceleration voltage of 200 kV. Specimens to be used for Cs-STEM were prepared



Figure 2.14. (a, b) Cross-sectional high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) images of the LSO(78 nm)/BSO(17 nm) films on STO substrate and the magnified LSO/BSO interface. Within the area marked by yellow dashes, the threading dislocations (TDs) that formed in the BSO film persist in the LSO film without any new dislocations forming at the interface, suggesting the coherent epitaxial growth of LSO on BSO. (c, d) The RSM (103) scans results of the LSO/BSO and LIO/BSO films on the STO substrate. The (103) peak of LSO is on the crimson vertical line, the (103) peak of LIO is on the sky blue vertical line, and the (103) peaks of BSO in both figures are located between the two lines.

primarily by focused ion beam milling (Helios 650 FIB; FEI, USA) and secondarily thinned by focused Ar-ion beam nano milling (M1040 Nano Mill; Fischione, USA). A cross-sectional high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) images of LSO/un-doped BSO heterostructures on STO substrate can be seen in Figure 2.14 (a). It can be confirmed that the large density of the TDs created in BSO on the substrate extend beyond the BSO layer to the LSO layer. The TD density of BSO deposited on the STO substrate is known as about 5×10^{10} cm⁻² [96], and a similar TD density can be seen in Figure 2.14 (a). Subsequently, an image of a higher-resolution interface can be found in Figure 2.14 (b). Here too, the TDs created in the BSO layer are maintained up to the LSO layer, but no formation of new TDs was found at the interface, indicating that the growth of LSO film is coherently epitaxial and not creating new dislocations near the interface. This is in contrast to the case of LGO/un-doped BSO heterostructures [84], where new dislocations, not being extended from the BSO layer, start to form right from the interface, preventing the coherent epitaxial growth. For the LIO/BSO interface in the previous chapter, we have already shown that the coherent epitaxial growth between the orthorhombic and cubic structures leads to structural modifications of the polar perovskite near the interface, resulting in interface polarization, which in turn enables formation of a 2DEG state [46.84]. Similarly, the coherent growth of LSO on BSO seems to contribute to generating the 2DEG state at the interface. Next, reciprocal space mapping (RSM) analyses were performed using a SmartLab with a Cu K α -1 source ($\lambda = 1.5406$ Å; Rigaku, Japan) at room temperature. An X-ray CBO system, a Ge (220) 2-bounce monochromator, and a 1dimensional semiconductor array detector (hybrid photon counting detector; HyPix-3000) were used for the high-resolution crystalline qualities. Figure 2.14 (c) shows the RSM scan around the peaks of the (103) plane of the LSO/un-doped BSO heterostructures on the STO substrate. All intensities of the 3 peaks are well confined in reciprocal space, and there is no polycrystalline growth. Among the two overlapping peaks, the upper peak belongs to the pseudocubic (103) plane of LSO and the lower peak belongs to the cubic (103) plane of BSO. The reciprocal space vectors $Q_x = 1.5325$ Å⁻¹ and $Q_z = 4.6181$ Å⁻¹ correspond to in-plane lattice and outof-plane lattice parameters $a_{LSO} = 4.1001$ Å, $c_{LSO} = 4.0816$ Å of the pseudocubic (103) plane of the LSO. And, the reciprocal space vectors $Q_x = 1.5319$ Å⁻¹ and $Q_z =$

4.5724 Å⁻¹ correspond to in-plane lattice and out-of-plane lattice parameters $a_{BSO} =$ 4.1014 Å and $c_{BSO} = 4.1224$ Å of the cubic (103) plane of the BSO. Considering that the bulk lattice constants of LSO and BSO are known as $a_{pc} = 4.053$ Å, $a_c = 4.116$ Å, respectively [78-80], the entire LSO is coherently grown on the BSO with its inplane lattice constant almost pinned with that of BSO, at least near the interface. While the in-plane lattice of the LSO is tensilely strained and coherently pinned with BSO, the out-of-plane lattice constant of the LSO is also expanded from the known bulk value. This can also describe the experimental results of Figure 2.7 (a) that, as the oxygen partial pressure during deposition decreases, the proportion of La in the LSO film decreases, which reduces the volume of the unit cell and at the same time the in-plane lattice constant is not pinned to that of BSO, resulting in no conductance enhancement at the interface. The reason for the broader peak along the Q_x direction of LSO than that of BSO is that there are 3 differently oriented domains of orthorhombic LSO when grown on cubic BSO, which causes the circumferential spread of LSO in RSM. This broadening can also be identified in the RSM (103) scan result of LIO/un-doped BSO heterostructures on the STO substrate in Figure 2.14 (d) [45,55]. There, among the two overlapping peaks, the upper peak belongs to the cubic (103) plane of the BSO and the lower peak belongs to the pseudocubic (103) plane of the LIO. The reciprocal space vectors $Q_x = 1.5241$ Å⁻¹ and $Q_z = 4.5441$ Å⁻¹ correspond to in-plane lattice and out-of-plane lattice parameters $a_{LIO} = 4.1227$ Å, $c_{LIO} = 4.1481$ Å of the pseudocubic (103) plane of the LIO. However, the BSO (103) peak is almost overlapped with the LIO pseudocubic (103) peak and cannot be distinctly distinguished. Given the bulk lattice constant of BSO, the in-plane lattice of the LIO seems to be compressively strained from BSO as opposed to that of the LSO. Here, it can be considered that the difference in strain direction between the

two interfaces (the LSO/BSO and LIO/BSO interfaces) makes the difference in the mobility of the 2DEG at the two interfaces. Considering that the resulting 2DEG state is created only near the interface and that recent theoretical studies have already reported that the mobility increases when BSO is subjected to tensile strain [97], it is not surprising that the BSO under tensile strain from the LIO at the interface shows relatively higher mobility than the BSO under larger compressive strain from the LSO at the interface. Of course, in our case of defect-limited transport, formation of extra defects around the interface, such as oxygen vacancies and misplacement, by the larger strain in the case of the LSO/BSO may have larger effects on the mobility.

2.3.4. Field-effect transistor using 2DEG channel

At the end of chapter 2.3, Field-effect transistor (FET) using 2DEG channel was fabricated using 0.2% BLSO as a channel layer and LSO as a gate oxide. First in the fabrication process, a 150 nm un-doped BSO buffer layer was grown on the entire area of the 5 mm×5 mm STO substrate. Next, a 12 nm 0.2% BLSO channel layer was deposited using a Si stencil line mask with a channel width of 140 μ m. Subsequently, 60 nm 4% BLSO source-drain contact layers were deposited using a butterfly-shaped stainless steel mask making the channel length 60 μ m. After the growth of contact layers, a 275 nm LSO dielectric layer was grown using a rectangular-shaped Si stencil mask. In the final step, a 4% BLSO gate contact layer was grown on the top of the LSO dielectric layer using a Si line mask with a width of 70 μ m, which covers the entire channel length with some overlap with the source and drain electrodes. The 3-dimensional schematic of the structure and the top view



Figure 2.15. A field-effect transistor (FET) using 0.2% BLSO as a channel layer and LSO as a gate oxide. After depositing the LSO dielectric on the channel layer, the conductance is enhanced due to the formation of 2DEG. (a) Schematic of the structure of the FET device. (b) The top view of the FET device observed by an optical microscope. The dashed lines are plotted to distinguish each layer. (c) The output characteristics of the FET device varying the gate voltage (V_{GS}) from -5 to 25 V with a 5 V interval. (d) The transfer characteristics of the FET device with the source-drain voltage (V_{DS}) maintaining 1 V. The source-drain current (I_{DS}) is shown by a red line and the leakage current (I_{GS}) is shown by a red dashed line. The calculated field-effect mobility (μ_{FE}) is shown by the blue circles. The FET device shows I_{on}/I_{off} ratio about 10⁶ and the maximum μ_{FE} close to 100 cm²·V⁻¹·s⁻¹ at room temperature.

of the FET device are shown in Figure 2.15 (a, b). Unlike the above experiments using 0.3% BLSO in chapter 2.3.2, 0.2% BLSO was selected as the channel layer in FET device to create an accumulation mode FET and reduce the impurity scattering in the 2DEG channel at the interface with LSO. Indeed, after depositing the 275 nm LSO layer, the resistance of the channel layer decreased from $1.5437 \times 10^9 \Omega$ to $6.2786 \times 10^5 \Omega$ due to the formation of 2DEG at the LSO/BLSO(0.2%) interface. The output characteristics of the FET device are shown in Figure 2.15 (c). Source-drain voltage (V_{DS}) was applied up to 10 V while gate voltage (V_{GS}) varied from -5 to 25 V with a 5 V interval. As the V_{GS} increases from -5 to 25 V, source-drain current (I_{DS}) also increases with V_{GS} , consistent with the behavior of a typical n-type FET device. Each of the 7 solid lines shows the same characteristics that the I_{DS} is proportional to the low V_{DS} and is pinched off at the drain end to saturate, whereby V_{DS} no longer affects the channel in the high V_{DS} limit. Thereafter, the transfer characteristics of the FET device are shown in Figure 2.15 (d). Based on the findings above, V_{GS} was swept from 25 to -5 V with $V_{DS} = 1$ V applied, which belongs to the linear region of the output characteristics. The results show clear switching on/off with little leakage current through the gate oxide, with the I_{on}/I_{off} ratio of about 10⁶. The field-effect mobility (μ_{FE}) was calculated using the following relation.

$$\mu_{FE} = \left(\frac{Lt}{W\kappa\varepsilon_0 V_{DS}}\right) \frac{\partial I_{DS}}{\partial V_{GS}} , \qquad (2.8)$$

L, t, W, and ε_0 are the channel length, the thickness of the gate oxide, the channel width, and the permittivity of the vacuum, respectively. The maximum μ_{FE} was calculated to be about 98.7 cm²·V⁻¹·s⁻¹, which is the highest value reported to date in FETs based on the BLSO channel layer using various gate oxides such as Al₂O₃ [52], HfO₂ [53], BaHfO₃ (BHO) [54], and LaInO₃ (LIO) [55], as shown in Table 1.1. Although the transconductance (g_m), defined as g_m = $\partial I_{DS}/\partial V_{GS}$, is slightly higher in the previously reported FETs using the LIO gate oxide than in the FET device using the LSO gate oxide, the relatively lower κ of the LSO gate oxide than that of the LIO makes the FET device to have higher μ_{FE} . Taken together, such high performance of the device can be attributed to the high conductivity of the channel due to the formation of the 2DEG at the LSO/BLSO(0.2%) interface, as well as the gate dielectric properties of LSO, which is chemically stable at high temperatures with high- κ , being one of the rare-earth scandates.

2.4. Conclusion

Using the self-consistent Poisson-Schrödinger band calculator, we introduced a new model named interface polarization model, where the polarization exists in 4 pseudocubic unit cells of the LIO from the interface and vanishes after that. By introducing this model, the n_{2D} variation as a function of the LIO thickness of particular LIO/BLSO(0.3%) samples could be described. HRTEM measurements provided evidence that supports this model, showing structural modifications occurring on a length scale equivalent to 2 - 3 pseudocubic unit cells of LIO at the LIO/BSO interface, and these modifications are a result of the coherent epitaxial growth of orthorhombic LIO on the cubic BSO. And next, after investigating the electrical and structural characteristics of the LSO/BSO heterostructures, interface polarization model was also proven applicable to the LSO/BSO heterostructures. High-mobility FETs using the 2DEG channel at room temperature were fabricated notwithstanding the high density TDs in the BLSO channel which impede the mobility of the channel. Therefore, if the mobility is improved by reducing the defect scattering, the 2DEG state of the LIO/BSO or LSO/BSO heterostructures will open up the possibilities to observe new quantum phenomena, and this will be covered in detail in chapter 4.

Chapter 3. 2-dimensional systems formed with BaSnO₃ – II. Expansion

3.1. Introduction

In the previous chapter, we focused on the 2-dimensional electron gas generated at the interface between polar orthorhombic LIO or LSO and non-polar cubic BSO. In particular, most of them were analyzed based on the experimental data of the interface with 0.3% BLSO, not the interface with un-doped BSO. As mentioned in chapter 2.3.2, the reason for this is that there are a lot of deep acceptors present in the BLSO films on STO substrates, which are attributed to the high density of threading dislocations (TDs) [14,21]. To counteract this, a small number of carriers from the La donors are required in the film; Since the $N_{DA,STO}$ of the BLSO film deposited on the STO substrate is obtained approximately $N_{\text{DA,STO}} = 6 \times 10^{19} \text{ cm}^{-3} \text{ by}$ previous studies [46], 0.3 - 0.4% La donor density in the BLSO film is valid to offset this. However, La donors itself act as a source for impurity scattering by activated carriers. It is necessary to fabricate and study heterostructures composed of un-doped BSO to reduce the influences of the 2-dimensional carriers generated at the perovskite interface from impurity-induced scattering as well as from TDs-induced scattering [11,98]. Therefore, in this chapter, I will expand on how to create a 2DEG state at the interface with LIO through structural improvement (particularly, termination layer control) of un-doped BSO. It is mainly analyzed through Atomic Force Microscopy (AFM) measurements. All measurements were made using a scanning probe microscope (Cypher, Asylum Research) with commercial tapping mode AFM tips (PR-T300; Probes), using AC Air Topography (tapping) mode at

room temperature. The resonance frequency, force constant, and radius of the tips were ~325 kHz, ~40 N/m, and ~8 nm, respectively. Not only these, the possibilities of forming novel types of 2-dimensional systems based on un-doped BSO will be theoretically calculated using self-consistent Poisson-Schrödinger (P-S) simulations; These include 2-dimensional hole gas (2DHG) at the LSO/un-doped BSO interface and 2DEG generated at the non-polar perovskite/un-doped BSO interfaces.

3.2. Termination layer control to enhance the 2DEG state at the interface



Figure 3.1. Sheet conductance (σ_s) before and after the formation of the interface between polar orthorhombic perovskite LaBO₃ (B = Sc, In) and 0.3% BLSO or undoped BSO. Little conductance enhancement occurs at the interface between LaBO₃ and undoped BSO deposited on STO substrate.

Figure 3.1 show the variation of sheet conductance (σ_s) before and after the formation of the interface between polar orthorhombic perovskite LaBO₃ (B = Sc,



Figure 3.2. (a) Surface topographic images of 150 nm BSO film deposited on STO substrate when the target-to-heater distance is 50 mm. (b, c) Surface topographic images after high-temperature(\sim 1200 °C) annealing of the films deposited under the same conditions. (d, e) Subsequently, images after depositing 2 nm LIO films on BSO and annealed BSO with step-terrace structure films, respectively. (f) On the other hand, when 10 nm LIO film is deposited on annealed BSO film, it can be confirmed that white particles presumed to be LaO_x are formed on the surface.

