



이학박사 학위논문

Study of Role of SnO₂ Termination of BaSnO₃ in Formation of 2DEG State at the LaInO₃/BaSnO₃ Interface

LaInO₃/BaSnO₃ 인터페이스에서 2DEG 상태 형성에 있어서 BaSnO₃의 SnO₂ 터미네이션의 역할에 대한 연구

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Abstract

Study of Role of SnO₂ Termination of BaSnO₃ in Formation of 2DEG State at the LaInO₃/BaSnO₃ Interface

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In recent years, oxide semiconductors have garnered significant attention in various fields such as electronics, optoelectronics, and energy conversion devices, thanks to their remarkable electronic and optical properties. Composed of transition metal oxides like, Indium Oxide (In₂O₃), Zinc Oxide (ZnO), and Indium Tin Oxide (ITO), oxide semiconductors have advantages over traditional semiconductors like Silicon (Si) or Gallium Nitride (GaN), offering high carrier mobility and density through effective doping. Moreover, oxide semiconductors generally have wide band gaps of 3 eV or higher, making them transparent to visible light and suitable for use as Transparent Conducting Oxides (TCO). The unique combination of these properties makes oxide semiconductors highly desirable for various electronic and optoelectronic applications.

This dissertation particularly focused on the oxide semiconductor Barium Stanate (BaSnO₃, BSO) and its intriguing properties. BSO, known for its wide band gap and high electron mobility, has gained attention, especially for its TwoDimensional Electron Gas (2DEG) formation at the interface with Lanthanum Indium Oxide (LaInO₃, LIO), commonly referred to as the LIO/BSO 2DEG.

The formation of conventional 2DEG has been extensively studied in various semiconductor systems, such as AlGaAs/GaAs, AlGaN/GaN, and MgZnO/ZnO, where the quantum well is created by the conduction band offset between different materials. In the case of GaAs, the modulation doping approach is utilized, while polarization-induced carrier accumulation occurs in GaN and ZnO. However, a different type of 2DEG behavior was discovered in 2004 at the interface of LaAlO₃ and SrTiO₃, showing distinct properties and formation mechanisms attributed to the "polar catastrophe" and charge transfer mechanism through the interface.

The LIO/BSO 2DEG behavior can be explained by the "interface polarization" model, where polar discontinuity occurs near the interface due to the breaking of centrosymmetry. According to this model, the role of the SnO₂ terminating layer of BSO is crucial for the formation of the 2DEG at the LIO/BSO interface. Conductance measurements of in-situ grown LIO/BSO heterostructures reveal that the 2DEG forms only when the BSO surface is SnO₂ terminated. The terminating layer can be controlled by additional SnO₂ deposition (dusting) on the BSO surface, resulting in SnO₂ termination. The terminating layer was confirmed using Coaxial Impact Collision Ion Scattering Spectroscopy (CAICISS). Additionally, an ex-situ method involving a 9:1 mixture of acetone and water was explored for SnO₂ termination on BSO surfaces. Furthermore, a previous report on LIO/BSO 2DEG formation through mask and heat treatment was discussed, providing valuable insights into achieving SnO₂ termination and the underlying mechanisms.

In conclusion, oxide semiconductors have been researched for their unique electronic and optical properties in various application fields, and among them, BSO is a material with high electron mobility, electron density, and significant potential. Particularly, the role of SnO₂ terminating layer at the LIO/BSO 2DEG interface is crucial. These research findings are expected to contribute to the development of applications utilizing LIO/BSO 2DEG, such as High Electron Mobility Transistors (HEMTs), as well as the exploration of new physical phenomena.

Keyword : BaSnO₃, LaInO₃, 2DEG, Termination, Interfacial polarization

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Chapter 1. Introduction

1.1. Overview of oxide semiconductors

This Ph.D. dissertation is devoted to a study on the critical effect of BaSnO₃ (BSO) termination and the research to achieve SnO₂ termination of BSO, focusing on the Two-Dimensional Electron Gas (2DEG) state at the BSO/LaInO₃ (LIO) interface.[1] Oxide semiconductors have recently attracted significant attention due to their unique electronic and optical properties, and their potential for a wide range of applications in electronics, optoelectronics, and energy conversion devices. Oxide semiconductors, which are often composed of transition metal oxides like Indium Oxide (In₂O₃), Zinc Oxide (ZnO), and Indium Tin Oxide (ITO), have unique properties that enable high carrier mobility and high carrier density through doping. These properties provide significant advantages over existing semiconductors such as Silicon (Si) or Gallium Nitride (GaN). Additionally, oxide semiconductors commonly have wide band gaps of 3 eV or more, making them transparent to visible light and suitable for use as Transparent Conducting Oxides (TCO). This combination of properties makes oxide semiconductors an attractive material for use in various electronic and optoelectronic applications. These properties have led to the commercialization of transparent conductive oxides such as ITO and Indium Gallium Zinc Oxide (IGZO), which are widely used in electronic devices. Furthermore, research is ongoing in the development of oxide semiconductors for high-temperature superconductors such as Yttrium Barium Copper Oxide (YBCO), materials with ferroelectricity such as Lead Zirconate Titanate (PZT), and solar cells utilizing the photovoltaic properties of organic halide oxides.[2-4] Overall, the

unique properties of oxide semiconductors hold promise for the development of advanced materials with improved performance and functionality.



Figure 1.1 BaSnO₃ Perovskite structure.

1.2. Oxide perovskite material, BaSnO₃ (BSO)

Figure 1.1 shows the crystalline structure of BSO which has a perovskite structure. Perovskite materials are characterized by their crystal structure, known as the ABX₃ structure. In this structure, A and B represent cations, while X represents anions. The B cations are bonded through BX_6 octahedra, creating a corner-sharing arrangement between the octahedra. As shown in Figure 1.2. perovskite materials have been extensively studied for their applications in optoelectronic devices, solar cells, lasers, and more.[2] Also, the unique properties of perovskite oxide materials, such as PZT, have attracted attention for their ferroelectric characteristics, leading to



Figure 1.2 Extensive research and promising applications of perovskite materials. [2,3,5,6]

the development of innovative ferroelectric devices.[3] In addition, perovskites are actively investigated for their potential in UV transparent devices, taking advantage of their wide bandgap.[3] Moreover, the combination of wide bandgap, high electron mobility, and high carrier density in perovskite materials positions them as promising candidates for high-power electronic devices.[5] These exceptional characteristics have established perovskites as versatile materials with vast potential in various fields. Perovskite materials have experienced significant advancements and are currently at the forefront of scientific and technological research, boasting numerous applications.

BSO is a material with a cubic perovskite structure, consisting of alternating nonpolar layers of BaO⁰ and SnO₂⁰. The space group of BSO is $Pm\overline{3}m$ which is centrosymmetric. BSO is a material with a large bandgap of 3.1 eV, and when doped with Lanthanum (La), it becomes an n-type material with high mobility of 320 cm²V⁻¹s⁻¹ that has been the subject of increasing research interest in recent years due to its unique electronic properties.[7] In addition, thermal stability due to oxygen vacancy

is a major issue in oxide semiconductors, but BSO is a thermally stable material with stable properties even after repeated thermal cycles.[7] The high thermal stability of BSO makes it a promising material for use in high-temperature applications. The lattice constant of BSO was found to be 4.116 Å using X-ray diffraction (XRD) measurements. This information is crucial for characterizing BSO's crystal structure and optimizing device performance.[8] BSO exhibits photoconductivity, a phenomenon commonly observed in semiconductor materials such as Si. Photoconductivity refers to the change in conductivity induced by photons with energies higher than the bandgap. While previous research suggests that BSO's photoconductivity primarily occurs in the ultraviolet range, it has been observed that photoconductivity in the yellow light range also occurs, particularly in lightly doped BLSO.

1.3. Wide bandgap semiconductor

Wide bandgap semiconductors are materials that have a large energy gap between the valence and conduction bands, typically greater than that of conventional semiconductors like Si (1.1 eV) or GaAs (1.42 eV).[9] These materials have unique electronic and optical properties that make them attractive for various applications, such as power electronics, optoelectronics, and photovoltaics. Among the wide bandgap semiconductors, oxide semiconductors have gained attention due to their tunable properties and high transparency in the visible light range. In addition, the bandgap of single crystal BaSnO₃ has been measured using optical absorption spectra, yielding a value of 3.1 eV.[8] Other measurements of the bandgap of BSO



Figure 1.3 Transmission spectra and absorption coefficient of BSO and BLSO single crystals. a) Transmission spectra of undoped BSO and BLSO single crystals. b) Absorption coefficient against photon energy for both undoped BSO and BLSO crystals.[7]

have been reported, including optical spectroscopy measurements ranging from 3.1-3.5 eV [7,11,12], 3.3 eV HAXPES measurements of 3.4 eV [13], and ARPES measurements of 3.7 eV.[14] In this dissertation, 3.1eV measured on a single crystal was used as the band gap of BSO. Due to its wide band gap of 3.1 eV, BSO has a high transmittance in the visible. As shown in **Figure 1.3**, BSO has a high transmittance of over 0.7, indicating its potential as a TCO.[7] The Figure 1.3 shows the transmission spectra and absorption coefficient (α) of BSO and BLSO single crystals, as reported in prior scientific studies. The transmission spectra were obtained through experimental measurements to determine the absorption coefficient of each undoped sample, as well as samples doped with a concentration of n = 2.39×10^{20} cm⁻³.

1.4. High electron mobility

When doped with La, BSO becomes n-type doped. La-doped BSO (BLSO) has been reported to have a mobility of over $320 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$ at room temperature in single crystals, even at carrier densities exceeding 10^{20} cm^{-3} which is higher than conventional semiconductor such as Si or GaN.[7] While films show $180 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ with a carrier density of 10^{20} cm^{-3} .[10] Compared to perovskite oxide materials such as ZnO or SrTiO₃ (STO), BLSO has a mobility several times higher, and even when compared to conventional semiconductors such as Si or GaN. In the case of films, however, carriers are trapped by the dislocation density. The acceptor density is dependent to the substrate on which BLSO are grown.[15,16] When grown on a STO



Figure 1.4 Electron mobility vs carrier density graph of reported BLSO.[10]

substrate, the carrier density was reported to be 6×10^{19} cm⁻³, while on an MgO substrate, using a BaHfO₃ (BHO) buffer, it is reported to be 4×10^{19} cm⁻³. BHO is

used as a buffer to reduce the lattice constant mismatch between MgO and BSO. Furthermore, if BSO is doped with potassium instead of barium [17] or doped with nitrogen instead of oxygen [18], it can be made into a p-type material, enabling the implementation of PN-junctions.

1.5. Thermal stability of BSO

Oxide semiconductor have been encountered challenges in maintaining oxygen stability. However, former research has focused on investigating BSO as a potential oxide material due to its exceptional oxygen stability.[19] As shown in Figure 1.5, the experimental procedure involved subjecting the BSO films to annealing at 530 °C in three different gases: air, O₂, and Ar. The resistance of the films was monitored over time to assess their stability. The second annealing process in O₂ aimed to remove oxygen vacancies, while the third annealing process in Ar created an oxygenvacancy-rich environment, allowing for the determination of the chemical diffusion constant. The results indicated a small resistance change of 1.7% when annealed in air and an 8% change when annealed in Ar gas. The resistance variations suggest the stability of oxygen atoms in BSO films. Thermal stability is an important issue in oxide semiconductors, but BLSO has the advantage of showing little change in its properties even after repeated thermal cycles. The reason why oxygen stability is important is that if oxygen vacancy unintentionally dopes, it becomes difficult to implement the same characteristics when creating a device. The oxygen stability of BSO indicates that it is a promising material for practical applications. Thermal stability is a crucial issue for oxide materials, as they can develop oxygen vacancies



Figure 1.5 a) The temperature profile and gas atmosphere were adjusted as shown in the upper panel, and the resulting resistance variation is plotted in the lower panel. The BSO film had a thickness of 100 nm, and the temperature was maintained at 530 °C for 5 hours. b) The resistance versus temperature plot illustrates the changes observed under different gas atmospheres. The resistance decreased (increased) by approximately 8% when annealed in an Ar (O₂) atmosphere for 5 hours at 530 °C, while it showed a minor change of about 1.7% in air.[19]

and undergo changes in properties under high temperature. BSO has excellent thermal stability compared to other materials, making it a desirable option for hightemperature applications.

1.6. Photoconductivity of BSO

The photoconductivity of BSO has been reported in previous studies.[20] As shown in **Figure 1.6**, an epitaxial film of BSO was grown on a MgO substrate to eliminate its contribution to the photoconductivity of the substrate due to its large



Figure 1.6 The time-dependent behavior of the photoconductivity of BSO and STO on both short and long time scales. The wavelength of the illumination is fixed at 330 nm. a) short time scale. b) long time scale.[20]

bandgap. Specifically, compared STO. BSO exhibited sustained to photoconductivity for a long time after exposure to light, whereas STO exhibited little sustained conductivity. Additionally, the photoconductivity of BSO increased to a value more than 25 times higher than that of STO after 3 hours of illumination. The spectral photoconductive response of the two materials shows the highest peak below 400 nm, indicating that electron-hole pair generation is the main mechanism of photoconductivity. The large and persistent photoconductivity of BSO appears to be related to deep-level defects with relatively large barriers for charge trapping and detrapping.

On the other hand, the conductance of lightly doped BLSO films exhibits an interesting behavior when exposed to yellow light (3000K fluorescent lamp) at room temperature. Over time, the conductance of the BLSO film tends to increase under such illumination conditions. This phenomenon is known as Persistent

Photoconductivity (PPC), where the conductance of the film remains elevated even after the light source is removed. Upon initial deposition, the resistance of the film may increase by several orders of magnitude, suggesting that carriers become slowly trapped within the material over a period of several days. Notably, the conductance does not show a significant increase when yellow light is carefully blocked at room temperature, indicating the dependence of this behavior on light exposure. As depicted in **Figure 1.7**, the conductance of Ba_xLa_{1-x}SnO₃ (BLSO) thin films in the very lightly doped region ($0.002 \le x \le 0.004$) often changes over time (days and weeks) from $10^{-12} \Omega^{-1}$ to $10^{-9} \Omega^{-1}$ or even lower. As shown in **Figure 1.8**, in order to investigate the effect of thermal annealing on conductance change, 0.2% BLSO thin films were prepared on STO substrates with degenerately doped 4 %BLSO contacts. It was found that the conductance of as-grown BLSO thin films increased over time. The films were annealed in the temperature range from 750°C to 900°C in vacuum or in air to examine the effect of thermal annealing on the conductance change. After



Figure 1.7 Time-dependent increase in conductance of lightly doped BLSO films under yellow light.



Figure 1.8 Influence of thermal annealing conditions on photoconductivity under yellow light. a) A sample annealed at 750°C in vacuum for 1 hour. In this case, no persistent photoconductivity was observed under yellow light. b) the sample annealed at 800°C showed variations in resistance. The sample annealed at 900°C in an oxygen atmosphere for 1 hour exhibited no change in resistance, indicating the absence of photoconductivity.

high-temperature thermal annealing, the increased conductance returned to the original low conductance values and remained stable over time. The large density of deep acceptor states acting as electron traps in BLSO suggests that the conductance increase is due to the electrons escaping from the low barrier potential wells of the electron trap states over time. High-temperature annealing makes the potential well deeper, preventing the trapped electrons from escaping. The density and the level of such trap states will be investigated using deep level transient spectroscopy to validate these assumptions.

References

- [1] S. Kim, M. Lippmaa, J. Lee, H. Cho, J. Kim, B. Kim and K. Char, *Adv. Mater. Interfaces* 9,2201781 (2022).
- [2] Y. Zhou, L. M. Herz, A. K. Y. Jen and M. Saliba, Nat. Energy 7, 794 (2022).
- [3] C. Ko, Y. Lee, Y. Chen, J. Suh, D. Fu, A. Suslu, S. Lee, J. D. Clarkson, H. S. Choe, S. Tongay, R. Ramesh and J. Wu, *Adv. Mater.* 28, 2923 (2016).
- [4] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang,
 Y. Q. Wang and C. W. Chu, *Phys. Rev. Lett.* 58, 908 (1987).
- [5] J. Kim, H. Yun, J. Seo, J. H. Kim, J. H. Kim, K. A. Mkhoyan, B. Kim and K. Char, ACS Appl. Electron. Mater. 4, 3623 (2022).
- [6] S. S. Williamson, Nat. Electron. 5, 14 (2022).
- [7] H. J. Kim, U. Kim, T. H. Kim, J. Kim, H. M. Kim, B.-G. Jeon, W.-J. Lee, H. S. Mun, K. T. Hong, J. Yu, K. Char and K. H. Kim, *Phys. Rev. B* 86, 165205 (2012).
- [8] U. Kim, C. Park, T. Ha, Y. M. Kim, N. Kim, C. Ju, J. Park, J. Yu, J. H. Kim and K. Char, *APL Mater.* 3, 036101 (2015).
- [9] S. Adachi, J. Appl. Phys. 58, R1 (1985).
- [10] H. Paik, Z. Chen, E. Lochocki, A. Seidner H., A. Verma, N. Tanen, J. Park, M. Uchida, S. Shang, B.-C. Zhou, M. Brützam, R. Uecker, Z.-K. Liu, D. Jena, K. M. Shen, D. A. Muller and D. G. Schlom, *APL Mater.* 5, 116107 (2017).
- [11] D. Seo, K. Yu, Y. Jun Chang, E. Sohn, K. Hoon Kim and E. J. Choi, *Appl. Phys. Lett.* 104, 022102 (2014).
- [12] T. N. Stanislavchuk, A. A. Sirenko, A. P. Litvinchuk, X. Luo and S.-W. Cheong, J. Appl. Phys. 112, 044108 (2012).
- [13] Z. Lebens-Higgins, D. O. Scanlon, H. Paik, S. Sallis, Y. Nie, M. Uchida, N. F.

Quackenbush, M. J. Wahila, G. E. Sterbinsky, D. A. Arena, J. C. Woicik, D. G. Schlom and L. F. J. Piper, *Phys. Rev. Lett.* **116**, 027602 (2016).