In) and 0.3% BLSO or un-doped BSO. As can be seen, little conductance enhancement occurs at the interface between LaBO₃ and un-doped BSO, which is due to the large deep acceptors present in the un-doped BSO film [44,56]. Generally,

to improve the structural characteristics of perovskite oxide thin films to increase carrier density and mobility, there have been various techniques implemented to decrease the density of TDs. These techniques involve controlling the buffer layer's thickness [13,14], adjusting the cation ratio according to target-to-substrate distance [99], and subjecting high-temperature heat treatment [100-102]. And, I tried to improve the film through the high-temperature heat treatment method among these various methods. Figure 3.2 (a, b, c) show the surface topographic images of 150 nm BSO film deposited on STO substrate before and after high-temperature annealing. As shown in Figure 3.2 (a), the BSO surface immediately after deposition has a very smooth surface without excess particles, which is the result of target-to-substrate adjustment during film growth, and details will be described in chapter 5; Target-tosubstrate = 50 mm is the best condition for BSO deposition, which is most stoichiometric. After that, high-temperature annealing was performed in the following conditions: maintaining 1200 °C for 1 h, with an oxygen flow of 30 ml/min, in GSL-1500X tube furnace. Several repeated experiments have shown that the above conditions including temperature and flow rate are optimal, and the hightemperature annealing results of BSO films under these conditions are shown in the Figure 3.2 (b, c), respectively [72,103]. When focusing on the sample with the 1200 °C annealed surface with distinct step-terrace structure after high-temperature annealing, magnified images of the central part of Figure 3.2 (b) and its line profile are shown in Figure 3.3. The height profile of Figure 3.3 (c) confirms that the width of one terrace is about 0.2 µm, and the spacing of each terrace is about 0.4 nm, which proves that single unit cell step-terrace structure is finely formed after hightemperature annealing. Based on several previously reported studies, the topmost



Figure 3.3. (a, b) Magnified surface topography and (c) its height profile of $1200 \,^{\circ}\text{C}$ annealed 150 nm BSO film deposited at a target-to-heater distance of 50 mm. The line profile result confirms that single unit cell step-terrace structures are formed on the surface.



Figure 3.4. The RSM (103) scans results of the BSO film deposited at a target-toheater distance of 50 mm (a) before and (b) after high-temperature(~1200 °C). The decrease in the Q_x interval of the BSO film after annealing implies structural improvement.

surface evolves to SnO₂-terminated atomically flat surface, and it has been also reported recently that the 2DEG state is only formed when the BSO surface is terminated mainly with a SnO_2 layer [72,103]. The relationship between the termination layer of BSO and the resulting direction of polarization of LIO layer for the generation of the 2DEG state will be discussed in detail in the very next chapter 3.3.1. The important point here is that since the as-grown BSO surface in Figure 3.2 (a) has mixed termination layers of both BaO and SnO₂ which is confirmed by coaxial impact collision ion scattering (Shimadzu, TALIS-9700) analyzer, the 1200 °C annealed BSO with a SnO₂-terminated surface is expected to be more advantageous in forming 2DEG states in the heterostructures with LIO or LSO. Next, the improved structural properties of this film after annealing can be proven not only from the AFM measurements but also from the RSM measurements. Figure 3.4 (a, b) show RSM (103) scans results of the BSO film on the STO substrate before and after high-temperature(~1200 °C) annealing. Comparing the two images, the Q_x interval of the BSO film after heat treatment is reduced by about 30% compared to before heat treatment, indicating structural improvement as TDs annihilation effect [72]. Hence, AFM analysis demonstrated that the high-temperature annealing treatment resulted in the successful formation of a smooth surface with atomically step-terrace morphology in BSO. Additionally, RSM measurements revealed that the structural properties in the bulk of the film were improved, leading to the decrease in TDs. Both surface and bulk improvements can enable 2DEG formation, especially between polar orthorhombic perovskite and un-doped BSO. The images of depositing LIO layer on the as-grown BSO film and the 1200 °C annealed BSO film are shown in Figure 3.2 (d, e, f), where Figure 3.2 (d, e) are the surface of the heterostructures film on which 2 nm LIO is deposited and Figure 3.2 (f) is the surface of the heterostructures film on which 10 nm LIO is deposited. When focusing on the



Figure 3.5. (a, b) Magnified surface topography and (c) its height profile of 2 nm LIO film on 1200 °C annealed 150 nm BSO film. The line profile result confirms that single unit cell step-terrace structures are maintained after LIO deposition.

sample with 2 nm LIO film on 150 nm distinct step-terrace structural BSO film, magnified surface topography of Figure 3.2 (e) and its line profile are shown in Figure 3.5. The height profile of Figure 3.5 (c) confirms that the width of one terrace and the spacing of each terrace are maintained after depositing 2 nm LIO, which means that single unit cell step-terrace structure is maintained after deposition. Unfortunately, when depositing 10 nm LIO, the step-terrace structure is maintained, but white particles (presumed to be LaO_x) are found to be generated on the surface [104,105]. So, depositing 2 nm LIO seems more stoichiometric, considering the surface state. Next, in order to check how much the electrical properties were improved, the Van der Pauw measurements were conducted on the LIO(2 nm)/undoped BSO(150 nm) sample and the LIO(2 nm)/step-terrace structural BSO(150 nm)



Figure 3.6. AFM topographic images of the annealed BSO films with single unit cell step-terrace structures after DI water etching for (a) 0 s, (b) 1 s, (c) 10 s, and (d) 60 s. As the etching time increases, the step-terrace structures fade little by little.



Figure 3.7. Sheet conductance (σ_s) of LIO/BSO 2DEG after LIO deposition as a function of deionized (DI) water etching time for the BSO and annealed BSO films. σ_s of 2DEG decreases as the etching time increases.

sample for comparison. Contrary to expectations, even if 2 nm LIO was deposited on the step-terrace BSO, conductance enhancement hardly occurred; it was almost similar to the case where 2 nm LIO was deposited on the as-grown BSO (in Figure 3.1). According to a study reported by Tohoku University, after ex-situ annealing at high-temperature(~1200 °C), a large amount of white particles was formed on the BSO surface, which was well cleared with deionized (DI) water, and the elemental analysis with inductively coupled plasma atomic emission spectroscopy revealed that these particles are BaO_x particles [105]. Based on this study, white particles were not found on the surface of our BSO film after high-temperature annealing through AFM measurements, but potential particles that were not revealed through AFM measurements can be present on the surface. so to remove them, the annealed BSO film was subjected to DI water etching, and then the surface was measured. Here, DI water etching was performed to hold the sample with a tweezer, soak it in DI water, and then stir it clockwise slowly. Figure 3.6 (a, b, c, d) show surface images of the same step-terrace BSO sample after etching for 0, 1, 10, and 60 seconds, respectively. As the etching time increases, the step-terrace structure of annealed BSO gradually fades. This is thought to be because as the etching time increases, the BaO layer under the topmost SnO2 is also affected by etching, making the step-terrace structure unstable. Proof of this phenomenon is also available from the electrical characteristic change trend in Figure 3.7. The difference of σ_s of LIO/BSO heterostructures after LIO deposition as a function of DI water etching time for the BSO and annealed BSO films are shown in Figure 3.7. In the case of the LIO/step-terrace BSO heterostructures, σ_s of about 10⁻⁷ Ω^{-1} is measured when 2 nm LIO is deposited on step-terrace BSO after etching for a short time (1 to 10 s), which is the highest value among LIO/un-doped BSO 2DEGs on STO substrate. As the DI water etching time of the step-terrace BSO became longer than 30 s, the degree of conductance enhancement after LIO deposition decreased, and finally in the case of LIO deposition after etching for 1 minute, there is no change in conduction before and after LIO deposition. On the other hand, as can be seen from the Figure 3.7, there was also conductance enhancement when LIO was deposited on the as-grown BSO after DI water etching, but it was less than 1 order than the former cases, and there was little change in conduction after 10 s or more of DI water etching of as-grown BSO [106]. In summary, when depositing LIO on step-terrace BSO that has undergone ex-situ annealing and subsequent DI water etching, conductance

enhancement of 10⁴ or more was obtained even with un-doped BSO, and through this method, 2DEG states which are little affected by impurity scattering from La dopants were created. In particular, since the impurity scattering by dopants has adverse effects on the low-temperature measurement of films, the low-temperature measurement was performed using LIO/step-terrace BSO sample (whose etching time is 1 s), and the results will be covered in chapter 4.

3.3. Possibilities of new 2-dimensional systems based on BaSnO₃

In chapter 2, the experimental results of the thickness dependence of LIO/BLSO(0.3%) and LSO/BLSO(0.3%) matched well with the theoretical analyses using the self-consistent Poisson-Schrödinger (P-S) band calculator. Conversely, using the P-S simulations, it is possible to construct new 2-dimensional systems that have not been reported experimentally so far and predict the possibility of formation of novel systems. Parameters used in P-S simulations include energy gap (E_g), conduction band offset to BSO (ΔE_{CB}), deep donor level (E_{DD}), deep donor density (N_{DD}), dielectric constant (κ), effective mass (m_e^*), and polarization (P), and so on [67]. I have run several simulations while adjusting these parameters appropriately and discovered the possibilities of forming new 2-dimensional systems: i.) 2-dimensional hole gas at the LaScO₃/BaSnO₃ interface, and ii.) 2-dimensional electron gas at SrHfO₃/BaSnO₃ interface. 2-dimensional charge carriers were formed at the interface of these new heterostructures, and theoretical calculations by P-S simulations expected to be the basis for experimental implementation in the future.



3.3.1. 2-dimensional hole gas at the LaScO₃/BaSnO₃ interface

Re-considering the formation mechanism, depending on the interface polarization model, the generation of 2DEG states at the LIO/BSO interface can be attributed to the sum of the polarization which is created only near the interface and the ΔE_{CB} between LIO and BSO. In this mechanism, the polarization direction at the

Figure 3.8. Structural diagrams of LIO/BSO heterostructures with (a) $(LaO)^+/(SnO_2)^0$ and (b) $(InO_2)^-/(BaO)^0$ interface. At the $(LaO)^+/(SnO_2)^0$ interface, the direction of the polarization is toward to BSO. At the $(InO_2)^-/(BaO)^0$ interface, on the other hand, the polarization is oriented in the opposite direction compared to its previous orientation. Band diagrams of the LIO/BSO heterostructures with (c) $(LaO)^+/(SnO_2)^0$ and (d) $(InO_2)^-/(BaO)^0$ interface calculated by the P-S simulations. The energy level at each interface is reduced as a result of polarization, along with the conduction band offset between LIO and BSO (ΔE_{CB}). In the case of the $(LaO)^+/(SnO_2)^0$ interface, 2DEG was formed at the interface. On the contrary, in the case of the $(InO_2)^-/(BaO)^0$ interface neither 2DEG nor 2DHG was formed.

interface depends on whether the first atomic layer of LIO at the interface is LaO⁺ or InO₂⁻. The direction of interface polarization determined by the first layer of LIO is represented in Figure 3.8 (a, b). At the $(LaO)^+/(SnO_2)^0$ interface, the direction of the polarization is toward to BSO. At the $(InO_2)^{-1}/(BaO)^0$ interface, on the other hand, the polarization is oriented in the opposite direction compared to its previous orientation. Figure 3.8 (c, d) show band diagrams of the LIO/BSO heterostructures with $(LaO)^{+}/(SnO_2)^{0}$ and $(InO_2)^{-}/(BaO)^{0}$ interface calculated by the P-S simulations. The energy level at each interface is reduced as a result of polarization, along with the ΔE_{CB} between LIO and BSO. In the case of the $(LaO)^+/(SnO_2)^0$ interface, 2DEG was formed at the interface. On the contrary, in the case of the $(InO_2)^{-}/(BaO)^0$ interface neither 2DEG nor 2DHG was formed [49]. If our 2DEG formation scenario is correct, then 2-dimensional hole gas (2DHG) can be form at $(InO_2)^-/(BaO)^0$ interface where the polarization has the same values with that of $(LaO)^+/(SnO_2)^0$ interface, opposite direction, and the valence band offset ($\Delta E_{\rm VB}$) is as large as the $\Delta E_{\rm CB}$ (= 1.6 eV). However, since the $\Delta E_{\rm VB}$ between LIO and BSO is known to be very small (about 0.3 eV), 2DHG at the interface can't occur even if polarization



Figure 3.9. Band alignments of (a) LIO/BSO and (b) LSO/BSO. Unlike the two heterostructures with similar conduction band offset (ΔE_{CB}), the difference in valence band offset (ΔE_{VB}) is large, in which ΔE_{VB} of the LSO/BSO is 5 times greater than that of the LIO/BSO.

direction is reversed. However, on the contrary, at the LSO/BSO interface, if only the polarization direction is reversed, 2DHG can be formed at the interface. Figure 3.9 shows the band alignments of the two heterostructures, resulting from the analyses of the Fowler-Nordheim (F-N) tunneling process in the LIO and LSO capacitors, respectively. Unlike similar ΔE_{CB} of the two heterostructures, the difference in ΔE_{VB} is large, confirming that the ΔE_{VB} of LSO/BSO is 5 times larger than that of LIO/BSO. Then, P-S simulations using LSO and un-doped BSO materials were implemented by changing only the polarization direction and other parameter values are set the same (especially, P = 61.5/61.5/23/10 μ C/cm² from the first LSO unit cell), which are obtained in chapter 2.3 [56]. The calculated band diagram of the LSO/un-doped BSO heterostructures is shown in Figure 3.10. From this band diagram, it can be seen that the direction of interface polarization is opposite to that in Figure 2.13, along with the large valence band offset, tilts the bands of the LSO upward at the interface. Then, from the interface to about 40 Å, the E_F becomes lower than the E_V , resulting in the generation of 2DHG near the


Figure 3.10. Band diagram of the LSO/un-doped BSO calculated by the P-S simulation. From the interface to about 4 Å, the Fermi level (E_F) becomes lower than the valence band level (E_V), resulting in the generation of 2-dimensional hole gas (2DHG) at the interface. The inset is a magnified image with n_{3D} near the interface.

interface. In the inset of Figure 3.10, the distribution of n_{3D} near the interface is shown. Compared to the n_{3D} that occurs at the interface of LSO/BLSO(0.3%), the n_{3D} of this system is about half as small, but considering that this heterostructures are with un-doped BSO, this value is comparable to the 2DEG states generated at the LSO/BLSO(0.3%) interface [56]. With these simulations, it was possible to describe that 2DHG as well as 2DEG can be formed at the perovskite oxides interface using the same mechanism as the 2DEG formation mechanism: i.) interface polarization + ii.) large band offset. In order to prove this experimentally, it is necessary to terminate the topmost surface of BSO layer with (BaO)⁰, after which (ScO₂)^{-/}(BaO)⁰ interface can be formed, and then the direction of interface polarization will be reversed towards the LSO layer. Since the (BaO)⁰ layer is an unstable layer that is particularly affected by the surrounding environment, such as moisture, no method of maintaining the topmost layer of BSO as (BaO)⁰-terminated surface has been found experimentally. Therefore, it seems that further research on this is needed. Of course, when the polarization direction is changed, not only the direction but also the polarization value can be changed, but if (BaO)⁰-terminated BSO is implemented experimentally, the possibility of 2DHG formation at the interface with LSO still exists.

3.3.2. 2-dimensional electron gas at the SrHfO₃/BaSnO₃ interface

Considering the mechanism of 2DEG formation at the interface, not only the combination of the polarization and conduction band offset for tilting the bands, but also only large conduction band offset can make 2DEG states at the perovskite oxides interface. In the case of the 2DEG systems including AlGaN/GaN [30-33], MgZnO/ZnO [34-37], and LIO/BLSO, all heterostructures have polarization discontinuity, which forms quantum well near each interface [44-51]. However, if there is large conduction band offset between two materials, it is also possible to form 2DEG states without polarization discontinuity at the interface. This is similar to the mechanism of modulation doping of AlGaAs/GaAs heterostructures without any polarization discontinuity [27-29]. The difference from the 2DEGs that occur in the three types of heterostructures mentioned above is that the polarization discontinuity at the interface is not required, so termination layer control to adjust polarization direction at the interface is also unnecessary. To verify this possibility through P-S simulations, materials with a large ΔE_{CB} to BSO were considered. And,

among the perovskite oxides, SrHfO₃ was chosen as the most suitable material. SrHfO₃ (SHO) is a non-polar orthorhombic perovskite of a GdFeO₃ type (*Pnma*) with an indirect band gap of 5.85 eV [62,107]. Its pseudocubic lattice constant (a_{pc}) is calculated as 4.087 Å [107,108], which is smaller than the lattice constant of BSO, 4.116 Å [7]. According to a very recently reported study, the conduction band offset between SHO and BSO was measured as 3.3 eV, resulting from the analysis of the Fowler-Nordheim (F-N) tunneling process in the SHO capacitors [107], and this value is more than twice as high as that between LIO and BSO. Figure 3.11 (a) shows



Figure 3.11. (a) A band alignment between SHO and BSO. (b) The structure in the P-S simulations is 30 nm SHO/150 nm un-doped BSO on MgO substrate. The manipulated variable parameters used in the simulations are conduction band offset (ΔE_{CB}), deep donor level (E_{DD}), and deep donor density (N_{DD}) in the SHO layer.

the band alignment between SHO and BSO obtained through the experimental results. Prior to proceeding with P-S simulations, among the parameters used in the simulation, dielectric constant (κ), effective mass (m_e^{*}), and polarization (P) can be used as experimentally obtained values (especially, P = 0 μ C/cm² in non-polar SHO) [107], but since there is no experimental data for other important parameters such as deep donor level (E_{DD}) and deep donor density (N_{DD}), the simulations were iterated while changing these values, and the degree of change is shown in the structure of

Figure 3.11 (b). After that, the band diagram of 30 nm SHO/150 nm un-doped BSO calculated by P-S simulation when changing i.) ΔE_{CB} , ii.) E_{DD} , and iii.) N_{DD} in the SHO layer, respectively, is summarized in Figure 3.12. The results of each situation are described in detail as follows.



Figure 3.12. Band diagrams of the 30 nm SHO/150 nm un-doped BSO calculated by the P-S simulations when varying (a) ΔE_{CB} , (b) E_{DD} , and (c) N_{DD} in the SHO layer, respectively.

i.) In the case of changing conduction band offset (ΔE_{CB}) to BSO

The simulations were performed while changing $\Delta E_{\rm CB}$ from 1.8 to 3.8 eV, wherein $E_{\rm DD}$ and $N_{\rm DD}$ were fixed to 2.5 eV below conduction band minimum (CBM) and 4×10^{20} cm⁻³, respectively. In the resulting band diagrams, it can be seen that n_{2D} of 10^{13} cm⁻² or more is formed at the interface from when the $\Delta E_{\rm CB}$ is 3.3 eV or higher. As mentioned in chapter 2.2.1, 2DEG states were formed at the LIO/BLSO interface when the total $\Delta E_{\rm CB}$ was practically 3.1 eV or higher (in other words, interface polarization values act like the 1.5 eV of $\Delta E_{\rm CB}$). Therefore, even if there is no polarization at the SHO/BSO interface, 2DEG states can be formed by a very large $\Delta E_{\rm CB}$ between SHO and BSO.

ii.) In the case of changing deep donor level (E_{DD}) of SHO

The simulations were performed while changing E_{DD} below conduction band

minimum (CBM) from 1.8 to 3.8 eV, wherein ΔE_{CB} and N_{DD} were fixed to 3.3 eV and 4×10^{20} cm⁻³, respectively. In the resulting band diagrams, it can be seen that n_{2D} of 10^{13} cm⁻² or more is formed at the interface from when the E_{DD} is 2.8 eV or lower. However, in contrast, n_{2D} is not generated at the SHO/BSO interface when the E_{DD} is above 2.8 eV. This is because even if there is a very large ΔE_{CB} between the two materials, if the E_{DD} of SHO is too large at the same time (i.e., the activation energy of SHO is also too large), there is not enough ΔE_{CB} to activate the deep donor states in SHO layer. Therefore, not only a large ΔE_{CB} but also E_{DD} below about 2.5 eV can be seen as an important factor in forming 2DEG at the SHO/BSO interface.

iii.) In the case of changing deep donor density (N_{DD}) of SHO

The simulations were performed while changing $N_{\rm DD}$ from 4×10^{19} to 4×10^{21} cm⁻³, wherein $\Delta E_{\rm CB}$ and $E_{\rm DD}$ were fixed to 3.3 eV and 2.5 eV, respectively. In the resulting band diagrams, it can be seen that n_{2D} of 10^{13} cm⁻² or more is formed at the interface from when the $N_{\rm DD}$ is 4×10^{20} cm⁻³ or higher. However, in contrast, n_{2D} is not generated at the SHO/BSO interface when the $N_{\rm DD}$ is below 4×10^{20} cm⁻³. This is because as the $N_{\rm DD}$ in the SHO layer decreases, the density of carriers passing to the BSO inevitably decreases. (i.e., carriers activated in deep donors farther from the interface are more difficult to move beyond the SHO layer to the BSO layer.) Therefore, sufficient $N_{\rm DD}$ of 10^{20} cm⁻³ or more, similar to that in LIO or LSO layers, must exist in the SHO layer, and combined with above-mentioned $\Delta E_{\rm CB}$ and $E_{\rm DD}$, high density n_{2D} can be created at the interface.

To sum up the results, even if there is no polarization, the SHO/BSO interface can form 2DEG states resulting from a very large conduction band offset, and n_{2D} at this

interface is much higher than that generated at the AlGaAs/GaAs interface with the same 2DEG formation mechanism [27-29].

3.4. Conclusion

First in this chapter, to exclude the effect of impurity scattering from La dopants in the LIO/BLSO(0.3%) heterostructures, I have experimentally demonstrated that the conductance enhancement of more than 10⁴ occurs even at the LIO/un-doped BSO interface, where the LIO layer was deposited on the step-terrace structural BSO layer undergone ex-situ high-temperature annealing and short-term DI water etching. Next, if the interface of the LSO/BSO heterostructures can be formed as $(ScO_2)^{-1}/(BaO)^0$ interface by terminating the topmost surface of BSO layer with (BaO)⁰, it is proved using P-S simulations that 2DHG states can be formed at the interface, in which the direction of interface polarization is reversed towards the LSO layer. Experimental implementation of this requires further research on how to maintain the topmost surface of BSO layer as the (BaO)⁰-terminated surface. Last, using iterative P-S simulations, it has been also demonstrated that the non-polar SHO/BSO interface can form 2DEG states due to a very large conduction band offset even in the absence of polarization. In fact, recently in our laboratory, we have confirmed several times that conduction increases when SHO film is deposited on un-doped BSO without termination layer control. However, since the degree of conductance enhancement varies greatly depending on the deposition conditions of SHO film (particularly, the oxygen partial pressure during deposition), a series of experiments to confirm the change in the resistance of the heterostructures by changing the deposition conditions seems to be necessary. In conclusion, there are

possibilities that novel 2-dimensional systems based on BSO, previously unreported, will be found experimentally in the future beyond theoretical predictions.

Chapter 4. Low-temperature characteristics of BaSnO₃-based systems

4.1. Introduction

Most of the studies on 2-dimensional electron gas (2DEG) generated at the polar LaAlO₃/non-polar SrTiO₃ (LAO/STO) interface are studies on physical phenomena generated at extreme low-temperature below 100 K [38,109-113]. Several fascinating physical phenomena such as superconductivity [39], ferromagnetism [40], Rashba spin-orbit coupling [41-43], and Shubnikov-de Haas oscillation are all measured at cryogenic temperature of several K [38,114,115]. This is due to the extremely low mobility of 2DEG at the LAO/STO interface near room temperature, which can be attributed to the characteristics of the electron states within the narrow Ti d-orbital bands, which acts as a hosting environment of 2DEG states at the STO layer [116]. However, in the case of STO-based 2-dimensional systems, since there are almost no other mobility-limiting scattering mechanisms such as dislocations, non-stoichiometry, and chemical dopants, these systems can have a very high mobility of 10,000 cm²·V⁻¹·s⁻¹ or more at low-temperature, along with which they represent attractive quantum phenomena when a high magnetic field is applied [109]. On the other hand, in the case of low-temperature measurements of BSO-based systems, studies on the temperature dependence of BLSO films with a thickness of several tens of nanometers or more have been mainly focused [7,13]. In addition, due to large density of the threading dislocations (TDs) created in BSO on the substrate and impurity scattering owing to La dopants, it was confirmed that the mobility of BLSO films didn't increase significantly and was limited at lowtemperature [7,13]. Therefore, in this chapter, I will focus on BSO-based systems, especially 2-dimensional systems, which include LIO/BSO 2DEG and δ -doped BSO. In order to eliminate the effect of impurity scattering due to La dopants and to reduce the dislocation density even a little, LIO/BSO 2DEG was made using step-terrace un-doped BSO films mentioned in the previous chapter and un-doped BSO films with a relatively small acceptor density deposited by Molecular-beam epitaxy (MBE), which was made from the other laboratory [12,117]. These samples are used to measure and analyze magnetoresistance (MR) under perpendicular and parallel magnetic fields as well as to measure and analyze temperature dependence of sheet resistance (R_s), sheet carrier density (n_{2D}), and electron mobility (μ). And not only this, fabrication of electric-double-layer transistor (EDLT) using ionic-liquid and application of liquid gating to BSO-based 2-dimensional systems at low-temperature are performed and analyzed.

4.2. Low-temperature measurement and analysis of the LaInO₃/BaSnO₃ 2DEG and δ-doped BaSnO₃

For low-temperature measurements, all samples were subjected to Hall-bar pattern (detailed in chapter 4.2.1), followed by Au contact deposition and Au wiring, and all samples were measured at extreme low-temperature using the same physical properties measurement system (PPMS; Quantum Design) equipped with a sample rotator, in which longitudinal and transverse transport properties could be measured. The temperature range applied in these measurements is 2 K to 300 K, and the magnetic field range is -7 T to 7 T.

4.2.1. Sample preparation



Figure 4.1. High-resolution X-ray diffraction (HRXRD) measurements of (a) a 150 nm step-terrace BSO film on STO substrate (by PLD), and (b) a 110 nm BSO film on MgO substrate (by MBE). Each θ -2 θ scan shows diffraction peaks corresponding to (002) of BSO film deposited by PLD or MBE. (c) Two rocking curves were measured at each (002) peak of BSO, with full width at half maximum (FWHM) of 0.06 ° (by PLD) and 0.366 ° (by MBE).



Figure 4.2. (a) The structure of δ -doped BSO. Each layer is 15 nm un-doped BSO/x nm 4% BLSO/150 nm un-doped BSO on STO substrate. (b) A Band diagram of δ -doped BSO calculated by the P-S simulation, which is the result when the 4% BLSO layer is set to be 3 nm. (c) Experimental results of R_s of the δ -doped BSO samples when varying the thickness of the 4% BLSO layer from 1.5 to 3 nm.

To make perovskite heterostructures with lower TD density, another un-doped BSO film deposited in D.G. Schlom's laboratory in Cornell University was included as one of the samples for low-temperature measurements. This film was grown on MgO substrate by MBE, and it has been reported that TD density is less than that deposited by PLD in other laboratory including us [12,72,117]. In particular, in the case of MBE, since Ba and Sn sources are used respectively, it is possible to easily control the composition of the topmost layer of the film, unlike in the case of PLD, so SnO₂-terminated BSO film could be obtained from them to form 2DEG in heterostructures. Figure 4.1 (a, b) show High-resolution X-ray diffraction (HRXRD) measurements of a 150 nm step-terrace BSO film on STO substrate (by PLD), and a 110 nm BSO film on MgO substrate (by MBE). Each θ -2 θ scan shows diffraction peaks corresponding to (002) of BSO film deposited by PLD or MBE. The absence of peaks related to other crystalline planes and secondary phases indicates that both BSO films were epitaxially grown well by PLD and MBE. Subsequently, Figure 4.1 (c) shows two rocking curves were measured at each (002) peak of BSO, with full width at half maximum (FWHM) of 0.06 ° (by PLD) and 0.366 ° (by MBE). Although the FWHM of BSO film deposited by MBE is larger, considering that the FWHM of BSO deposited on MgO substrate by PLD was previously reported as $0.63 \circ [45]$, it can be seen that the quality of the thin film deposited by MBE is similar to or higher than that deposited by PLD. Two heterostructures were fabricated by depositing each 5 nm LIO film on these high-quality un-doped BSO films (At this time, as mentioned in the previous chapter, step-terrace BSO was subjected to DI water etching for about 5 s, after then LIO film was deposited). In addition to these samples, another BSO-based 2-dimensional system was prepared, which is called δ doped BSO. The theoretical and experimental analyses of δ -doped BSO is described in detail in the following papers: i.) Y. Kim, Ph. D. dissertation, Seoul National University (2021) [71]. ii.) Y. Kim et al., Appl. Phys. Lett. 118, 052101 (2021) [118], and it is omitted in this dissertation. A sample structure of δ -doped BSO is represented in Figure 4.2 (a). The band diagram of δ -doped BSO calculated by P-S simulation in Figure 4.2 (b) confirms that the conductive layer is confined to a few nm only in the 4% BLSO layer, which could be a 2-dimensional conductive layer in a different sense. The actual experimental results related to this are shown in Figure



Figure 4.3. Structure of each sample for low-temperature measurements (a) LIO(5 nm)/step-terrace BSO(150 nm) on STO substrate (by PLD). (b) LIO(5 nm)/BSO(110 nm) on MgO substrate (by MBE). (c) δ -doped BSO(2 nm) on STO substrate (by PLD).