- [14] B. S. Joo, Y. J. Chang, L. Moreschini, A. Bostwick, E. Rotenberg and M. Han, *Curr. Appl. Phys.* 17, 595 (2017).
- [15] K. Ellmer, Nat. Photonics 6, 809 (2012).
- [16] J. Son, P. Moetakef, B. Jalan, O. Bierwagen, N. J. Wright, R. Engel-Herbert and S. Stemmer, *Nat. Mat.* 9, 482 (2010).
- [17] H. M. Kim, U. Kim, C. Park, H. Kwon and K. Char, *APL Mater.* 4, 056105 (2016).
- [18] J. Wang and B. Luo, Ceram. Int. 46, 25678 (2020).
- [19] H. J. Kim, U. Kim, Kim, T. H. Kim, H. S. Mun, B.-G. Jeon, K. T. Hong, W.-J.Lee, C. Ju, K. H. Kim and K. Char, *Appl. Phys. Express* 5, 061102 (2012).
- [20] J. Park, U. Kim and K. Char, Appl. Phys. Lett. 108, 092106 (2016).

Chapter 2. Overview of 2DEG: From Conventional Systems to Interfacial Polarization Model

2.1. 1. Introduction

The 2DEG where electrons are confined in a narrow quantum well has been a very fertile ground for discovering novel phenomena as well as for use in semiconductor applications such as HEMTs.[1,2] The quantum well in conventional 2DEGs (AlGaAs/GaAs, AlGaN/GaN, and MgZnO/ZnO) are formed by the conduction band offset between the two materials.[1-4] Two different approaches have been studied for conventional semiconductor 2DEGs: the modulation doping approach is used for GaAs while polarization-induced carrier accumulation occurs in GaN and ZnO.[1,2,5,6] On the other hand, 2DEG-like behavior was also found at LAO/STO interfaces in 2004.[8] The LAO/STO 2DEG exhibits distinct properties compared to conventional semiconductor 2DEGs like AlGaAs/GaAs, AlGaN/GaN, and MgZnO/ZnO. Additionally, their formation mechanism differs from that of the aforementioned semiconductor 2DEGs. The 'polar catastrophe', and the resulting charge transfer mechanism through the interface, has been considered as the primary mechanism for 2DEG between LAO and STO.[7] Recently, sheet conductance enhancement by four order of magnitudes was reported at the LIO/BSO interface.[9,10] The LIO/BSO 2DEG is described by a model in which polar discontinuity occurs only near the interface ('interface polarization' model) due to the inversion symmetry breaking at the interface. [9,11]

2.2. Conventional 2DEG system: Modulation doping approach (AlGaAs/GaAs)

From the 1980s, the AlGaAs/GaAs 2DEG has been widely studied for HEMT applications.[1,2] The high mobility of electrons in AlGaAs/GaAs 2DEGs is achieved by reducing impurity scattering through modulation doping. Since GaAs does not suffer from unintentional doping, the electron mobility in GaAs can be increased by modulation doping the larger bandgap AlGaAs with a Si dopant. In the AlGaAs/GaAs system, a quantum well is formed at the interface due to the conduction band offset between the two materials.[2] GaAs has the zinc blende structure in the $F\overline{4}3m$ space group and it is thus a non-centrosymmetric crystal. Despite the non-centrosymmetric crystal structure, the spontaneous polarization of GaAs and AlGaAs is almost zero.[12,13] The piezoelectric polarization is negligible because the lattice constant of AlGaAs is nearly the same as that of GaAs.[12,13] Since there is no polarization in GaAs and AlGaAs, no polarization discontinuity exits at the interface, and a quantum well is formed only by the conduction band offset. Therefore, in the AlGaAs/GaAs system, the effect of crystalline direction or terminating layer, which may determine the direction of the polarization, can be ignored.

The **Figure 2.1** illustrates the band structure of an AlGaAs/GaAs 2DEG system. In this configuration, a dopant is introduced using Si in the AlGaAs region, which has a larger bandgap compared to GaAs. The dopant is strategically placed behind the interface, with a spacer to prevent direct contact with the interface. This is a modulation doping technique, which has become a groundbreaking method for enhancing the mobility of AlGaAs/GaAs 2DEG. The Si dopant creates deep acceptor centers, leading to a reduction in the electron mobility within the 2DEG. Conversely, the spacer region lacks such dopants, resulting in higher mobility. It is worth noting that this system relies solely on the band offsets between the two materials for the formation of a quantum well, as there is no polarization effect present in either material. The unique band structure depicted in the figure showcases the intricate interplay between dopant placement and the resulting electron mobility characteristics in the AlGaAs/GaAs 2DEG system.



Figure 2.1 Band structure of AlGaAs/GaAs 2DEG system with modulation doping. Schematic representation of the band structure in an AlGaAs/GaAs 2DEG system with modulation doping, illustrating the use of Si dopants for modulation doping.

2.3. Conventional 2DEG system: Polarization-induced carrier accumulation (AlGaN/GaN and MgZnO/ZnO)

On the other hand, the AlGaN/GaN and MgZnO/ZnO interfaces form 2DEGs due to polarization-induced doping.[5,6] Both GaN and ZnO have the wurtzite structure belonging to the *P*6₃*mc* space group. As shown **Figure 2.2**, the crystals consist of hexagonally arranged Ga-N binary layers in an alternating stacking sequence, which is non-centrosymmetric. If the crystal direction is [0001], the binary layers are terminated with Ga and it becomes Ga-face. If it is the opposite direction, it becomes N-face. Because of their non-centrosymmetricity, GaN has a spontaneous polarization of 2.90 μ C cm⁻² and Al_{0.32}Ga_{0.68}N has a spontaneous polarization (*P*_{sp}) of 4.56 μ C cm⁻².[5,12] The total polarization (*P*_{tot}) in such wutzites is determined by the sum of spontaneous polarization and piezoelectric polarization, and its difference between AlGaN and GaN determines the polarization discontinuity at the interface. In AlGaN/GaN, the direction of the spontaneous polarization is



Figure 2.2 Polarization in AlGaN/GaN system with Ga-Face and N-Face orientations

determined by the crystal orientation due to the inversion symmetry breaking. When the wurtzite lattice is viewed along the [0001] or 0001 crystallographic directions, the dipoles between the two constituent atoms are all aligned in one direction, determining the polarization direction. The Ga face [0001] presents spontaneous polarization toward the GaN from AlGaN, and the N face $[000\bar{1}]$ presents spontaneous polarization in opposite direction.[5] In addition to the spontaneous polarization, there exists the piezoelectric polarization (P_{pe}) effect due to the lattice mismatch between GaN and AlGaN in a AlGaN/GaN heterostructure.[5] The direction of the piezoelectric polarization is determined by the direction of the spontaneous polarization and the type of strain in each layer. The P_{sp} and P_{pe} of GaAs, AlGaAs, GaN, AlGaN, ZnO, and MgZnO can be found in Table 2.1, where the ratio of Al and Mg alloying is 32%, respectively. As shown in Table 2.1, the total polarization in AlGaN is $P_{tot} = P_{sp} + P_{pe} = 4.56 \ \mu C \ cm^{-2} + 1.17 \ \mu C \ cm^{-2} = 5.73 \ \mu C$ cm⁻² at its maximum when AlGaN is under tensile strain on relaxed GaN, and 4.56 μ C cm⁻² at its inimum when the AlGaN layer is fully relaxed on GaN.[5,12,14] Therefore, the polarization discontinuity (ΔP) at the interface of AlGaN/GaN is ΔP = $P_{AIGaN} - P_{GaN} = 2.83 \ \mu C \ cm^{-2}$ at its maximum and $\Delta P = 1.66 \ \mu C \ cm^{-2}$ at its minimum. In the case of the GaN/AlGaN structure, the GaN layer can be subjected to compressive strain on relaxed AlGaN. In this case, ΔP becomes -2.70 μ C cm⁻². In addition to the polarization discontinuity at the interface, the formation of a 2DEG at the interface is aided by the conduction band offset, which is 1.1 eV for the Al_{0.32}GaN_{0.68}/GaN interface. Unlike an AlGaAs/GaAs 2DEG, intentional doping in the wider bandgap AlGaN is not required due to the existence of intrinsic deep donors. The N vacancies as well as the O and Si impurities in GaN were considered as native defects generating intrinsic donors and these donors become deep donors

when the Al ratio in AlGaAs is above 0.4.[15-17] In the case of ZnO, Zn and O are playing the same role as Ga and N in GaN.[7,18]

Figure 2.3 shows the 1D band structure of AlGaN/GaN 2DEG, which was calculated using the Poisson-Schrödinger (P-S) calculator by Snider.[19] The simulation was specifically performed for the Ga-face orientation of the structure. The plot represents the energy levels along the z-axis, with z=0 corresponding to the interface between the AlGaN and GaN layers. The calculated results demonstrate the formation of a 2DEG precisely at the interface (z=0), indicating the confinement of electrons within a confined region.