Structure	Sheet resistance (k Ω)	Sheet carrier density (cm ⁻²)	Electron mobility (cm ² ·V ⁻¹ ·s ⁻¹)
LIO/step-terrace BSO (by PLD)	400	Not measurable	Not measurable
LIO/BSO (by MBE)	11	1.05×10^{13}	60.56
δ-doped BSO (by PLD)	6.46	3.26×10 ¹³	29.61

Table 4.1. Electrical properties of all three samples measured using a Keithley 4200

 SCS at room temperature.

4.2 (c), when δ -doped BSO samples were fabricated by varying the thickness of the 4% BLSO layer from 1.5 nm to 3 nm, it was confirmed that even a thickness difference of about 0.5 nm resulted in a large R_s difference of more than 1 order of magnitude. Considering that the confinement length of 2DEG generated at the LIO/BSO interface is 2 nm, a sample with a thickness of 4% BLSO layer of 2 nm was selected among the δ -doped samples for low-temperature measurements. Finally, the following 3 samples shown in Figure 4.3 (a, b, c) are samples for low-temperature measurements: i.) LIO(5 nm)/step-terrace BSO(150 nm) on STO substrate by PLD. ii.) LIO(5 nm)/BSO(110 nm) on MgO substrate by MBE. iii.) δ -doped BSO(2 nm) on STO substrate by PLD, and before low-temperature experiments, measurements using Keithley 4200 SCS at room temperature were preceded, and the results of electrical properties of all samples are shown in Table 4.1. As expected, it can be confirmed that the R_s of the LIO/BSO sample using MBE-grown BSO is more than



Figure 4.4. (a) Fabrication process of Hall-bar pattern, Au contact deposition, and Au wiring for low-temperature measurement. The fabrication process of all samples including this sample (LIO/BSO by MBE) is the same. (b) Top view of the completed Hall-bar patterned sample with the Au contact pads under an optical microscope.

l order smaller than that using PLD-grown step-terrace BSO (This is due to the lower TD density of the former film.), whose difference will be particularly noticeable at low-temperature and will be described in the next chapter 4.2.2. In low-temperature measurements using PPMS, since the temperature is extremely low, even a very small noise can cause a signal to fluctuate greatly. In order to prevent this and make more precise measurements, all samples were subjected to additional fabrication steps such as Hall-bar pattern, Au contact deposition, and Au wiring, a flow chart of which is shown in figure 4.4 (a). The Hall-bar geometry was patterned using photolithography and ion-milling process. Photolithography was performed using a maskless aligner (Nano System Solutions, Inc., DL-1000A1) and AZ5214e photoresist. Etching was physically performed by an Ar-ion miller (Korea Vacuum Tech, KVET-IM2000L). The incident angle and beam voltage were 45 ° and 400 V for etching, respectively, and 80 ° and 200 V for surface treatment. After etching process, the photoresists were removed using acetone and Dimethyl Sulfoxide (DMSO) sonification. Au deposition for contact pads was performed using an E-

beam evaporator (Korea Vacuum Tech, KVET-IM2002L) and a stencil mask made of invar FeNi36. The E-beam power for deposition was 7 kV, and the deposition rate was 0.55 angstrom per second. Wiring was carried out using 20 μ m thick Au wires, and silver paste was used for fixing between the Au wires and the Au contact pads. The top view of the completed Hall-bar patterned sample with the Au contact pads under an optical microscope is shown in Figure 4.4 (b). From the microscope, it is confirmed that the length and width of the channel are 300 μ m and 150 μ m, respectively. During measurements, the Van der Pauw and Hall measurements can be performed simultaneously using 6 Au contact pads. After all preparations were completed, low-temperature measurements using PPMS was performed.

4.2.2. Temperature dependence of sheet resistance

Figure 4.5 (a) shows temperature-dependent transport properties of all Hall-bar patterned samples. First, in the case of the LIO/step-terrace BSO sample (crimson), the R_s only increased as the T decreased, and the measurement signal was cut off below 100 K. This sample, which showed a relatively high R_s at room temperature, seems to transition to an insulator as the temperature decreases. Considering the reason, R_s at low-temperature was significantly higher compared to the quantum of resistance $h/2e^2 = 12.9 \text{ k}\Omega$, indicating that it is under strong localization regimes [110,113]. In these regimes, the temperature dependence of R_s follows the Mott variable-range hopping (VRH) model in general, represented by the equation $\rho = \rho_0 \exp(T_0/T)^{(1/(d+1))}$), where d = 2 or 3 is the dimensionality [110,119], and the rise in R_s occurs because the energy available for hopping decreases as the temperature decreases. On the other hand, the other 2 samples (LIO/BSO and δ -doped BSO



Figure 4.5. Temperature-dependent transport properties of all Hall-bar patterned samples. (a) Change of sheet resistance (R_s) as a function of temperature (T) for 3 samples. (b) Magnified graph of the area indicated by the red dash in (a). Upturn of sheet resistance of both samples occurs around 100 K.

samples) don't show a rapid increase in R_s as the temperature decreases, and R_s is less than the quantum of resistance (12.9 k Ω). The magnified situation for this is shown in Figure 4.5 (b), showing that as the temperature decreases, the R_s of both samples decrease, R_s minimum (R_{upturn}) occurs at around 100 K, after which R_s increases again. Unfortunately, the presence of R_{upturn} at low-temperature means that 2 samples don't have complete metallic behavior. Rather typically, R_s -T graph of this type and the existence of R_{upturn} are from weak localization (WL) [113,120,121] or Kondo effect [122,123], where anisotropic negative magnetoresistance in the next chapter 4.2.3 will indicate that the cause of this phenomenon is from WL.

4.2.3. Negative magnetoresistance

Magnetoresistance (MR) measurements can give additional insight into the role of localization effects, especially important in 2-dimensional systems such as LIO/BSO heterostructures and δ -doped BSO. The MR is calculated according to the following formula: MR (%) = $[{R_s(\mu_0 H) - R_s(0)}/{R_s(0)}] \times 100$. Figure 4.6 (a, b) show negative magnetoresistance (nMR) of the LIO/BSO sample, in which MR as a function of B-field applied perpendicular or parallel to the surface is shown at various temperatures. The solid lines are MR data when out-of-plane B-field is applied. On the other hand, the dotted lines are MR data when in-plane B-field is applied. When B-field is parallel to the current, in-plane MR shows different B-field dependence and smaller MR values than those of out-of-plane MR, and such anisotropic nMR indicates that the temperature dependence on Rs is due to 2dimensional WL [121,124,125]. Similar trends in anisotropic nMR are also confirmed in magnetic field dependence measurements of δ -doped BSO sample. Figure 4.7 (a, b) show negative magnetoresistance (nMR) of the δ -doped BSO sample, in which MR as a function of B-field applied perpendicular or parallel to the surface is shown at various temperatures. Similar to the measurement results of the previous sample, anisotropic nMR can be confirmed according to the direction of the B-field. In both samples, the nMR increases as the temperature decreases and the nMR increases as the B-field increases, and the out-of-plane MR has a larger value than the in-plane MR at the same temperature. The measurement results most similar to these measurement results were found in the LAO/Fe-doped STO interface described in the following paper: H. Xue et al., Phys. Rev. B 98, 085305 (2018) [121]. Summing up the report, when the interface between LAO and Fe-doped STO is formed, the scattering sources by Fe dopants rise at the interface, increasing the WL effect by disorder, and the out-of-plane MR, which typically shows positive MR (pMR) at the LAO/STO interface, changes to nMR. In addition, since n_{2D} generated at the interface is reduced by Fe doping, the spin-orbit coupling (SOC) that depends on n_{2D} is weakened, and the weak antilocalization (WAL) effect that depends on SOC

is also weakened, resulting in nMR even in-plane MR. The detailed configurations of WL and WAL are shown in Figure 4.8 (a, b); A schematic diagram of 2 timereversal electron trajectories in a closed quantum diffusion path and typical magnetoresistance behavior of thin films under the interaction of scattering processes of intervalley and intravalley, and the resulting interference effects are shown. Among the interferences, destructive interference induces WAL in thin films of excellent quality with large SOC. However, when disorder caused by point defects or dislocations is dominant, intervalley scattering becomes more significant, constructive interference predominates, resulting in either suppressed WAL or the typical WL in thin films of moderate quality [126,127]. Then, analyzing the MR of our samples based on the previous LAO/Fe-doped STO heterostructures case, due to the high density of TDs present in the films, the WL effect is quite large, resulting in negative out-of-plane MR of several tens of percent. Furthermore, our samples have relatively smaller SOC due to n_{2D} lower than 1 order than n_{2D} generated at the LAO/STO interface($n_{2D} = 3 \times 10^{14} \text{ cm}^{-2}$) [38], which weakens WAL effect and is considered to have negative in-plane MR rather than well-known in-plane MR in the form shown below in Figure 4.8 (b). Of course, since there is almost no thickness of conductive layer in the in-plane direction, the value of nMR is much smaller than that of the former. At this time, anisotropic nMR of 2 samples is due to WL effect acting differently on 2-dimensional systems, which means that the value of in-plane MR is smaller than that of out-of-plane MR because the sheet carrier is confined in 2-dimensions only [124,125]. The B-field dependence of 3-dimensional systems in the opposite situation is shown in Figure 4.9 (a, b), and the 0.4% BLSO sample was selected as a control to compare the differences with the previous 2 samples. When comparing out-of-plane MR and in-plane MR, it is confirmed that the 2 types of the

MR are almost overlapped, which means isotropic nMR unlike the previous



Figure 4.6. Negative magnetoresistance (nMR) of the LIO/BSO sample. (a) MR as a function of B-field applied perpendicular or parallel to the surface at various temperatures. The solid lines are MR data when out-of-plane B-field is applied. On the other hand, the dotted lines are MR data when in-plane B-field is applied. (b) Magnified graph of the area indicated by the black line in (a).



Figure 4.7. Negative magnetoresistance (nMR) of the δ -doped BSO sample. (a) MR as a function of B-field applied perpendicular or parallel to the surface at various temperatures. The solid lines are MR data when out-of-plane B-field is applied. On the other hand, the dotted lines are MR data when in-plane B-field is applied. (b) Magnified graph of the area indicated by the black line in (a).



Figure 4.8. (a) A schematic diagram of 2 time-reversal electron trajectories in a closed quantum diffusion path. (b) Typical magnetoresistance behavior of thin films under the interaction of scattering processes of intervalley and intravalley, and the resulting interference effects. As a result of the pseudospin and Berry phase of π , the phenomenon of backscattering is inhibited through destructive interference. This suppression leads to weak antilocalization (WAL) in thin films of excellent quality. However, when short-range disorder caused by point defects or dislocations is present, intervalley scattering becomes more significant, resulting in either suppressed weak localization or the typical weak localization (WL) in thin films of moderate quality.



Figure 4.9. Negative magnetoresistance (nMR) of the 0.4% BLSO sample, which was selected as a control group for comparison of differences with the previous 2 samples. (a) MR as a function of B-field applied perpendicular or parallel to the surface at various temperatures. The solid lines are MR data when out-of-plane B-field is applied. On the other hand, the dotted lines are MR data when in-plane B-field is applied. (b) Magnified graph of the area indicated by the black line in (a).



Figure 4.10. Angle-dependent magnetoresistance (MR) of the LIO/BSO sample. 0 $^{\circ}$ (or 180 $^{\circ}$) corresponds to the case where the sample and the magnetic field are perpendicular (namely, out-of-plane B-field), and 90 $^{\circ}$ (or 270 $^{\circ}$) corresponds to the case where the sample and the magnetic field are parallel (namely, in-plane B-field). Angle-dependent measurements were made at 2 K with the B-field of 0.5 T, 3 T, and 6 T, respectively.

2 samples with anisotropic nMR, because this system is 3-dimensional. So there is no difference in transverse and longitudinal mobility from the perspective of the 3dimensional carrier, in other words, the previous anisotropic nMR of the 2 samples proves that these systems are 2-dimensional systems [124,125]. As the last experiments for B-field dependence, angle dependence experiments of the LIO/BSO sample were performed by rotating the sample, and the results are shown in Figure 4.10. Angle-dependent measurements were made at 2 K with the B-field of 0.5 T, 3 T, and 6 T, respectively. In the graph, 0 ° (or 180 °) corresponds to the case where the sample and the magnetic field are perpendicular, and 90 ° (or 270 °) corresponds to the case where the sample and the magnetic field are parallel. For all B-fields, nMR has minimum values around 90 ° (or 270 °) and conversely, MR has maximum values around 0 ° (or 180 °), which shows that anisotropic nMR can also be confirmed in angle-dependent measurements [111].

4.2.4. Hall measurement



Figure 4.11. (a) Change of Hall resistance (R_{XY}) as a function of out-of-plane Bfield at various temperatures for both LIO/BSO and δ -doped BSO samples, showing a linear behavior for all measured temperatures. Data from the LIO/BSO sample are shown as solid lines, and data from the δ -doped BSO sample are shown as dotted lines. Temperature dependence of (b) sheet carrier density (n_{2D}) and (c) electron mobility (μ). No carrier freeze-out effect occurs as the temperature decreases, meaning that these samples have high oxygen stability even at low-temperature.

Figure 4.11 (a) shows change of Hall resistance (R_{XY}) as a function of out-of-plane B-field at various temperatures for both LIO/BSO and δ -doped BSO samples, in which data from the LIO/BSO sample are shown as solid lines, and data from the δ doped BSO sample are shown as dotted lines. They show linear behavior for all measured temperatures. Temperature dependence of n_{2D} and μ are plotted in Figure 4.11 (b, c), which are calculated from the slopes in Figure 4.11 (a) and the R_s in Figure 4.5 (b). n_{2D} generated at the LAO/STO interface typically decreases with decreasing temperature [38,110,113]. In contrast, however, n_{2D} at our interfaces of 2 samples are almost temperature-independent, which indicates that carrier freeze-out effect is almost non-existent in our samples when the temperature decreases. In general, as the temperature decreases, free electrons in the conduction band move to the oxygen vacancy (V_o) level, resulting in the carrier freeze-out effect. But, since BSO has very little V_o states, there is little such movement, which means that the carrier freeze-out effect is weakened. In other words, no carrier freeze-out effect is considered to be due to the high oxygen stability, which is one of the biggest advantages of BSO over other perovskite oxides [11]. However, in both samples, μ doesn't increase but rather decreases when the temperature goes down. This is because, as expected, the increase in μ is limited by the disorder present in the films, i.e., a large density of defects and dislocations, despite the fabrication of the LIO/BSO sample using MBE-grown BSO, which is expected to have lower TDs.

4.3. Ionic-liquid gating for carrier modulation

As discussed in chapter 4.2, the following methods are needed to improve the transport properties at low-temperature based on the results of the B-field-dependent measurements and the Hall measurements: i.) Significantly reducing disorder (defects or dislocations) in films. ii.) Increasing n_{2D} to enhance SOC effect. Among them, the former method is lowering TDs by using lattice-matched substrates with BSO, whose possibilities will be examined in chapter 5. Here, the second method was chosen: Carrier modulation in oxides using electrolyte gating in electric-double-layer transistor (EDLT) to improve transport properties at low-temperature by modulating n_{2D} generated at the interface. In this method, the dielectric in conventional field-effect transistor (FET) is replaced with an electrolyte, an ionic-liquid (IL). In an EDLT, an IL is capable of electrostatic accumulation of n_{2D} up to approximately 10^{15} cm⁻² on the surface, which is more than 1 to 2 orders compared to solid-gate FETs [105,128-132]. Therefore, if n_{2D} is significantly increased using IL gating, not only can the SOC effect of 2-dimensional systems be enhanced, but also μ enhancement by IL gating can be expected, considering the well-known $\mu \propto$

 $n^{d/2}$ relationship. (if d = 1, 3-dimensional carrier and if d = 3, 2-dimensional carrier) [133]. Since there have been prior reports that applied IL gating on BSO (K. Fujiwara *et al.*, Appl. Phys. Lett. **110**, 203503 (2017)) [105] and La-doped BSO film (H. Wang *et al.*, Phys. Rev. Mater. **3**, 075001 (2019)) [131], in this dissertation, IL gating was applied focusing only on LIO/BSO heterostructures. After that, the low-temperature measurements were carried out again and the results were compared and analyzed with the data in chapter 4.2.

4.3.1. Sample preparation for ionic-liquid gating

To configure the LIO/BSO EDLT, the following steps were added to the Hall-bar patterned LIO/BSO sample: First, the surfaces except for the channel region and the contact pads were coated with approximately 1 μ m thick photoresist (PR, AZ 5214E) to prevent the BSO in this region from being modulated by gating. Second, an additional Au wire as a gate electrode to apply the gate voltage (V_{GS}) was placed directly above the channel region at intervals of about 1 mm to avoid contact with each other. Last, a drop of IL fell on the sample immediately before loading it into the PPMS to minimize water contamination. At this time, the liquid used in these experiments was diethylmethyl ammonium bis(trifluoromethylsulfonyl)imide, which is also known as [DEME]⁺[TFSI]⁻. To describe the IL gating process in detail, when V_{GS} is applied positively to the EDLT, cations of the IL (in this case, [DEME]⁺) move toward the surface of the sample and accumulated. (In contrast, anions of the IL (in this case, [TFSI]⁻) are move toward the gate electrode and accumulated). Then, charges are balanced by accumulation of electrons on the side of the interface



Figure 4.12. (a) Schematic diagrams with the addition of steps required for the Hallbar patterned sample for ionic-liquid gating. PR coating to prevent gating of undoped BSO and gate electrode for top gating were added. (b) Top view of the LIO/BSO sample immediately before dropping the liquid under an optical microscope. (c) Change of sheet resistance (R_s) and leakage current (I_{GS}) as a function of gate voltage (V_{GS}) at 230 K. V_{GS} was applied up to 7 V at 1 V intervals, and at the time of application, a time interval of 20 minutes per voltage was set to make enough time for [DEME]⁺ and [TFSI]⁻ in the ionic-liquid to align.

between the sample and the [DEME]⁺, forming an electric-double-layer. Figure 4.12 (a) shows a schematic of the completed LIO/BSO EDLT, and Figure 4.12 (b) shows the top view of the sample under an optical microscope just before a drop of liquid, in which the PR coated surfaces (excluding the LIO/BSO channel layer) and the gate electrode are observed. Before carrying out full-scale temperature- and B-field-dependent low-temperature experiments, some tests were conducted to demonstrate the feasibility of gating using IL: The sheet resistance (R_s) of the channel and the

leakage current (I_{GS}) between the channel and the gate electrode were tested when the V_{GS} was applied. Before using IL, it was baked in a hot plate at 110°C for 12 hours to remove moisture contained in IL. And the V_{GS} was then applied at 230 K and held for 20 minutes before the next bias was applied, which was to stabilize IL and give enough time for [DEME]⁺ and [TFSI]⁻ in the liquid to align [134]. Figure 4.12 (c) shows change of R_s (green solid line with circles) and I_{GS} (red dotted line with triangles) as a function of V_{GS} at 230 K, where V_{GS} was applied up to 7 V at 1 V intervals, and a time interval of 20 minutes was set per voltage. It is confirmed that the R_s of the LIO/BSO EDLT decreases as the applied V_{GS} increases, and confirmed that the I_{GS} maintains less than 1 μ A up to 7 V (A rapid increase in I_{GS} was observed from 8 V or higher). In addition, when the gate bias is removed, the reversibility of R_s to the pre-bias R_s after a sufficient time has elapsed was also confirmed. Based on these gating tests, the feasibility of IL could be demonstrated, and temperature- and B-field-dependent low-temperature experiments of EDLT were then performed in the PPMS.

4.3.2. Temperature dependence of sheet resistance

Figure 4.13 (a) shows temperature- and gate voltage-dependent transport properties of a LIO/BSO EDLT, where change of R_s as a function of T at different V_{GS} (0 to 7 V at intervals of 1 V). Each V_{GS} was applied at 230 K and kept for 20 min for [DEME]⁺ and [TFSI]⁻ in the liquid to align. After cooling the LIO/BSO EDLT to 2K while keeping the V_{GS} constant, all measurements were carried out while raising the temperature. The anomalies observed in R_s within the temperature range from 200 K to 230 K are attributed to the freezing point of the [DEME]⁺[TFSI]⁻,



Figure 4.13. Temperature- and gate voltage-dependent transport properties of a LIO/BSO EDLT. Change of sheet resistance (R_s) as a function of temperature (T) at different V_{GS} (0 to 7 V at intervals of 1 V).

whose irregularities are frequently observed in other EDLTs. Considering the instability of E-field-applied IL around room temperature, the range of temperature during measurements was set from 2 K to 230 K. After one R_s-T measurement for one V_{GS} is completed, the following new V_{GS} was applied at 230 K. Analyzing the measurement results, up to V_{GS} = 3 V, the decrease in R_s is monotonic as V_{GS} increases. At V_{GS} = 4 V, this monotonous decrease is getting bigger, and at 5 V \leq V_{GS} \leq 7 V, the R_s decreases compared to before cases, but almost overlaps. Specifically, at V_{GS} = 7 V, the R_s is rather larger than that of 6 V, which is due to the instability of IL at high voltage (It can be seen that the fluctuation of the data point increases as it approaches 230 K). Unfortunately, even with EDL gating, it is still hard to induce complete metallic behaviors of the sample, showing that as the temperature decreases, the R_s minimum (R_{upturn}) still occurs, followed by an upturn in which the R_s increases again at extremely low-temperature. These results demonstrate that even with the increase of n_{2D} by IL gating and the corresponding increase of μ , the side

effects of WL still present in this sample can't be negligible.



4.3.3. Negative magnetoresistance

Figure 4.14. Negative magnetoresistance (nMR) of the LIO/BSO EDLT. MR as a function of B-field applied perpendicular to the surface at 2 K for different applied V_{GS} (0 to 7 V at intervals of 1 V). A tendency for MR to decrease as the applied V_{GS} increases is confirmed.

Figure 4.14 shows negative magnetoresistance (nMR) of the LIO/BSO EDLT, in which MR as a function of the B-field applied perpendicular to the surface at 2K is shown when different V_{GS} (0 to 7 V at intervals of 1 V) are applied. Here, the tendency for MR to decrease as the applied V_{GS} increases is confirmed (Of course, when $V_{GS} = 6$ V, similar to the previous temperature- and gate voltage-dependent low-temperature experiments, the decrease is largest among all V_{GS}). This seems to be because as the gate bias applied to the EDLT increases, n_{2D} increases accordingly and the ratio of the WL effect, which have an effect on MR, decreases, and the MR approaches the positive MR (pMR) observed in conventional 2-dimensional systems [112,128]. In fact, in the case of the LAO/STO heterostructures, which have little

WL effect due to almost no dislocations, it has been reported a number of times that the pMR from the orbital motion effect emerges when the perpendicular B-field is applied [112,113]. Focusing on the case of $V_{GS} = 6$ V, the MR comparisons before and after the gate bias is applied are shown in Figures 4.15 and Figures 4.16, respectively: First, Figure 4.15 (a, b) show MR as a function of B-field applied perpendicular to the surface at various temperatures before and after applying V_{GS} = 6 V, where the solid lines are MR data after V_{GS} is applied and the dotted lines are MR data without applying V_{GS} . Next, Figure 4.16 (a, b) show MR as a function of B-field applied parallel to the surface at various temperatures before and after applying $V_{GS} = 6$ V. Similarly, the solid lines are MR data after V_{GS} is applied and the dotted lines are also MR data without applying V_{GS} . It was confirmed that the magnitude of out-of-plane MR and in-plane MR of the LIO/BSO EDLT measured at all temperatures (2, 10, 50, and 100 K) consistently and significantly decreased when a gate bias of 6 V was applied. However, even if n_{2D} was significantly increased through carrier modulation using IL gating, the WAL-type MR shape as shown in Figure 4.8 (b) was not obtained [127]. In particular, in the case of in-plane MR, no matter how much the value of the MR was reduced to around 1%, the pMR in the low B-field regime could not be confirmed. This reason can be inferred from the characteristics of Sn 5s orbitals in BSO: In s orbitals, angular momentum (secondary, azimunthal) quantum number (notated as l) is 0, and spin-orbit coupling term in Hamiltonians (H_{SOC}) is typically *l*-dependent, so when *l* is 0, the SOC effect is very small or close to 0. Therefore, the SOC-dependent WAL effect is bound to be very small in BSO-based systems, so, even if n_{2D} is increased over 10^{14} cm⁻² using gating, WAL-type MR can't be obtained. Rather, it is possible to obtain only one trend in both out-of-plane MR and in-plane MR, in which the values of nMR are reduced due

to the decrease in WL effect through carrier modulation using IL gating.



Figure 4.15. (a) MR as a function of B-field applied perpendicular to the surface at various temperatures before and after applying $V_{GS} = 6$ V. The solid lines are MR data after V_{GS} is applied. On the other hand, the dotted lines are MR data without applying V_{GS} . (b) Magnified graph of the area indicated by the black line in (a).



Figure 4.16. (a) MR as a function of B-field applied parallel to the surface at various temperatures before and after applying $V_{GS} = 6$ V. The solid lines are MR data after V_{GS} is applied. On the other hand, the dotted lines are MR data without applying V_{GS} . (b) Magnified graph of the area indicated by the black line in (a).



Figure 4.17. Temperature dependence of (a) sheet carrier density (n_{2D}) and (b) electron mobility (μ) of the LIO/BSO EDLT at different V_{GS} (0 to 7 V at intervals of 1 V). As V_{GS} increases, n_{2D} continues to increase, while μ starts to decrease after 4 V is applied.

Temperature and gate voltage dependence of n_{2D} and μ of the LIO/BSO EDLT at different V_{GS} (0 to 7 V at intervals of 1 V) are plotted in Figure 4.17 (a, b). Similar to the results of not applying gating to the sample in the previous chapter 4.2.4, the calculated n_{2D} for each gate bias applied are almost temperature-independent, which indicates that carrier freeze-out effect is still non-existent after IL gating when the temperature decreases. Up to $V_{GS} = 6$ V, the larger the gate bias applied to this LIO/BSO EDLT, the more n_{2D} is modulated, and the maximum modulation of n_{2D} reaches up to approximately 2.5×10^{14} cm⁻² with $V_{GS} = 6$ V, which is higher than 1 order compared to that modulated in conventional solid-gate FETs [53-56]. Therefore, n_{2D} obtained from low-temperature gating experiments demonstrates that IL gating can be carried out effectively for 2-dimensional carrier accumulation in the 2-dimensional LIO/BSO system. Nevertheless, when the gate bias is applied, μ doesn't fully follow the trend of n_{2D} . Up to $V_{GS} = 3V$, μ increases as n increases at all measured temperatures according to the relationship $\mu \propto n^{1/2}$ [11]. At 4 V $\leq V_{GS} \leq$ 6 V, however, n_{2D} starts to increase significantly, but μ starts to decrease conversely according to the relationship $\mu \propto n^{-1}$ [11], so that μ at V_{GS} = 6 V becomes less than one-third than μ at V_{GS} = 3 V for all measured temperatures. At V_{GS} = 7 V, μ increases again, but the value doesn't exceed a maximum of 50 cm²·V⁻¹·s⁻¹ at all measured temperatures. This increasing and then decreasing trend of µ is quite consistent with the well-known typical trend of μ versus n_{3D} for La-doped BSO film [11,98]: Until the ratio of La dopant reaches 2% (until 2% BLSO), as the dopant ratio increases, the number of activated carriers increases, and at the same time, μ increases along with n. This is because increasing electron carriers compensate for screening of charged defects. However, if the ratio of La dopants exceeds 2% (over 2% BLSO), the effect of dopants acting as scattering sources (also called ionized impurities) gradually increases, so even if there are more activated carriers compared to the former, μ can't be increased but rather decreases due to a significant number of these impurities. The electron mobility limit mechanism in the bell-shaped curve of the μ as a function of n, where charged dislocations are the dominant scattering origin that limit the µ in the low La-doped regime while in the high La-doped regime, the ionized-dopant scattering dominates, is described in detail in the following dissertation: U. Kim, Ph. D. dissertation, Seoul National University (2015) [98]. Then, in order to compare the relationship between μ and n_{2D} of our LIO/BSO EDLT as well as other BSO-based EDLTs reported to date, Figure 4.18 provides points showing all the data measured at 150 K using IL gating and a line fitted to the relation $\mu \propto n_{2D}^{3/2}$ [133]. In this graph, green circle points are data of the LIO/BSO EDLT, which are obtained from Figure 4.17 at 150 K. And 2 other BSO-based EDLTs for comparison are shown in the graph. First, sapphire square points are data of 50 nm 2% BLSO with applying $V_{GS} = 0 \sim 4 V$ (from H. Wang *et al.* at Minnesota University)



Figure 4.18. μ as a function of n_{2D} at 150 K for BSO-based EDLTs. All data of the LIO/BSO EDLT were obtained from Figure 4.17 (green circles). For comparison, other BSO-based EDLTs are also shown: i.) 50 nm 2% BLSO with applying $V_{GS} = 0 \sim 4 \text{ V}$ (from H. Wang *et al.* at Minnesota University, sapphire squares) and ii.) 248 nm BSO with applying $V_{GS} = 0 \sim 6 \text{ V}$ (from K. Fujiwara *et al.* at Tohoku University, crimson triangles). The dotted line represents a line fitted to the relation $\mu \propto n_{2D}^{3/2}$. at 150 K [131]. Next, crimson triangle points are data of 248 nm BSO with applying

 $V_{GS} = 0 \sim 6 \text{ V}$ (from K. Fujiwara *et al.* at Tohoku University) at 150 K, too [105]. In the low n_{2D} regimes (n_{2D} < 2×10¹³ cm⁻²), as the gate bias is applied, n_{2D} and μ increase simultaneously, showing higher μ for the same n_{2D} than the crimson triangle points gating a single thick BSO layer. This seems to be due to the characteristics of the band structure of the LIO/BSO heterogeneous system, in which the carrier is transferred from the LIO layer to the interface without any dopants. In the high n_{2D} regimes (n_{2D} > 6×10¹³ cm⁻²), however, as n_{2D} becomes larger, μ becomes smaller, which is observed in all 3 systems shown in the graph. (In particular, for n_{2D} above 10^{14} cm⁻², the tendency of green and crimson points is almost overlapped.) Expectedly, the presence of bell-shaped curves of μ versus n_{2D} in both LIO/BSO and thick BSO systems at the high n_{2D} regimes means that other extrinsic scattering sources are still present in these systems such as interface roughness scattering which is already reported in conventional MgZnO/ZnO heterostructures [135] or δ -doped STO [136], and this scattering impedes transport properties under higher n_{2D} regimes. Therefore, if problems such as degradation of the sample surfaces due to the electrochemical reaction caused by IL gating can be solved, μ can be expected to continue to increase along n_{2D} , as in the trend of the low n_{2D} regimes.