Polarization characteristics of various systems, including the AlGaN/GaN system, the MgZnO/ZnO system, and the AlGaAs/GaAs system discussed in Chapter 2.2 and Chapter 2.3, have been compiled and presented in Table 2.1. This table



Figure 2.3 one-dimensional band structure calculation of AlGaN/GaN 2DEG for Ga-face orientation

provides a comprehensive overview of the polarization properties exhibited by each system. By referring to Table 2.1, one can gain insights into the specific types of
polarization, such as spontaneous polarization (P_{sp}) and piezoelectric polarization (P_{pe}) , associated with these materials. The summarized data allows for a comparative analysis of the polarization behavior among the different systems, enabling a better understanding of their unique characteristics and their implications in device performance and functionality.

Top/bottom Layer x=0.32	Top layer Stress	Top $P_{\rm sp}$ [μ C cm ⁻²]	Top P _{pe}	Bottom P _{sp}	Bottom P _{pe}	ΔP
AlGaAs/GaAs	Tensile	0^{a}	<1×10 ^{-3 a,b}	0 ^a	0 ^a	0
AlGaN/GaN	Relaxed	$4.56^{b,c}$	0^{c}	2.90 ^c	0^{c}	1.66
AlGaN/GaN	Tensile	$4.56^{b,c}$	$1.17^{b,c}$	2.90 ^c	0^{c}	2.83
GaN/AlGaN	Compressive	2.90°	-1.04 ^c	4.56 ^{b,c}	0^{c}	-2.70
MgZnO/ZnO	Tensile	7.43 ^{b,d}	1.10 ^{b,d}	5.40 ^d	0	3.13
^a Ref. [13], ^b Ref. [12], ^c Ref. [5], ^d Ref. [4]						

Table 2.1 Polarization of GaAs, AlGaAs, GaN, AlGaN, ZnO and MgZnO

2.4. Polar catastrophe model (LaAlO₃ (LAO)/SrTiO₃ (STO))

Ohtomo and Hwang discovered a conducting layer at the interface between LAO and STO. While LAO and STO are insulating, the LAO/STO interface exhibits a high carrier density. The behavior of LAO/STO 2DEG is explained by a mechanism distinct from conventional 2DEGs.[7,8] The very high sheet carrier density found at LAO/STO interfaces, larger than 3×10^{14} cm⁻², is much higher than those in the conventional semiconductor 2DEGs.[20] The origin of such high carrier density has not been fully understood yet, but several origins have been proposed, such as oxygen vacancies, interfacial mixing and the polar catastrophe.[7,21-23]

Among these, the polar catastrophe model is widely accepted. According to the polar catastrophe model, the internal potential diverges as the thickness of the LAO layer increases but the divergence catastrophe can be avoided if half an electron per unit cell $(3 \times 10^{14} \text{ cm}^{-2})$ charge transfer across the interface occurs and it compensate electrostatic potential at the $(\text{LaO})^+/(\text{TiO}_2)^0$ interface.[7] This is why the polar catastrophe model is called a 'charge transfer' model.[7] In this model, the $(\text{AlO}_2)^-/(\text{SrO})^0$ interface is expected to form a Two-Dimensional Hole Gas (2DHG), which has been reported to be experimentally observed.[24] The termination of the interface, either $(\text{AlO}_2)^-/(\text{SrO})^0$ or $(\text{LaO})^+/(\text{TiO}_2)^0$ thus determines whether a 2DEG or a 2DHG forms at the interface in this model.

Figure 2.4 shows the concept of polar catastrophe model between LAO and STO. In Figure 2.4ab, an unreconstructed interface is depicted where the STO planes are electrically neutral, while the LAO planes possess alternating net charges. An electric potential (V) diverges as the thickness increases. Figure 2.4c proposes the addition of half an electron to the last Ti layer. This induces an interface dipole, causing the electric field to oscillate around zero and ensuring a finite potential. Similarly, Figure 2.4d illustrates the avoidance of divergence at the AlO₂/SrO/TiO₂



Figure 2.4 Polar catastrophe at interfaces between LAO and STO.[7]

interface by removing half an electron from the SrO plane in the form of oxygen vacancies.

2.5. Interfacial polarization model of LIO/BSO

BSO is a cubic perovskite semiconductor with a wide band gap (3.1 eV).[25,26]LIO is an orthorhombic perovskite with a large band gap of 5.0 eV and its pseudocubic lattice constant is 4.117 Å which is almost matched to the BSO cubic lattice constant of 4.116 Å.[27,28] The space group of BSO is $Pm\bar{3}m$ which is centrosymmetric. The orthorhombic LIO is in the space group of Pnma which is also centrosymmetric. Therefore, neither LIO nor BSO can have spontaneous polarization in their bulk form. However, within a few unit cells near the interface where the translation symmetry is broken, a polar state can exist in the growth direction in LIO. LIO and BSO are both insulating materials individually. However, when BSO is doped differently with La and deposited with LIO on top, a significant increase in conductance is observed at the interface between the two materials, as shown in the **Figure 2.5**.[9,10]



Figure 2.5 a) Schematic diagram of a LIO/BLSO 2DEG. b,c) The sheet conductance varies with the La concentration at the LIO/BLSO interfaces on an STO substrate (b). On an MgO substrate(c).[9.10]

Therefore, an "interfacial polarization" model has been proposed to explain the 2DEG formation at LIO/BSO interfaces.[9] Experimentally, the LIO/BSO conductance reaches a maximum value when the LIO thickness is four unit cells and starts to decrease for thicker layers.[10,11] It has been shown that this experimental result can be explained by the 'interface polarization' model through a self-consistent P-S calculation.[11,12]

2.6. Analyzing the LIO/BSO interface with Poisson-Schrödinger simulation

As shown in **Figure 2.6**a, the BSO lattice consists of a sequence of nonpolar layers of $(BaO)^0$ and $(SnO_2)^0$. Since the $(BaO)^0$ and $(SnO_2)^0$ layers in BSO are neutral, spontaneous polarization is not possible. On the other hand, the LIO has a sequence of polar layers of $(LaO)^+$ and $(InO_2)^-$. The $(LaO)^+/(InO_2)^-$ and $(InO_2)^-/(LaO)^+/(InO_2)^-$ and $(InO_2)^-/(LaO)^+/(InO_2)^-$ and $(InO_2)^-/(LaO)^+/(InO_2)^-$ and $(InO_2)^-/(LaO)^+/(InO_2)^-/(InO_2)^$

formed at the interface, but for BaO termination $(LaO)^+/(InO_2)^-/(BaO)^0$, no 2DEG can be formed, nor can a 2DHG form due to the very small valence band offset. Since LIO/BSO 2DEG formation is determined by the LIO polarization direction at the interface, the 2DEG formation will be sensitive to the terminating layer of the BSO crystal. To examine this, we studied the LIO/BSO conductance by controlling the termination of the BSO surface via in-situ additional SnO₂ depositions.



Figure 2.6 a) Schematic illustration of the $(LaO)^+/(SnO_2)^0$ interface $(SnO_2 \text{ termination})$ and $(InO_2)^-/(BaO)^0$ interface (BaO termination). At the $(LaO)^+/(SnO_2)^0$ interface, the direction of the polarization is toward to BSO. At the $(InO_2)^-/(BaO)^0$ interface, direction of the polarization is the reverse of the previous one. b) Calculated band diagram at the SnO₂ termination and BaO termination interface using a self-consistent P-S calculation. In addition to the conduction band offset between the two materials, the energy level is lowered due to polarization at the interface. In the case of SnO₂ termination, 2DEG was formed at the interface, but in the case of BaO termination neither 2DEG nor 2DHG can be formed.[30]

Reference

- [1] H. L. Störmer, R. Dingle, A. C. Gossard, W. Wiegmann and M. D. Sturge, *Solid State Commun.* 29, 705 (1979).
- [2] T. Mimura, S. Hiyamizu, T. Fujii and K. Nanbu, Jpn. J. Appl. Phys. 19, L225 (1980).
- [3] M. A. Khan, J. N. Kuznia, J. M. Van Hove, N. Pan and J. Carter, *Appl. Phys. Lett.*60, 3027 (1992).
- [4] A. Tsukazaki, A. Ohtomo, T. Kita, Y. Ohno, H. Ohno and M. Kawasaki, *Science* 315, 1388 (2007).
- [5] O. Ambacher, J. Smart, J. R. Shealy, N. G. Weimann, K. Chu, M. Murphy, W. J. Schaff, L. F. Eastman, R. Dimitrov, L. Wittmer, M. Stutzmann, W. Rieger and J. Hilsenbeck, *J. Appl. Phys.* 85, 3222 (1999).
- [6] H. Tampo, H. Shibata, K. Maejima, A. Yamada, K. Matsubara, P. Fons, S. Kashiwaya, S. Niki, Y. Chiba, T. Wakamatsu and H. Kanie, *Appl. Phys. Lett.* 93, 202104 (2008).
- [7] N. Nakagawa, H. Y. Hwang and D. A. Muller, Nat. Mater. 5, 204 (2006).
- [8] A. Ohtomo and H. Y. Hwang, *Nature* **427**, 423 (2004).
- [9] U. Kim, C. Park, Y. M. Kim, J. Shin and K. Char, APL Mater. 4, 071102 (2016).
- [10] Y. Kim, Y. M. Kim, J. Shin and K. Char, APL Mater. 6, 096104 (2018).
- [11] Y. M. Kim, T. Markurt, Y. Kim, M. Zupancic, J. Shin, M. Albrecht and K. Char, *Sci. Rep.* 9, 16202 (2019).
- [12] Y. Kim, S. Kim, H. Cho, Y. M. Kim, H. Ohta and K. Char, *Phys. Rev. Appl.* 17, 014031 (2022).
- [13] S. Adachi, J. Appl. Phys. 58, R1 (1985).

- [14] A. D. Bykhovski, B. L. Gelmont and M. S. Shur, J. Appl. Phys. 81, 6332 (1997).
- [15] D. C. Look, D. C. Reynolds, J. W. Hemsky, J. R. Sizelove, R. L. Jones and R. J. Molnar, *Phys. Rev. Lett.* **79**, 2273 (1997).
- [16] C. G. Van de Walle, C. Stampfl and J. Neugebauer, J. Cryst. Growth 189-190, 505 (1998).
- [17] C. Wetzel, T. Suski, J. W. Ager Iii, E. R. Weber, E. E. Haller, S. Fischer, B. K. Meyer, R. J. Molnar and P. Perlin, *Phys. Rev. Lett.* 78, 3923 (1997).
- [18] M. Yano, K. Hashimoto, K. Fujimoto, K. Koike, S. Sasa, M. Inoue, Y. Uetsuji,
 T. Ohnishi and K. Inaba, J. Cryst. Growth 301-302, 353 (2007).
- [19] I. H. Tan, G. L. Snider, L. D. Chang and E. L. Hu, J. Appl. Phys. 68, 4071 (1990).
- [20] S. Thiel, G. Hammerl, A. Schmehl, C. W. Schneider and J. Mannhart, *Science* 313, 1942 (2006).
- [21] W. Siemons, G. Koster, H. Yamamoto, W. A. Harrison, G. Lucovsky, T. H. Geballe, D. H. A. Blank and M. R. Beasley, *Phys. Rev. Lett.* 98, 196802 (2007).
- [22] G. Herranz, M. Basletić, M. Bibes, C. Carrétéro, E. Tafra, E. Jacquet, K. Bouzehouane, C. Deranlot, A. Hamzić, J. M. Broto, A. Barthélémy and A. Fert, *Phys. Rev. Lett.* 98, 216803 (2007).
- [23] L. Qiao, T. C. Droubay, T. Varga, M. E. Bowden, V. Shutthanandan, Z. Zhu, T. C. Kaspar and S. A. Chambers, *Phys. Rev. B* 83, 085408 (2011).
- [24] H. Lee, N. Campbell, J. Lee, T. J. Asel, T. R. Paudel, H. Zhou, J. W. Lee, B. Noesges, J. Seo, B. Park, L. J. Brillson, S. H. Oh, E. Y. Tsymbal, M. S. Rzchowski and C. B. Eom, *Nat. Mater.* 17, 231 (2018).
- [25] H. J. Kim, U. Kim, Kim, T. H. Kim, H. S. Mun, B.-G. Jeon, K. T. Hong, W.-J. Lee, C. Ju, K. H. Kim and K. Char, *Appl. Phys. Express* 5, 061102 (2012).

- [26] H. J. Kim, U. Kim, T. H. Kim, J. Kim, H. M. Kim, B.-G. Jeon, W.-J. Lee, H. S. Mun, K. T. Hong, J. Yu, K. Char and K. H. Kim, *Phys. Rev. B* 86, 165205 (2012).
- [27] H. M. Park, H. J. Lee, S. H. Park and H. I. Yoo, Acta Cryst. C 59, i131 (2003).
- [28] U. Kim, C. Park, T. Ha, Y. M. Kim, N. Kim, C. Ju, J. Park, J. Yu, J. H. Kim and K. Char, *APL Mater.* 3, 036101 (2015).
- [29] M. Zupancic, W. Aggoune, T. Markurt, Y. Kim, Y. M. Kim, K. Char, C. Draxl and M. Albrecht, *Phys. Rev. Mater.* 4, 123605 (2020).
- [30] S. Kim, M. Lippmaa, J. Lee, H. Cho, J. Kim, B. Kim and K. Char, *Adv. Mater. Interfaces* 9, 2201781 (2022).

Chapter 3. In-situ Study for Understanding the Role of Terminating Layer on 2DEG State Formation at the LIO/BSO Interface

3.1. Introduction

The "interfacial polarization" model has been proposed to explain the formation of the 2DEG at LIO/BSO interfaces. As mentioned in Chapter 2.5 and Chapter 2.6, the interfacial polarization model has been further validated through a self-consistent P-S calculation, which provides an explanation for the observed experimental results. To experimentally demonstrate the difference between the $(InO_2)^{-}/(LaO)^{+}/(SnO_2)^{0}$ and $(LaO)^{+}/(InO_2)^{-}/(BaO)^{0}$ interfaces at the LIO/BSO 2DEG interface, following the interfacial polarization model, we conducted in-situ experiments involving the simultaneous deposition of multiple layers.

All samples were fabricated using Pulsed Laser Deposition (PLD) with a KrF excimer laser with a 248 nm wavelength, an abbreviation for Pulsed Laser Deposition, which is a deposition technique employing pulsed lasers. **Figure 3.1**a illustrates the schematic of PLD, while Figure 3.1b shows the picture of PLD. The PLD technique represents a prominent approach for depositing films onto substrates. PLD involves the rapid heating of the target material's surface using short pulses of laser energy, leading to an explosive release of material in the form of a plasma plume. This ejected material subsequently deposits onto the substrate, resulting in film formation. One notable advantage of PLD is the ability to precisely control the film's thickness through the manipulation of laser shots. The fluence on the target

was in the range of 1.4~1.5 J/cm² and the deposition was performed at 750 °C and 100 mTorr oxygen pressure. The samples were cooled down in 600 Torr of oxygen after deposition to room temperature. The targets were supplied by Toshima Manufacturing Co.. To make electrical contacts, indium contacts were pressed on the 4 corners of a sample in the Van der Pauw geometry. The electrical measurements were carried out with Keithley 4200 SCS. All electrical measurements were taken at room temperature.



Figure 3.1 a) Schematic illustration of PLD and image of BSO plume. b) Photograph of the PLD system

3.2. Growth rate measurement of SnO₂ using X-ray Reflectometry (XRR)

Figure 3.2 shows a SnO₂ growth rate measurement by X-Ray Reflectometry (XRR). The SnO₂ film was grown in the (101) direction of the rutile structure (a = b = 4.74 Å, c = 3.18 Å) on a (1012) Al₂O₃ substrate.[1,2] The inset of Figure 3.2 shows the X-ray diffraction (XRD) pattern of the SnO₂ sample. As shown Figure 3.2, the thickness of a SnO₂ film grown with 525 laser pulses was 204 Å, determined by

analyzing the positions of maxima of Kiessig fringes. The growth rate of SnO₂ was thus 0.389 Å per 1 pulse of laser deposition. To evaluate the growth direction and quality of SnO₂, we measured an X-ray diffraction pattern of a 150 nm thick SnO₂ film on ($10\overline{12}$) Al₂O₃ as shown in the inset of Figure 3.2. In order to convert the measured SnO₂ growth rate to the layer deposition rate of perovskite-type BSO, we considered the unit cell volume difference of each crystal structure. **Figure 3.3** shows a schematic image of the SnO₂ rutile structure, showing its structural arrangement and crystallographic features. In the rutile structure, each unit cell volume (71.51 Å³) contains two Sn atoms, whereas in perovskite BSO, a single Sn atom is contained in a half unit cell (34.87 Å³). By taking into account the packing density difference between the rutile and perovskite SnO₂, the growth rate of the SnO₂ layer for the perovskite structure was adjusted to be 0.379 Å per 1 pulse of laser deposition. For



Figure 3.2 SnO₂ X-ray spectrum and growth rate measurement using XRR. SnO₂ is grown by 525 laser pulses with the laser energy fluence of 1.4 J cm⁻² in 100 mTorr O₂ atmosphere at 750 °C. The results of XRR measurement of SnO₂ sample. Inset presents X-ray diffraction spectrum of 150 nm SnO₂ on (1012) Al₂O₃ substrate. The growth direction of SnO₂ is (101) direction.[1]



Figure 3.3 Crystal structure of SnO₂ in the rutile structure. The lattice parameters are a = b = 4.7374 Å and c = 3.1864 Å. Each unit volume of 71.512 Å³ contains 2 Sn atoms.

example, to obtain a single monolayer of SnO_2 with the perovskite structure, a 6pulse laser deposition of SnO_2 (2.27 Å) is needed. If an as-grown BSO surface has a ratio of 50:50 of BaO and SnO_2 , its surface can be changed to mainly SnO_2 terminated BSO with 1.03 Å of SnO_2 or 3-pulse laser deposition (1.14 Å), assuming all the SnO_2 ends up on top of the BaO layer.