4.4. Conclusion

In summary, temperature- and B-field-dependent low-temperature measurements were carried out using BSO-based 2-dimensional systems, including LIO/stepterrace PLD-grown BSO, LIO/MBE-grown BSO, and δ -doped BSO systems. All samples were subjected to additional fabrication steps including Hall-bar pattern and Au contact deposition for precise measurements at low-temperature. The temperature-dependent measurements showed that the LIO/BSO and δ -doped samples were under weak localization regimes rather than the complete metallic behavior regions, and the B-field-dependent measurements showed that the values of in-plane MR are less than those of out-of-plane MR. Here, this anisotropic nMR of 2 samples is due to WL effect acting differently on 2-dimensional systems in which the carriers are confined in only 2-dimensions. After that, fabrication of electric-double-layer transistor using ionic-liquid and application of liquid gating to BSO-based 2-dimensional systems are performed to improve transport properties by modulating the carriers at low-temperature. Using IL gating, carriers were significantly modulated to more than 1 order, indicating that the feasibility of reversible liquid gating for carrier modulation in BSO-based 2-dimensional systems, but electron mobility didn't increase as much as n_{2D} . This is because, despite the efforts so far, unresolved obstacles such as interface roughness scattering remain between our samples and the IL. Further studies related to the interface between the samples and IL are needed to address these obstacles. In order to measure quantum phenomena such as Shubnikov-de Haas oscillation or Quantum Hall effect in 2DEG systems, the μ should be higher than $10^4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at cryogenic temperature with significant B-field. However, even with MBE-grown BSO with a relatively small acceptor density, the LIO/BSO interface has yet to show it. Therefore, considering another solution, it is to further reduce the TDs of the films by using lattice-matched substrates with BSO, as mentioned in chapter 4.3 above. The availability of novel substrates not reported to date for fabricating BSO-based heterostructures will be discussed in chapter 5.

Chapter 5. Efforts to improve electrical properties of La-doped BaSnO₃

5.1. Introduction

The dissimilarity in the mobility of the BLSO single crystals and the BLSO films on substrate has been ascribed to the presence of large density threading dislocations within the epitaxial films [14,21]. In the case of BLSO films on STO substrate, μ as a function of n_{3D} creates an upwardly convex curve, which implies the threading dislocations that limit the mobility in the low-doping region, while the impurity scattering is dominant in the high-doping region. These threading dislocations (TDs) are due to lattice mismatch between the BSO films and substrates, the TDs are shown in Figure 5.1 (a, b) when BSO film is deposited on the STO and MgO substrate,



Figure 5.1. (a) Cross-sectional bright field transmission electron microscope (TEM) image of a BSO film deposited on STO substrate. (b) Cross-sectional high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) image of a BSO film on a MgO substrate with threading dislocations indicated by red dotted lines.



Figure 5.2. (a) Electron traps in BSO film as deep acceptors. (b) Carrier density of BLSO layer with BSO buffer layer on MgO substrate versus La doping of BLSO layer. The green circles represent the measured carrier density and the thick line represents the fully activated carrier density.

respectively. STO has a smaller lattice constant(-5.12%) than BSO, so BSO film deposited on the STO substrate is under compressive strain, while MgO has a larger lattice constant(+2.45%) than BSO, so BSO film deposited on MgO is under tensile strain. In both cases, it can be confirmed by Transmission Electron Microscope (TEM) measurement that threading dislocation density of about 10¹¹ cm⁻² exists in both BSO films. TDs reduce the mobility by scattering, and the dangling bonds along threading dislocation lines act as electron traps, also called deep acceptors. From the model of Figure 5.2 (a) [46,69], the phenomenon of deep acceptors not being able to accept electrons to produce holes in the valence band at room temperature is due to the significantly high activation energy required for electrons to transition to the impurity level as compared to the thermal energy available. However, deep acceptors can accept free electrons present in the conduction band, as it is thermodynamically favorable to lower the energy of electrons. As deep acceptors don't spontaneously ionize to create holes but accept free electrons in the conduction band, the behavior of deep acceptors is suitable for electron traps. The electrical properties of La-doped BSO (BLSO) film deposited on the MgO substrate shown in Figure 5.2 (b) show that relatively smaller amount of carrier density was measured than the carrier density
when 100% activated. Through the comparison of green circles(measured values) and black line(100% activation line), the electron traps density as the deep acceptors density present in this BLSO film is calculated as $N_{\text{DA,MgO}} = 4 \times 10^{19} \text{ cm}^{-3}$, and $N_{\text{DA,STO}} = 6 \times 10^{19} \text{ cm}^{-3}$ in the case of BLSO film deposited on the STO substrate through a similar method. These deep acceptors as electron traps are also well-known in other conventional heterostructures like GaN on sapphire. Table 5.1 shows deep acceptor

Material	N _{DA} (cm ⁻³)	E _a (eV)
GaAs	1×10^{16}	0.38
GaN	1×10^{17}	1.2
ZnO	1×10^{15}	0.2
BSO on STO substrate	6×10 ¹⁹	1.55
BSO on MgO substrate	4×10 ¹⁹	1.55

Table 5.1. Deep acceptor density (N_{DA}) of conventional semiconductors and BSO film on STO and MgO substrate.

density (N_{DA}) BSO film on STO and MgO substrates and N_{DA} of conventional semiconductors including GaAs, GaN and ZnO [14,21,46,51,69,137-142]. As can be seen from the Table 5.1, the N_{DA} of conventional semiconductors is 2 to 4 orders less than BSO film because most of these materials grow the same film on the same substrate (For example, GaAs film on GaAs substrate [27-29,137,138]), and film growth technology has been developed much more (for decades). Therefore, in order to improve the electrical properties of BLSO film, the TDs of the film and the resulting N_{DA} must be reduced, and if N_{DA} is successfully reduced, more activated carrier density is expected to be generated, and further contribute to the improvement of carrier mobility. To this end, in this chapter, I tried to improve the electrical

properties of BLSO film through three attempts. First, the film was grown using new, previously unreported substrates whose lattice constant is matched with the BLSO film. Second, a new previously unreported buffer layer whose lattice constant is matched with the BSO buffer layer was used. Last, it was checked whether the BLSO film deposited on the STO substrate was effectively improved in electrical characteristics through adjustment of target-to-substrate spacing or subsequent high-temperature heat treatment. HRXRD and AFM measurements were mainly used in chapter 5, and the characteristics of the previously reported BLSO film and the new characteristics were compared and analyzed.

5.2. Change of substrate – LaInO₃ substrate

The lattice constant of BSO is larger than that of most commercial perovskite oxide substrates. In Figure 5.3 (a), BLSO films versus LaAlO₃ [143], LSAT [144], SrTiO₃ [21], NdScO₃ [50], MgO [14] substrates show a large lattice mismatches. So, they possess a high density of threading dislocations with low electric properties of the BLSO films. To alleviate this problem, I used a new, non-commercially used substrate, a LaInO₃ (LIO) substrate. The LIO substrate is a GdFeO₃-type orthorhombic perovskite substrate [62]. Its pseudocubic lattice constant (a_{pc}), calculated from the three lattice constants (a = 5.722 Å, b = 5.94 Å, and c = 8.215 Å) in the orthorhombic perovskite structure, is 4.117 Å(+0.17 %), and this corresponds very well to that of BSO. Growth of LIO single crystals was carried out in Leibniz Institute for Crystal Growth (IKZ) [145]. And, cutting of the crystals into several substrates with (100), (110) surface orientation and chemical mechanical polishing of the substrates for epitaxy was performed by CrysTec GmbH, Berlin, Germany.



Figure 5.3. (a) The difference in lattice constant(expressed as a percentage) between BSO and frequently used perovskite oxide and MgO substrates. (b) Schematic model of each unit cell for the relationship between the orthorhombic (red) and pseudocubic (black) structure.

According to the schematic mode shown in Figure 5.3 (b), the cubic film grows with (110) surface orientation on the orthorhombic substrate with (100) surface orientation, and on the contrary, the cubic film deposited on the orthorhombic substrate with (110) surface orientation can be confirmed to have (100) surface orientation [47]. So, it is believed that (110)-oriented BLSO film grows on the LIO (100) substrate, and (100)-oriented BLSO film grows on the LIO (110) substrate.

5.2.1. LaInO₃ substrate in (100) orientation

Figure 5.4 (a) shows the structural properties of (110)-oriented 50 nm 1% BLSO film deposited on a LIO (100) substrate. θ -2 θ scan shows diffraction peaks corresponding to (110), (220) of BLSO and (200), (400) of LIO substrate. The absence of peaks related to other crystalline planes and secondary phases suggests that the (110)-oritented BLSO film has been epitaxially grown well, following the alignment of the LIO (100) substrate. Rocking curve presented as an inset was measured at the (110) peak of BLSO, with full width at half maximum (FWHM) of 0.235 °. Unlike the FWHM of the BLSO film deposited on the STO reported to be



Figure 5.4. (a) High-resolution X-ray diffraction (HRXRD) measurement of the 50 nm 1% BLSO film on LIO (100) substrate. θ -2 θ scan shows diffraction peaks corresponding to (110), (220) of BLSO and (200), (400) of LIO substrate. Rocking curve presented as an inset was measured at the (110) peak of BLSO, with full width at half maximum (FWHM) of 0.235 °. (b, c) Atomic force microscopy (AFM) topography and its height profile of 50 nm 1% BLSO films on LIO (100) substrate. Microcracks with a height of 2 ~ 3 nm are observed.

about 0.03 degrees [11,45], a relatively large FWHM was measured, which seems to be due to the BLSO film growing in the direction (110). However, apart from growing well on the substrate, this BLSO film was insulating when measured as Van der Pauw method using Keithley 4200 SCS, and the reason can be inferred from the AFM measurement results in Figure 5.4 (b, c). From the topography and its height profile, it can be seen that the surface has large density microcracks of about 3 nm. In general, the microcracks of film are well known to occur when the film is under a large tensile strain. Considering the case of (110)-oriented BLSO film deposited on the LIO (100) substrate, the BLSO film is under both 2% tensile strain in [010]_{orthorhombic} direction and 0.2% compressive strain in [001]_{orthorhombic} direction at the interface between the substrate and the film. And then, it can be expected that the film surface is torn by the tensile strain applied in the direction of [010], forming microcracks. These interfere with the movement of the carrier, resulting in the film being insulating. For this reason, despite the fact that this film was grown epitaxially well on the LIO (100) substrate, it was no longer possible to use this LIO (100) substrate, and next experiments were continued using a LIO (110) substrate.



5.2.2. LaInO₃ substrate in (110) orientation

Figure 5.5. (a) High-resolution X-ray diffraction (HRXRD) measurement of the 50 nm 1% BLSO film on LIO (110) substrate. θ -2 θ scan shows diffraction peaks corresponding to (110), (220), and (330) of LIO substrate. The peaks of the BLSO are too close to the peaks of the LIO to be distinguished. Rocking curve presented as an inset was measured at the (220) peak of LIO, with full width at half maximum (FWHM) of 0.03 °. (b) Sheet resistance (R_s), carrier density (n_{3D}), and electron mobility (μ) of 1% BLSO films of different thicknesses deposited on STO substrate (crimson empty squares) and LIO (110) substrate (sky blue empty squares).

Figure 5.5 (a) shows the structural properties of (100)-oriented 50 nm 1% BLSO film deposited on a LIO (110) substrate. θ -2 θ scan shows diffraction peaks corresponding to (110), (220), and (330) of LIO substrate. Rocking curve presented as an inset was measured at the (220) peak of LIO, with full width at half maximum (FWHM) of 0.03 °. Unfortunately, the peaks of the BLSO are too close to the peaks of the LIO to be distinguished. However, by measuring the electrical properties of the film using the Van der Pauw method, it can be expected that 1% BLSO has been

epitaxially deposited on the LIO (110) substrate without any microcracks. Sheet resistance (R_s), carrier density (n_{3D}), and electron mobility (μ) of 1% BLSO films of different thicknesses deposited on STO substrate (crimson empty squares) and LIO (110) substrate (sky blue empty squares) are represented in Figure 5.5 (b). Compared to the case of BLSO film on STO substrate, the n_{3D} of the BLSO film on the LIO (110) substrate is about 20% larger than that of STO substrate, which can be interpreted as having a relatively low deep acceptor density. Considering the case of (100)-oriented BLSO film deposited on the LIO (110) substrate, the BLSO film is under both 0.2% tensile strain in [-110]_{orthorhombic} direction and 0.2% compressive strain in [001]_{orthorhombic} direction at the interface between the substrate and the film. As such, since there is a very small lattice mismatch of about 0.2%, it is reasonable for the BLSO film on the LIO (110) substrate to have smaller TDs, resulting in a smaller deep receptor density. In fact, another recent study on the LIO (110) substrate showed that the 2% BLSO film deposited on this substrate had less TDs than those of the STO substrate through transmission electron microscopy (TEM) and highresolution scanning transmission electron microscopy (HRSTEM) [146,147]. On the other hand, unlike the trend of increased carrier density of the BLSO film on LIO (110) substrate, the mobility of the film didn't improve at all. According to the bellshaped curve of the μ versus n_{3D} function, it is reported that μ is proportional to $(n_{3D})^{1/2}$ [11]. Considering the unincreased mobility, it can be assumed that there are other defects when using this new substrate, and the cause of this problem was found through AFM measurements. In Figure 5.6, AFM topographic images of the LIO



Figure 5.6. AFM topographic images of the LIO (110) substrates after thermal annealing at (a) 600 °C, (b) 650 °C, (c) 700 °C, and (d) 750 °C for 1 hour in the furnace with the oxygen flow. White particles appearing on the surface after thermal annealing have been reported as GaO_x particles.

(110) substrates after thermal annealing at 600 °C, 650 °C, 700 °C, and 750 °C for 1 hour in the furnace with the oxygen flow were shown. After 650 °C annealing, white particles increase rapidly on the surface, and at 750 °C, more than half of the surface is covered with white particles. According to a study reported by IKZ that provided this new substrates [146,147], deterioration of the surface of the substrate is caused by an unintentional Ga-contamination. When LIO single crystals melt and grow, Ga impurities were segregated during the crystal growth and associated with losses of In, which are substituted by unintentional Ga. It partially occupy lattice sites of In in the perovskite and form the $La(In,Ga)O_3$ crystals as alternatives. Thus, when the substrate is in the annealing process, Ga ions become mobile, forming GaO_x particles on the surface. From the SEM/EDS mapping, it can be confirmed that there are unintentional Ga impurities in the LIO (110) substrate [146,147]. Since the BLSO film is deposited at a temperature of 750 °C, there are many GaO_x particles on the LIO surface when deposited, and these particles enter the BLSO film and act as another defect, resulting in not increasing the mobility of the BLSO film. Therefore, it is expected that the electrical properties of the BLSO film can be significantly improved only by solving the defects of this new substrate itself. So far, Gacontamination has not been resolved, so this substrate can no longer be used, and the second attempt was made to improve the electrical properties of the BLSO film.

5.3. Change of buffer layer – Sr_{1-x}Ba_xHfO₃ film

In several studies related to BSO, un-doped BSO buffer layer is usually inserted between the BLSO film and the substrates to reduce the TDs in the BLSO film. The BSO buffer layers with a thickness of about $150 \sim 200$ nm are reported as optimal condition and improves the conductance of the BLSO film about twice as much as when the BSO buffer layer is not used. However, even with this thick buffer layer, the TDs density present is still around 10^{11} cm⁻² [14,21]. In addition, considering the deep acceptors derived from TDs, since the band gap of BSO is 3.1 eV, there is also a problem that the defect states in the BSO buffer layer can be affected by visible light. To make a buffer layer that is not affected by ambient light while reducing TDs, two ultra-wide band gap perovskites, SrHfO₃ (SHO) and BaHfO₃ (BHO), were used.



Figure 5.7. (a) Non-polar orthorhombic perovskite (*Pnma*) SrHfO₃ structure, and (b) non-polar cubic perovskite BaHfO₃ structure. Both figures were generated using VESTA software.

As shown in Figure 5.7, SHO is a non-polar orthorhombic perovskite of a GdFeO₃

type (*Pnma*) with an indirect band gap of 5.85 eV [62,107]. Its pseudocubic lattice constant (a_{pc}) is calculated as 4.087 Å [107,108], which is smaller than the lattice constant of BSO [7], 4.116 Å. On the other hand, BHO is a non-polar cubic perovskite, with a bulk lattice constant of 4.171 Å and a direct band gap of 6.1 eV [54,148]. Due to their significantly wider band gaps when compared to that of BSO, these materials share the characteristic of being non-conductive insulators that can't be doped with n-type impurities and remain unaffected by visible light. For use as a buffer layer for the BLSO films, the lattice constant of the buffer layer must match that of BLSO. In this experiment, SHO and BHO were mixed in an appropriate pulse ratio to make a mixed (Sr,Ba)HfO₃ film, and the lattice constant of the mixed film were calculated. In PLD system, sequential deposition with two targets is an established practice as long as the solid solutions of two targets are known to exist without phase separation, which is determined by pulse number and deposition rate [84]. From Figure 5.8 (a), experiments show that the lattice constant of the mixed film mixed film.



Figure 5.8. (a) Graph of lattice constant change of $Sr_{1-x}Ba_xHfO_3$ (SBHO) film according to pulse ratio to BHO target of SHO target. (b) plume images of SHO, BHO, and SBHO whose lattice constant is matched with that of BSO.

(Sr,Ba)HfO₃ film increases when the pulse ratio of the BHO target is greater than that of the SHO target, which is due to BaO is larger than SrO. When the pulse ratio of is 27(SHO):5(BHO), it was possible to fabricate a (Sr,Ba)HfO₃ film whose lattice constant is exactly matched with that of BSO, and the film at this appropriate ratio becomes a Sr_{0.85}Ba_{0.15}HfO₃ (SBHO) film. In subsequent experiments, SBHO films were produced using a single target in which SHO and BHO were mixed in a ratio of 85:15, respectively, and electrical and structural properties were analyzed. Since the SHO ratio in the single target is more than 5 times larger than the BHO ratio, it was confirmed in Figure 5.8 (b) that the plume image of this target is similar to that of the SHO target. First, the photoconductivity of BSO and SBHO was measured to compare the defect states in the BSO and SBHO films. Each 160 nm thick BSO and SBHO film channel was deposited on the STO substrate in the same shape using a Si stencil mask with a line width of 240 µm and a line length of 100 µm. Subsequently, 4% BLSO was deposited on the channel layers as contact layers using a butterflyshaped stainless steel mask, which can serve as good metallic contact layers because 4% BLSO is highly degenerately doped. Then, the area between the contact layers was illuminated using optical fiber as shown in Figure 5.9 (a) [149]. The top view of the BSO and SBHO channel layers observed under the optical microscope in Figure 5.9 (b) shows that the samples were well-deposited as expected. Keithley 4200 SCS was used to measure photoconductance, which was maintained for several minutes



Figure 5.9. (a) Sample structure and measurement method for photoconductivity of BSO and SBHO channel layers. (b) Top view of the BSO and SBHO channel layers observed under an optical microscope. (c) Graph of change in photocurrent during switch on/off using optical fiber in which the wavelength of light is about 577 nm.

after applying bias voltage of 40 V. The light source is a 450W Xe lamp with a UV monochromator system, which was used in this experiment to illuminate yellow light of about 577 nm wavelength among visible light. Figure 5.9 (c) shows the change in photocurrent of the BSO and SBHO channels while the optical fiber switch is turned on and off. When the switch is turned on and off, a rapid change in photocurrent occurs in the BSO channel, but the SBHO channel is not greatly affected by switch on/off. Since the energy of yellow light at a wavelength of 577 nm is calculated as 2.15 eV, the results of this experiment show that the defect states in SBHO is much deeper than those in BSO. Alternatively, if the defect states density of SBHO is much less than that of BSO, it can also be explained as a reason for the results of this experiment where the photocurrent in SBHO didn't change. Either way, since SBHO is made by mixing SHO and BHO, which has ultra-wide band gap, so it has less impact from defect states than BSO. It implies this film can be applied as a more suitable buffer layer than the un-doped BSO buffer layer. Figure 5.10 (a) shows the structural properties of 100 nm $Sr_{0.85}Ba_{0.15}HfO_3$ film deposited on a STO substrate, whose lattice constant is consistent with that of BSO. θ -2 θ scan shows diffraction peaks corresponding to (001), (002), (003) of SBHO and (001), (002), (003) of STO



Figure 5.10. (a) High-resolution X-ray diffraction (HRXRD) measurement of the 100 nm $S_{0.85}B_{0.15}HO$ film on STO substrate. θ –2 θ scan shows diffraction peaks corresponding to (001), (002), (003) of $S_{0.85}B_{0.15}HO$ and (001), (002), (003) of STO substrate. Rocking curve presented as an inset was measured at the (002) peak of $S_{0.85}B_{0.15}HO$, with full width at half maximum (FWHM) of 0.04 °. (b) Sheet resistance (R_s), carrier density (n_{3D}), and electron mobility (μ) of 1% BLSO films with BSO buffer (crimson empty squares) and $S_{0.85}B_{0.15}HO$ buffer (green empty squares) layer. AFM topographic images of (c) $S_{0.85}B_{0.15}HO$ film and (d) 1% BLSO film on $S_{0.85}B_{0.15}HO$ buffer layer on STO substrate.

substrate. Rocking curve presented as an inset was measured at the (002) peak of SBHO, with full width at half maximum (FWHM) of 0.04 °. Considering that the FWHM for (002) peak of the BSO film deposited on the STO substrate was reported as 0.09 °, it can be seen that the SBHO film is epitaxially deposited with a quality as high as that of the BSO film. This can also be seen in AFM images in Figure 5.10 (c, d), and the film roughness of 150 nm SBHO film was measured to be about 600 pm, and when 1% BLSO film was deposited on it, the film roughness was reduced to less than 300 pm. Compared to the report that the 1% BLSO film on the BSO buffer layer is about 800 pm, it can be confirmed that the BLSO film has a lower roughness when using the SBHO buffer layer than when using the BSO buffer layer, which proves that this film is smoother. However, by comparing the electrical properties against expectations, Figure 5.10 (b) shows that the electrical properties when using the SBHO buffer layer are not significantly improved compared to when using the BSO buffer layer. R_s, n_{3D}, and μ of 1% BLSO films with BSO buffer (crimson empty)

squares) and SBHO buffer (green empty squares) layer are almost same. Predictably, although the defect states of SBHO are deeper than those of BSO, there are still around 10^{11} cm⁻² of TDs between the STO substrate and SBHO film, and since TDs density hasn't been critically reduced, there seems to be a high level of carriers which are trapped in electron traps. The use of the SBHO buffer layer to reduce photoconductivity can improve the problems of the BSO buffer layer to some extent, but if TDs are not directly reduced, electrical properties including n_{3D} can't be improved. As an alternative to this, referring to studies related to other attempts [72,99-102,150], the structure of the film can be improved through adjustment of target-to-substrate spacing or subsequent high-temperature heat treatment, which will be described in the following chapter 5.4.

5.4. Change of target-to-substrate distance

One of the most influential factors in the electrical properties of 1% BLSO among studies reported to date is the distance between target and substrate. The R_s of the 100nm 1% BLSO film as a function of the target-to-substrate distance (45 mm < $d_{ts} \leq 55$ mm) is shown in Figure 5.11. Unusually, when the target-to-substrate (d_{ts}) is larger than 54 mm, the R_s increases rapidly to more than 2 orders. The reason for this unique phenomenon is that the cation ratio changes rapidly, even with a distance difference of just 1 to 2 mm. During the deposition process of BLSO by PLD method with an oxygen pressure of 100 mTorr, the Sn and Ba atoms that are ablated experience significant collisions with O₂ molecules that are directed towards the substrates. In each scattering event, the lighter Sn experiences a higher scattering angle compared to the heavier Ba. As the plume moves, Sn undergoes more repeated



Figure 5.11. Sheet resistance (R_s) of a 100 nm 1% BLSO films as a function of the target-to-substrate distance (45 mm $< d_{ts} \le 55$ mm). R_s increases rapidly when the d_{ts} is greater than 54 mm.

collisions with the O_2 molecules, resulting in a wider distribution of angles toward the substrate compared to Ba. As a result of the scattering of plumes with O_2 molecules, the ratio of Ba atoms increases with increasing d_{ts}, while at low oxygen pressure or short d_{ts}, Sn-excess BLSO films are formed than stoichiometrically equivalent BLSO films. In fact, there is a prior report using Rutherford backscattering spectrometry (RBS) measurements that the Sn/Ba ratio decreases from 1.04 to 0.97, as the d_{ts} increase by just 5 mm [99,104]. The significant decrease in the electrical properties of 1% BLSO with increasing d_{ts} appears to be due to more carriers provided by La dopants being trapped under Ba-rich conditions. The cause of this phenomenon is related to the relative ease of Sn to La substitution in Ba-rich environments. This forms acceptor-like defects and is presumed to balance out the shallow donors in the BLSO film with excess Ba. As a result, the activation of free electrons by La dopants is hindered, leading to a quick decrease in n_{3D} and μ in the Ba-excess BLSO films. In addition, in these films, the excess Ba combines with O₂ molecules to form BaO_x particles [105], which can be confirmed by AFM measurements. In Figure 5.12 (a, b, c), surface topographic images of 150 nm undoped BSO films deposited on STO substrates when the d_{ts} is 50 mm, 52 mm, and 55 mm, respectively. As the d_{ts} increases from 50 mm to 55 mm, the white particles on the surface increase rapidly, and according to the descriptions above, these particles are BaO_x particles created by combining excess Ba with O₂ molecules. Then, high-temperature (~1200 °C) annealing was performed in a furnace with oxygen flow for 1 h to reduce the TD density as well as to create an atomically flat stepterrace surface of BSO. Figure 5.12 (d, e, f) shows the surface changes of samples with d_{ts} of 50, 52, and 55 mm after high-temperature(~1200 °C) annealing. In the



Figure 5.12. Surface topographic images of 150 nm BSO films deposited on STO substrates when the target-to-heater distance is (a) 50 mm, (b) 52 mm, and (c) 55 mm, respectively. And, surface changes of (d) 50 mm, (e) 52 mm, and (f) 55 mm samples after high-temperature(\sim 1200 °C) annealing for 1 hour in the furnace with the oxygen flow. The holes found in (e) and (f) are caused by the escape of particles, which seem to be BaO_x.

case of the sample with d_{ts} of 50 mm without white particles on the surface before annealing, a surface with a distinct step-terrace structure could be obtained after annealing. However, in the case of sample with d_{ts} of 52 mm, the surface of the faint step-terrace structure was identified, and in the case of sample with d_{ts} of 55 mm, which had the most particles on the surface, it was confirmed that many holes were formed at the same time as irregular step-terrace structure after hightemperature($\sim 1200 \,^{\circ}$ C) annealing. These holes appear to be traces of highly mobile BaO_x particles escaping from the film when the atoms on the surface moves during the high-temperature annealing process to create an atomically flat surface. When focusing on the sample with d_{ts} of 50 mm with no holes on the surface with distinct step-terrace structure after high-temperature annealing, enlarged images of the central part of Figure 5.12 (d) and its line profile are shown in Figure 3.3. As it can be seen in chapter 3.2, the height profile of Figure 3.3 (c) confirms that the width of one terrace is about 0.2 µm, and the spacing of each terrace is about 0.4 nm, which proves that single unit cell step-terrace structure is finely formed after hightemperature annealing. Based on several previously reported studies [72,103], the topmost surface evolves to SnO₂-terminated atomically flat surface. The improved structural properties of this film after annealing can be confirmed not only from the AFM measurements but also from the RSM measurements. As it can be seen again in chapter 3.2, Figure 3.4 (a, b) show RSM (103) scans results of the BSO film deposited at a target-to-heater distance of 50 mm before and after hightemperature(~1200 °C). Comparing the two images, the Q_x interval of the BSO film after annealing decreased by about 30% compared to before annealing, indicating the structural enhancement that is the TDs annihilation effect. Therefore, AFM measurements confirmed that the atomically flat step-terrace surface of BSO was

successfully formed after high-temperature annealing treatment, and RSM measurements confirmed that annihilated TDs occurred due to improvement of structural properties inside the bulk as well as the surface of the film. Based on the



Figure 5.13. Seat resistance (R_s) of a 100 nm 1% BLSO film as a function of the target-to-substrate distance (45 mm $< d_{ts} \le 55$ mm) expressed by pre-annealing (red line) and post-annealing (purple line).

results of the heat treatment experiments of the BSO film, 1% BLSO film was subjected to high-temperature annealing of the same process (in a furnace with oxygen flow for 1 h), followed by structural and electrical properties measurements. The atomically flat step-terrace surface was created the same as in previous experiments, but the expected increase in conductivity was rarely measured. As shown in Figure 5.13, the electrical characteristics of samples with d_{ts} of 50 and 52 mm are measured after high-temperature annealing, but there is little decrease in R_s. In other words, despite some improvements in structural properties such as surface and TDs annihilation effect through high-temperature annealing, the film still appears to have many electronic traps that trap carriers.