3.3. Electrical properties of LIO/BSO as a function of SnO₂ thickness

3.3.1 2DEG conductance as a function of SnO₂ thickness on MgO

To examine the 2DEG conductance as a function of SnO₂ thickness, we prepared differently terminated BSO films by an additional SnO₂ deposition on asgrown BSO. As shown **Figure 3.4**a, we deposited the in-situ LIO/BSO samples on top of an 80 nm thick BaHfO₃ (BHO) buffer layer on MgO substrates. The BHO buffer layer was used for strain relaxation since its cubic lattice constant 4.171 Å is between that of MgO (4.212 Å) and that of BSO (4.116 Å).[3,4] After depositing a 200 nm thick BSO layer, we deposited a few additional pulses of SnO₂ on the BSO surface for termination control, followed by 10 nm thick LIO deposition. As shown in Figure 3.4b, the heterostructure grown without additional SnO₂ deposition at the interface was basically insulating, with a sheet conductance of $<1 \times 10^{-11} \Omega^{-1}$. The



Figure 3.4 LIO/BSO 2DEG conductance as a function of additional SnO_2 . a) Schematic illustration of in-situ LIO/BSO 2DEG on MgO with additional SnO_2 deposition on BSO layer. b) The sheet conductance of LIO/BSO on MgO substrate as a function of additional SnO_2 thickness. The 2DEG conductance increases until 1.1 Å of SnO_2 and the conductance decreases as the thickness of SnO_2 increases beyond 1.1 Å.

highest sheet conductance of $2.56 \times 10^{-6} \Omega^{-1}$ was achieved with a 3-pulse (1.1 Å) SnO₂ deposition at the interface. The sheet conductance slowly decreased to $3.64 \times 10^{-7} \Omega^{-1}$ ¹ for a 5-pulse (1.9 Å) SnO₂ deposition and then rapidly dropped to $7.79 \times 10^{-10} \Omega^{-1}$ at 6 pulses of SnO₂. The highest sheet conductance measured here is about 2 times higher than what has been reported in the past for samples grown on MgO in an exsitu process.[5] The sample with 3 pulses of SnO₂ dusting (1.1 Å) showed 2.09 $cm^2V^{-1}s^{-1}$ mobility with 1.07×10^{13} cm⁻² carrier density. This mobility value is higher than our previous ex-situ made sample (mobility $< 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ at $\sim 1.0 \times 10^{13}$ cm⁻² 2D carrier density).[5] The dramatic effect of the SnO₂ deposition at the interface on the sheet conductance shows that the termination control of the BSO surface is crucial for obtaining a high-mobility 2DEG at a LIO/BSO interface. Considering that the peak point is at the 3-pulse deposition (1.1 Å) of SnO₂, the optimal SnO₂ layer thickness is 1.1 Å, which suggests that the Ba:Sn ratio of the thick as-grown BSO film is close to 50:50. In such case the surface of the BSO film requires about 1/4 unit cell (1.029 Å) of SnO₂ to complete the SnO₂ terminating layer. This is consistent with an ab initio calculation which reported that both SnO₂ and BaO terminations on the BSO surface are energetically equally stable.[6]

3.3.2 2DEG conductance as a function of SnO₂ thickness on STO

We also investigated the conductance of LIO/BSO 2DEGs on STO substrates. **Figure 3.5**a shows a schematic diagram of these samples. The 10 nm LIO was deposited on 200 nm thick undoped BSO with a few pulses of SnO₂ deposition at the



Figure 3.5 LIO/BSO 2DEG on STO conductance as a function of additional SnO₂. a) Schematic illustration of in situ LIO/BSO 2DEG on STO with SnO₂ dusting on BSO layer. b) The sheet conductance of LIO/BSO on STO substrate as a function of additional SnO₂ thickness. This trend was similar to the samples made on MgO substrates in Figure 3.4.

interface. The 2DEG conductance as a function of SnO₂ deposition thickness is shown in Figure 3.5b. The maximum 2DEG conductance was achieved at 1.1 Å of SnO₂ and decreases thereafter. This trend is similar to the samples made on MgO substrates shown in Figure 3.4b. However, the highest sheet conductance of $4.47 \times 10^{-7} \Omega^{-1}$ on the STO substrate is about 6 times lower than what was obtained on MgO substrates, as shown in Figure 3.4b. This difference can be attributed to the different deep acceptor density of BSO films grown on different substrates.[5] The deep acceptor density in BSO grown on MgO was 4×10^{19} cm⁻³ and 6×10^{19} cm⁻³ on STO.[7-9] In our earlier work, we reported that the LIO/BSO(undoped) heterostructures on STO, made by ex-situ processes, were insulating with the sheet conductance lower than $10^{-10} \Omega^{-1}$.[10] In contrast, here we report a sheet conductance of LIO/BSO(undoped) on STO as high as $4.47 \times 10^{-7} \Omega^{-1}$ when made by the in-situ SnO₂ termination control process.

3.3.3 Percolation threshold

The percolation threshold is a fundamental concept that holds key significance in comprehending the diverse range of conductive behaviors observed in various systems. It serves as a pivotal parameter for understanding the conductivity variations within these systems. As shown **Figure 3.6**, in a two-dimensional n × n lattice, where each site can be occupied by a conducting site with a probability *p* or represent the volume fraction of a conductive material like $(InO_2)^{-/}(LaO)^{+/}(SnO_2)^{0}$, the percolation threshold, denoted as p_c , represents a critical value. This critical value marks the point at which there is a sudden, discontinuous change in the percolation probability, P_r , which measures the likelihood of the existence of a conductive path from one side of the lattice to the other. In this context, we can define *p* as the fractional ratio of SnO₂ on the surface termination of BSO.



Two phase random resistor network

Figure 3.6 Illustration of the percolation phenomenon in 2-dimensional $n \times n$ lattice. Each site can be either occupied by a conducting site with a probability p or by a volume fraction of Sn. The percolation probability, P_r , represents the likelihood of a path existing from the left side to the right side of the lattice and is an increasing function of p. The percolation threshold, p_c , marks the point where there is a discontinuous change in P_r . It is observed that p_c decreases as the quantum well thickness increases.



Figure 3.7 The percolation threshold p_c in two-dimentional lattice. a) Percolations probabilities of two phase composition, for a 2D hexagonal (triangular) lattice for increasing lateral mesh size. The percolation threshold, p_c , is indicated to be 0.5. b) In the case of a cubic two-dimensional lattice with a thickness of h=1, the percolation threshold is found to be p_c =0.5929. On the other hand, for a cubic thin plate with a thickness of h=4, the percolation threshold is p_c =0.3998.[11]

As the probability p increases, the percolation probability P_r also increases, indicating a higher likelihood of the presence of a conductive path. However, it is at the percolation threshold p_c where a significant transition occurs. Below the percolation threshold, P_r is relatively low, suggesting the absence of a connected conductive path. However, once p_c is surpassed, there is a sudden jump in P_r , indicating the emergence of a continuous conductive pathway throughout the lattice.

As shown in **Figure 3.7**, The percolation threshold p_c is influenced by various factors, and one important factor is thickness of conducting path or the quantum well thickness.[11] In general, as the quantum well thickness increases, the percolation threshold p_c decreases. This means that it becomes easier for a conductive path to form as the quantum well becomes thicker. Furthermore, the percolation probabilities of two-phase compositions in different lattice structures exhibit interesting patterns. For example, in a 2D hexagonal (triangular) lattice, the percolation threshold p_c has a fixed value of 0.5, regardless of the lateral size. On the

other hand, for a cubic two-dimensional lattice with a thickness of h=1, p_c is determined to be 0.5929, indicating a higher probability of percolation compared to the hexagonal lattice.[11] Considering that BSO is a cubic perovskite, the presence of a single layer of SnO₂ on the BSO surface determines the formation of the LIO/BSO 2DEG. Therefore, it is believed that an approximate SnO₂ thickness of 59 % of SnO₂ termination is required for an increase in conductivity to be observed.

These findings highlight the significant role of the percolation threshold in understanding the conductive properties of various systems. By identifying and analyzing the percolation threshold, researchers can gain insights into the transition from an insulating state to a conductive state, allowing for a better understanding of conductivity variations in different materials and structures.

3.4. Coaxial Impact Collision Ion Scattering Spectroscopy (CAICISS)

Ion Scattering Spectroscopy (ISS), also known as low-energy ion scattering spectroscopy, is a technique used in surface analysis. It involves bombarding a sample surface with noble gas ions or alkali metal ions, such as helium, neon, or lithium ions, typically in the energy range of keV. ISS provides valuable information about the surface composition and structure of materials. One of the key characteristics of ISS is its surface sensitivity, which allows for the analysis of only the outermost atomic layers of the material. The sampling depth, or the distance from which the ions probe into the material, is typically on the order of angstroms (Å). This makes ISS particularly useful for studying surface layers and interfaces. In ISS, the de Broglie wavelength of the ions is negligible, measuring around 10^{-4} Å. This means that the scattering process can be described using classical two-body elastic collisions, simplifying the analysis of the scattering events.

Co-axial Impact Collision Ion Scattering Spectroscopy (CAICISS) is a specialized form of ISS. It is used to selectively observe the backscattered ions along their incident trajectory, where the scattering angle is 180 degrees. CAICISS provides valuable insights into head-on collisions between incident ions and surface atoms. This specific type of scattering event allows for the determination of the surface atomic positions independently of the subsurface atomic positions. CAICISS can be contrasted with high-energy ion scattering techniques, such as Rutherford Backscattering Spectrometry (RBS). RBS typically uses high-energy particles, such as alpha particles, in the MeV energy range. Unlike ISS, RBS provides information about the atomic positions relative to the subsurface atomic positions. In contrast, ISS, including CAICISS, focuses on determining the surface atomic positions independently of the subsurface atomic positions of surface atomic positions of surface atomic structure and contributing to a deeper understanding of the surface composition and structure of materials.

The incident ions in CAICISS cannot penetrate into the subsurface layers, resulting in the formation of what is known as "shadow cones." These shadow cones arise due to the limited depth of ion penetration. At the edges of these shadow cones, the ion flux becomes focused, leading to an increase in the backscattering flux. This phenomenon occurs when there is another atom located precisely on the edge of the shadow cone. By analyzing the shadow effect and observing changes in

backscattering intensity, it becomes possible to determine the atomic structure of the surface. At the critical angle, the edge of the shadow cones incidentally interacts with a surface atom. However, as the edge of the shadow cones moves further away, it is no longer incident on an atom, resulting in a decrease in backscattering intensity. Conversely, when the edge of the shadow cones reaches the position of a second-layer atom, the backscattering from the second layer becomes increased. By carefully analyzing these variations in backscattering intensity and understanding the shadow effect, it becomes possible to extract valuable information about the atomic structure and arrangement of the surface atoms in CAICISS experiments.

To analyze the termination of the BSO surface, we used CAICISS, (Shimadzu, TALIS-9700) analyzer. The CAICISS is a direct technique to analyze the composition of the terminating atomic layer.[12] All CAICISS data were measured through a collaborative effort with the University of Tokyo. As shown **Figure 3.8**a, an incident Ne⁺ ion beam was aligned with the [111] direction of BSO. Due to the incident beam direction alignment, the second layer from the top will be hidden from the ion beam by the shadow cone in a perovskite structure except for the exposed edges. We measured the Time-of-Flight (TOF) of backscattered Ne⁺, which was only affected by the atomic mass of the scattering cations of the BSO surface.[12]

Figure 3.8b shows the TOF spectra of three different samples. In the case of the as-grown BSO, backscattering peaks from both Ba and Sn are equally large. This indicates the presence of both Ba and Sn on the surface. For the sample with an additional 1.1 Å SnO₂ deposition, the Ba peak intensity decreased significantly,



Figure 3.8 CAICISS spectrum of three different samples (as-grown BSO / additional 1.1 Å SnO₂ deposition on BSO / additional 1.9 Å SnO₂ deposition on BSO). a) Measurements were performed at [111] direction with a Ne ion beam. Ne ions are backscattered by the topmost atomic layer, and the inner ions are hidden by the shadowing cone. b) The CAICISS spectrum of the As-grown BSO shows that the intensity of both the Ba and Sn peaks are quite large. The Ba peak intensity is significantly decreased in the additional SnO₂ spectrum. The additional SnO₂ layer deposited BSO samples are SnO₂ dominant. However, there are no significant differences between 1.1 and 1.9 Å of additional SnO₂.

showing that the additional SnO_2 deposition does indeed change the terminating layer composition of the BSO surface. This change in the spectrum suggests that the

SnO₂ dusting process effectively transforms the BSO surface into an SnO₂ termination. However, the Ba peak did not completely disappear even after 1.9 Å thick SnO₂ deposition. Surprisingly, the overall shape of the TOF spectrum did not exhibit significant changes compared to the previous sample. However, it is important to note that the Ba peak did not completely vanish. As shown in **Figure 3.9**, This phenomenon can be attributed to the surface not being atomically flat, which exposes Ba atoms next to Ne ions. Although the surface may have a dominant Sn termination, a partial exposure of Ba atoms can still occur, thus explaining the persistent presence of the Ba peak in the TOF spectrum.

The electrical data of Chapter 3.3 can be analyzed in conjunction with the surface characterization results. After SnO₂ termination, the 2DEG conductance becomes evident, providing further support for the understanding that the presence of SnO₂ on the surface plays a crucial role in 2DEG conductance. However, interestingly, excessive SnO₂ deposition does not exert a significant influence on the CAICISS results, indicating that the conductance is not drastically affected. On the other hand, the formation of SnO₂ defects resulting from SnO₂ deposition may lead to a reduction in conductance. This observation highlights the importance of maintaining the optimal SnO₂ thickness for achieving desirable conductive properties in the LIO/BSO 2DEG system.



Figure 3.9 The schematic image of the exposure of Ba atoms despite the SnO_2 termination through CAICISS by the Ne ion beam. The incomplete disappearance of the Ba peak can be attributed to the non-atomically flat surface, which results in the exposure of Ba atoms adjacent to Ne ions.

3.5. Surface morphology analysis using Atomic Force Microscopy (AFM)

As shown in **Figure 3.10**, the surface of BSO was determined by the Atomic Force Microscopy (AFM) morphology images. The images included the as-grown BSO sample, the BSO sample subjected to 3 pulses, which was anticipated to achieve the optimal termination, and the BSO sample with an excessive deposition of SnO₂ obtained through 5 pulses. Despite the substantial differences observed in the electrical data, the AFM surface images did not exhibit easily discernible variations. The surface roughness values were determined as 615 pm for the as-grown BSO sample, 667 pm for the BSO sample treated with 3 pulses, and 709 pm for the BSO sample with 5 pulses. These results indicate that the surface morphology of the BSO



Figure 3.10 AFM morphology images of (a) as-grown BSO, (b) after 3-pulse (1.1 Å) dusting on BSO, (c) after 5-pulse (1.9 Å) dusting on BSO.

samples did not show significant changes based on the number of pulses used during the SnO_2 deposition process. It is likely due to the fact that the sample surface isn't atomically smooth, exposing Ba atoms on the edges of the small islands to the Ne⁺ ion beam in CAICISS.

3.6. Structure properties with Scanning Transmission Electron Microscopy (STEM)

Figure 3.11a,b show the High Angle Annular Dark Field Scanning Transmission Electron Microscope (HAADF-STEM) cross section images of an LIO film grown on a BSO film terminated with an optimal 3-pulse deposition of a 1.1 Å SnO₂ layer at the interface. Figure 3.11d,e show the effect of depositing an additional 4.2 Å (11 pulses) SnO₂ layer on BSO. Figure 3.11c shows a schematic diagram of the sample shown in Figure 3.11a,b and Figure 3.11f shows a schematic diagram of the sample corresponding to Figure 3.11d,e. In both cases, LIO was epitaxially grown on BSO. Since the contrast between Ba and La and between Sn and In is very small, the LIO/BSO interface in most previous reports was not easy to see.[5,7,10,13]



Figure 3.11 STEM images of BSO/LIO. a,b) HAADF-STEM image of LIO on optimally SnO₂ terminated BSO (3-pulse dusting). c) Schematic diagram of LIO on SnO₂ terminated BSO film on an MgO substrate. d,e) HAADFSTEM image of LIO with excessive SnO₂ (11-pulse dusting) on BSO. The red rectangular lines of (b) and (e) are guides for the interfacial region. f) Schematic diagram of LIO with excessive SnO₂ dusting on BSO film on an MgO substrate.

However, the interface is more clearly visible at lower magnification, as can be seen by comparing images in Figure 3.11a,d. The higher magnification images in Figure 3.11b,e show clearly that the growth of subsequent LIO remains epitaxial regardless of the additional SnO_2 deposition thickness. However, there exist areas with more visible darker contrast in Figure 3.11e near the interface which suggests that defectrelated strain exists near the interface. For the thicker SnO_2 layer, the offstoichiometry can be accommodated by creating defects such as Sn_{Ba} or V''_{Ba} , which are known to form during the growth of BSO in Sn-rich conditions of molecular beam epitaxy.[14] Although the film maintains epitaxial growth at the interface, the sheet conductance with 4.2 Å SnO₂ deposition was just $1.52 \times 10^{-9} \Omega^{-1}$, which is 3 orders of magnitude lower than the highest conductance of $2.56 \times 10^{-6} \Omega^{-1}$, obtained with the optimal SnO₂ coverage shown in Figure 3.4(b).

3.7. Conclusion

In summary, we have shown that the use of SnO₂-terminated BSO is crucial for obtaining a conducting interface at a LIO/BSO interface. It is very likely that the polarization direction at the LIO/BSO interface is sensitively affected by the termination of the BSO. We have shown that the BSO termination could be controlled by additional SnO₂ deposition of just a few laser pulses. The electrical conductance increased by more than 4 orders of magnitude with optimal SnO₂ termination. We confirmed the termination of the BSO surfaces by CAICISS. Since the optimal sheet conductance was found when 1/4 unit cell (1.1 Å) of SnO₂ was added at the interface, the as-grown BSO surface was found to have nearly equal amounts of BaO and SnO₂ as the terminating layer after PLD deposition.