5.5. Conclusion

In this chapter, I tried to improve the reduced n_{3D} and μ of the BLSO film through three methods such as using non-commercial LIO substrates whose lattice constants are matched with those of BLSO, inserting a mixed $Sr_{0.85}Ba_{0.15}HfO_3$ buffer layer replacing the BSO buffer layer, optimizing target-to-substrate spacing to 50 mm, and subsequent 1200 °C high-temperature annealing for structural enhancement of surface and bulk of the BLSO film. As a result, all attempts had only a slight improvement in electrical properties and didn't significantly reduce the deep acceptors density that traps the carrier. However, BSO films with SnO_2 -terminated step-terrace surface obtained through high-temperature annealing, the last of these attempts, played a crucial role in forming 2-dimensional electron gas at the interface of perovskite heterostructures. If other methods in the future can improve carrier density and mobility by more effectively reducing threading dislocation density, the 2DEG states of BSO-based heterostructures and the electrical properties of BLSO will open up the possibilities of observing new physical phenomena, especially in low-temperature measurements.

Chapter 6. Summary

BSO is a promising perovskite oxide with several exceptional characteristics compared to other perovskite oxides. It has high electron mobility with high carrier density, excellent transparency in the visible spectrum, and high oxygen stability as well as chemical stability, where these excellent properties of BSO make it an intriguing material for a wide range of applications such as transparent field-effect transistors, energy harvesting, optoelectronics, and high-power devices. My research described in this dissertation is particularly focused on 2-dimensional systems formed with BSO, LIO, and LSO.

Using the self-consistent Poisson-Schrödinger band calculator, we introduced a new model named interface polarization model, and 2DEG variation as a function of the LIO thickness of particular LIO/BLSO(0.3%) samples could be described by introducing this model. Not only that, interface polarization model was also proven applicable to the LSO/BSO interface, and the electrical and structural measurements and analyses of the LSO/BSO heterostructures demonstrate that 2DEG states are also formed at this interface. High-mobility FETs using the 2DEG channel and LSO gate dielectric were fabricated, showing mobility close to 100 cm²·V⁻¹·s⁻¹ at room temperature, which is the highest value reported to date in FETs based on the BSO channel and other gate oxides.

Next, in order to exclude the effect of impurity scattering from La dopants in the LIO/BLSO(0.3%) heterostructures, I have experimentally demonstrated that the conductance enhancement of more than 10⁴ occurs at the LIO/un-doped step-terrace structural BSO interface, where the BSO went through ex-situ high-temperature heat treatment and subsequent short-term DI water etching.

The possibilities of forming novel types of 2-dimensional systems, unreported to date, based on BSO are theoretically calculated using self-consistent Poisson-Schrödinger simulations, including 2DHG generated at the LSO/BSO interface and 2DEG generated at the SHO/BSO interfaces. Using iterative simulations by varying adjustments of related parameters, 2-dimensional charge carriers could be formed at each interface of these new heterostructures.

Temperature- and B-field-dependent low-temperature measurements were carried out using BSO-based 2-dimensional systems including LIO/step-terrace PLD-grown BSO, LIO/MBE-grown BSO, and δ -doped BSO systems. The temperature- and B-field-dependent measurements confirmed that the samples were under localization regimes. In order to reduce this adverse effect and improve transport properties, EDLTs with IL gating applied to BSO-based 2-dimensional systems were fabricated, and carriers of more than 10^{14} cm⁻² order were successfully accumulated at low-temperature. This indicates the feasibility of reversible electrolyte gating for carrier modulation in BSO-based 2-dimensional systems.

Finally, I tried to improve n_{3D} along with μ of the BLSO film through following methods such as using non-commercial LIO (110) substrates whose lattice constants are matched with those of BLSO, inserting a mixed $Sr_{0.85}Ba_{0.15}HfO_3$ buffer layer replacing the BSO buffer layer, optimizing target-to-substrate spacing to 50 mm, and subsequent 1200 °C high-temperature annealing for structural enhancement of surface and bulk of the BLSO film.

Continuous research and development of BSO-based systems is expected to further increase the potential for discovery of novel scientific phenomena as well as expand their commercialization in the future.

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- Y. Jang, S. Hong, J. Seo, <u>H. Cho</u>, K. Char, Z. Galazka. "Thin film transistors based on ultra-wide bandgap spinel ZnGa₂O₄". *Appl. Phys. Lett.* 116, 202104 (2020).
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List of presentations

- 1. <u>**H. Cho**</u>, Y. M. Kim, K. Char. "Effect of perovskite dielectric Ba_xSr_{1-x}HfO₃ on BaSnO₃". Workshop on Oxide Electronics 25, October 2018. (Poster)
- 2. <u>**H. Cho**</u>, Y. M. Kim, K. Char. "Effect of perovskite dielectric Ba_xSr_{1-x}HfO₃ on BaSnO₃". American Physical Society Meeting, March 2019. (Oral)
- 3. <u>H. Cho</u>, D. Song, Y. Kim, B. Kim, K. Char. "High-Mobility Field-Effect Transistor Using 2-Dimensional Electron Gas at the LaScO₃/BaSnO₃ Interface". Korea Dielectric Symposium 17, February 2022. (Poster)
- 4. <u>H. Cho</u>, D. Song, Y. Kim, B. Kim, K. Char. "High-Mobility Field-Effect Transistor Using 2-Dimensional Electron Gas at the LaScO₃/BaSnO₃ Interface". Workshop on Oxide Electronics 28, October 2022. (Poster)
- <u>H. Cho</u>, D. Song, Y. Kim, B. Kim, K. Char. "High-Mobility Field-Effect Transistor Using 2-Dimensional Electron Gas at the LaScO₃/BaSnO₃ Interface". Workshop on Functional Materials Science 4, June 2023. (Poster)
국문초록

페로브스카이트 산화물 BaSnO₃ 기반 시 스템에서 2차원 전자 가스의 수송 특성

조형민 서울대학교 물리천문학부

바륨 주석 산화물로도 알려진 BaSnO₃(BSO)는 지금까지 보고된 몇 가지 우수한 특성을 가진 유망한 물질이다. 다른 페로브스카이트 산화물 에 비해 BSO가 갖는 우수한 특성은 다음과 같다: 첫째, BSO는 n형 도 펀트(특히, La dopant)로 쉽게 도핑될 수 있으며, 높은 캐리어 밀도(n_{3D} ~10²⁰ cm⁻³)와 높은 전자 이동성(단결정의 경우 µ ~ 320 cm² · V⁻¹ · s^{-1} 및 박막의 경우 $\mu \sim 70 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)을 가지고 있어 상온에서 다른 페로브스카이트 산화물 중 가장 높다. 이 특성은 전자 장치에서 효 율적인 전하 수송을 달성하여 장치 성능을 향상시키는 데 필수적이다. 둘째, BSO는 가시 스펙트럼에서 우수한 투명도를 가지고 있어 빛이 상 당한 흡수나 산란 없이 통과할 수 있다. 이러한 특성으로 인해 투명 디 스플레이, 태양 전지, 그리고 센서와 같은 광전자 장치에 적합하다. 셋째, BSO는 높은 온도에서도 전기적, 광학적 특성을 유지하면서 우수한 열 안정성을 보여준다. 이러한 안정성은 전력 전자 장치 및 고체 산화물 연 료 전지와 같은 고온 작동과 관련된 애플리케이션에 매우 중요하다. 넷 째, BSO는 우수한 화학적 안정성을 보여주며 다양한 환경에서 열화에 대한 내성을 보여준다. 이러한 안정성은 특히 가혹한 조건이나 부식성

환경에서 장기적인 장치 신뢰성과 성능에 유리하다. BSO의 이러한 우수 한 특성은 투명 전계 효과 트랜지스터, 에너지 하베스팅, 광전자 및 고 출력 장치를 포함한 광범위한 응용 분야에 흥미로운 재료가 된다.

본 논문에서는 주로 BSO와 다른 페로브스카이트 산화물 사이의 헤테 로 구조, 특히 LaInO₃/BaSnO₃와 LaScO₃/BaSnO₃ 헤테로 구조에 대한 연구를 진행하고 있으며, 각 계면에 2차원 전자 가스(2DEG)가 형성되 어 있다. 자체 일관성 있는 포아송-슈뢰딩거 시뮬레이션의 계산과 고해 상도 투과 전자 현미경으로 검증된 이종 구조의 구조적 변조의 확인에 기반한 계면 분극 모델의 도입으로 LaInO₃/BaSnO₃ 계면에서 2DEG의 분석이 재확인되었다. 그리고, 전기적, 구조적 특성 분석을 통해 LaScO₃/BaSnO₃ 계면에서 기존에 보고되지 않은 2DEG가 발생한 것을 확인하고, 그 결과를 LaInO₃/BaSnO₃ 계면과 비교하였다. 계면 분극 모 델은 LaScO₃/BaSnO₃ 시스템에 적용되었는데, 분극은 계면에서 LaScO₃ 의 4 개의 유사 입방 단위 셀에만 존재하고 이후에는 LaInO₃/BaSnO₃ 계면처럼 소멸된다. 자체 일관성 있는 포아송-슈뢰딩거 방정식의 계산 에 따르면, LaScO₃/BaSnO₃ 헤테로 계면에서 생성되는 n_{2D}의 LaScO₃ 두께 의존성은 이 모델과 일치하며, 나아가 양자 우물의 단일 서브 밴드 를 예측한다. 마지막으로 전도성 2DEG 채널과 LaScO3를 게이트 유전 체로 사용하여 상온에서 100 cm²·V⁻¹·s⁻¹에 가까운 높은 전계 효과 이동도를 갖는 페로브스카이트 산화물로만 구성된 전계 효과 트랜지스터 가 시연되었다.

다음으로, BSO를 기반으로 한 다른 유형의 2차원 시스템을 형성할 수 있는 가능성이 자체 일관성 있는 포아송-슈뢰딩거 시뮬레이션을 사용하 여 이론적으로 계산되었다. 여기에는 LaScO₃/BaSnO₃ 계면에서 생성되 는 2차원 홀 가스(2DHG)와 SrHfO₃/BaSnO₃ 계면에서 생성되는 2차원

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전자 가스(2DEG)가 포함된다. 에너지 갭, BSO에 대한 전도대 오프셋, 깊은 도너 수준, 깊은 도너 밀도, 유전 상수, 유효 질량 및 분극화와 같 은 관련 매개변수를 다양하게 조정하여 시뮬레이션을 실행한 결과, 2차 원 전하 캐리어가 이러한 새로운 헤테로 구조의 계면에 형성될 수 있었 다. 시뮬레이션에 의한 이론적 계산은 향후 후속 실험의 기초가 될 것으 로 기대된다.

LaInO₃/BaSnO₃ 이종 구조는 최근 상온에서 전계 효과 소자를 포함하 여 우수한 수송 특성을 갖는 2DEG를 구현하기 위한 유망한 플랫폼으로 연구되고 있으나, 그 저온 거동은 여전히 잘 이해되지 않고 있다. 따라 서, 본 논문에서는 LaInO₃/BaSnO₃ 계면에서 형성되는 2DEG의 저온 특 성에 대한 자세한 연구가 수행되었다. 수직 및 평행 자기장에서 측정된 음의 자기 저항과 홀 측정으로부터 저온에서 전자 이동성이 증가하지 않 는다는 것은 이 시스템이 박막의 결함 및 스레딩 전위를 포함한 높은 밀 도의 무질서 상태로 인해 약한 국소화 체제 하에 있음을 시사한다. 그 후, 이온성 액체를 이용한 전기 이중 층 트랜지스터의 제작 및 BSO계 2차원 시스템으로의 액체 게이팅을 수행하여 저온에서 캐리어를 변조하 여 수송 특성을 향상시켰다. 이온-액체 게이팅을 사용함으로써 캐리어 는 1차 이상으로 크게 변조되었으며, 이는 BSO 기반 2차원 시스템에서 캐리어 변조를 위한 가역적 액체 게이팅의 가능성을 나타낸다.

마지막으로, BSO 기반 시스템의 전기적 특성을 개선하기 위한 몇 가 지 시도가 도입되었고, 1% La-doped BSO(BLSO)를 사용하여 사전 테 스트되었다. 먼저, 박막은 격자 상수가 BLSO 박막과 일치하는 사방 정 계 구조를 가진 이전에 보고되지 않은 새로운 LaInO₃ 기판을 사용하여 성장되었다. 둘째, 격자 상수가 BSO 버퍼 층과 일치하는 이전에 보고되 지 않은 새로운 Sr_{1-x}Ba_xHfO₃ 버퍼 층이 사용되었다. 마지막으로, BLSO 박막의 전기적 특성이 타겟-기판 간격 조정 혹은 후속 고온 열 처리를 통해 효과적으로 개선되는지 확인하였다. 그런 다음, 기존에 보 고된 BLSO 박막과 상기 시도를 포함하는 BLSO 박막의 특성을 비교 및 분석하였다.

Keywords: BaSnO₃, LaInO₃, LaScO₃, 페로브스카이트 산화물들, 이차원 전자 가스, 전계 효과 트랜지스터, 저온 측정, 이온-액체 게이팅

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