References

- [1] S. Kim, M. Lippmaa, J. Lee, H. Cho, J. Kim, B. Kim and K. Char, *Adv. Mater*. *Interfaces* 9, 2201781 (2022).
- [2] H. Mun, H. Yang, J. Park, C. Ju and K. Char, APL Mater. 3, 076107 (2015).
- [3] H. J. Kim, U. Kim, Kim, T. H. Kim, H. S. Mun, B.-G. Jeon, K. T. Hong, W.-J. Lee, C. Ju, K. H. Kim and K. Char, *Appl. Phys. Express* 5, 061102 (2012).
- [4] T. Maekawa, K. Kurosaki and S. Yamanaka, J. Alloys Compd. 407, 44 (2006).
- [5] Y. Kim, Y. M. Kim, J. Shin and K. Char, APL Mater. 6, 096104 (2018).
- [6] A. Slassi, M. Hammi and O. El Rhazouani, J. Electron. Mater. 46, 4133 (2017).
- [7] Y. M. Kim, T. Markurt, Y. Kim, M. Zupancic, J. Shin, M. Albrecht and K. Char, *Sci. Rep.* 9, 16202 (2019).
- [8] Y. Kim, S. Kim, H. Cho, Y. M. Kim, H. Ohta and K. Char, *Phys. Rev. Applied* 17, 014031 (2022).
- [9] J. Shin, Y. M. Kim, Y. Kim, C. Park and K. Char, *Appl. Phys. Lett.* 109, 262102 (2016).
- [10] U. Kim, C. Park, Y. M. Kim, J. Shin and K. Char, APL Mater. 4, 071102 (2016).
- [11] M. K. Horton and M. A. Moram, Appl. Phys. Lett. 110, 162103 (2017).
- [12] T. Ohnishi, K. Shibuya, M. Lippmaa, D. Kobayashi, H. Kumigashira, M. Oshima and H. Koinuma, *Appl. Phys. Lett.* 85, 272 (2004).
- [13] Y. M. Kim, Y. Kim and K. Char, Commun. Mater. 2, 73 (2021).
- [14] N. G. Combs, W. Wu and S. Stemmer, Phys. Rev. Mater. 4, 014604 (2020).

Chapter 4. Ex-situ Study for the Terminating Layer Control at the LIO/BSO Interface

4.1. Introduction

2DEG in AlGaAs/GaAs, AlGaAs/GaN, and MgZnO/ZnO systems has been widely studied in conventional 2DEGs such as HEMTs.[1-5] Not only from an application but also due to the intriguing physical phenomena observed in 2DEGs, such as the Quantum Hall Effect (QHE) and Fractional Quantum Hall Effect (FQHE). [5-7] Since the discovery of 2DEG in AlGaAs/GaAs, achieving high mobility has been essential for measuring quantum phenomena like QHE. The modulation doping method, proposed in 1978, enabled achieving electron mobility greater than 10^4 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at carrier densities of 10^{15} - 10^{17} cm⁻³ at room temperature.[8] Over the next 20 years, the mobility in AlGaAs/GaAs improved further, reaching up to $10^7 \text{ cm}^2\text{V}^-$ ¹s⁻¹.[9] Efforts to enhance mobility in 2DEG systems, including AlGaAs/GaAs, have been crucial in exploring new physical phenomena. In contrast, a new 2DEG phenomenon has been discovered between LAO and STO oxides, and various mechanisms, such as polar catastrophe, have been proposed to explain it.[10,11] In 2016, a 2DEG in LIO/BSO was discovered, and an interface polarization model was proposed to explain the LIO/BSO system.[11,12] Especially, BSO attracted attention due to its large bandgap of 3.1eV and high mobility of 320 cm²V⁻¹s⁻¹ at room temperature for n-type doping in single-crystal form with a high carrier density of 8x10¹⁹ cm⁻³.[14,15]. GaN, another representative large bandgap material exhibits mobility as 100 cm²V⁻¹s⁻¹ at 10²⁰ cm⁻³ at room temperature.[16] In the case of BSO film, the mobility is lower compared to single crystals with values around 70 cm²V⁻ $^{1}s^{-1}$ deposited by pulsed laser deposition in 2012, reaching 150-180 cm²V⁻¹s⁻¹ for

molecular beam epitaxy grown BSO films in 2016-2017.[14,15,17,18] The reduction in mobility in BSO films has been attributed to charge traps resulting from dislocations between the substrate (e.g., STO, MgO) and to solve this issue, the use of LIO single crystal substrates has been suggested.[19]

In our previous research, electron mobility of LIO/BSO 2DEG $\mu < 1 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ to $\mu = 2.09 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ was achieved at a carrier density of 10^{13} cm^{-2} with undoped BSO.[20,21] It was reported that the interface between LIO and BSO with SnO₂ termination in BSO is crucial for formation of LIO/BSO 2DEG.[21]. The SnO₂ terminated BSO was achieved using an in-situ method of dusting SnO₂. However, excessive SnO₂ deposition led to a decrease in the conductance of LIO/BSO 2DEG. For formation of LIO/BSO 2DEG, SnO₂ terminated BSO is essential, but in-situ control has its limitations for a perfect SnO₂ terminated BSO. If the surface can be treated through chemical treatment to achieve a perfect termination, it would aid in increasing the conductance of LIO/BSO 2DEG and contribute to future research for enhancing electron mobility.

Also, we explored the mask and heat treatment method, which involves using a stencil mask to create a van der Pauw structure for measurement. Although we first explored the mask and heat treatment method, which involves using a stencil mask to create a van der Pauw structure for measurement, we later found that this method had been previously used to achieve unintentional termination in the 2DEG structure. We investigated how it could be applied to achieve termination in BSO, but we found that this method had limitations in achieving reliable termination in BSO structures. In the previous report, a stencil mask was used to deposit a 4% metallic BLSO

structure for measurement purposes. The mask was placed on the substrate, and then a thin layer of metal was deposited through the openings of the mask.

Our future goal in studying BSO termination is to achieve high mobility in LIO/BSO and to apply it to low-temperature measurements of field-effect transistors using LIO/BSO or the 2DEG structure. We believe that achieving reliable termination in BSO is a key step towards achieving this goal. In addition to studying the effectiveness of these methods, we also investigated the mechanisms underlying termination in BSO. Specifically, we studied the role of SnO₂ termination in BSO and how it can be achieved through both ex-situ methods.

4.2. Surface engineering with chemical treatment

Table 4.1 provides a comprehensive overview of the chemical characteristics of BaO and SnO₂. BaO is known for its high solubility in water, leading to the formation of Barium Hydroxide (Ba(OH)₂) upon reaction. It exhibits reactivity with ethanol while remaining unreactive towards acetone. Conversely, SnO₂ is remarkable insolubility in water, as it does not dissolve in both ethanol and acetone. This distinctive behavior enables the selective etching of BaO on the BSO surface when utilizing water as a treatment medium. Furthermore, it is noteworthy that barium hydroxide exhibits a relatively low boiling point of 780 °C under 1 atm. Consequently, any residual barium hydroxide on the film can easily evaporate within the low-pressure, high-temperature environment of the chamber. Such information

BaO		SnO ₂
Rapidly Soluble (1.5 g/100g at 20 °C) BaO + H ₂ O = Ba(OH) ₂	Water Solubility	Insoluble
Soluble	Ethanol Solubility	Insoluble
Insoluble	Acetone Solubility	Insoluble
1972 °С	Melting Temperature	1800 - 1900 °С
Ba(OH)2		
780 °C (1 atm)	Boiling Temperature	

Table 4.1 Chemical characteristics comparison of BaO and SnO₂. BaO reacts with water to form $Ba(OH)_2$, and $Ba(OH)_2$ not only dissolves in water but also has a relatively low boiling point of 780 °C at 1 atm.

is critical for understanding the etching process and the subsequent behavior of BaO on BSO.

As shows in **Figure 4.1**, during the wet etching process, the BaO is selectively removed through chemical etchants or solutions. As wet etching progresses, the BaO layer, which is soluble in water, is gradually etched away, resulting in an increasing proportion of SnO_2 on the surface. When treating the sample with the solution, sonication is performed until the water surface ripples and vibrates. Figure 4.1c is a schematic diagram of the chemical etching of the BSO surface to achieve SnO_2 termination. This ideal surface termination is composed of a single unit cell thickness, where BaO is preferentially etched, primarily leaving behind the SnO_2 -terminated surface. The detailed schematic visually demonstrates the transformation of the BSO



Figure 4.1 Schematic illustration of the ex-situ method for SnO_2 terminated BSO and LIO/BSO 2DEG. a) Deposition of BSO film onto substrate. b) The ex-situ chemical treatment with bath sonification. c) Schematic illustration of the chemical treatment process, where the BSO surface undergoes termination with SnO_2 . d) Deposition of LIO film on ex-situ treated BSO film.

surface from its initial state of mixed BaO and SnO₂ composition to the desired surface termination primarily composed of SnO₂. Upon completion of wet etching,

the ideal surface represents a single unit cell thick BSO surface terminated with SnO₂. Afterward, a deposition of the LIO film was carried out on the BSO film that had undergone ex-situ treatment.

However, **Figure 4.2** presents the results of an experimental investigation conducted to examine the effects of water leaching on the BSO surface, followed by the deposition of LIO. When LIO was deposited on the BSO sample with 10 seconds of water leaching, did it exhibit 2DEG conductance, but it did not reach the conductance level of $2.56 \times 10^{-6} \Omega^{-1}$ achieved through the in-situ method with dusting technique.[21] Moreover, with prolonged exposure with water, a significant decrease in conductance was observed, resulting in insulating behavior. A plausible explanation for the decrease in conductance with longer leaching time is the rapid reactivity of BaO with water. It is postulated that the water molecules react with BaO, causing a severe etching effect that extends beyond the surface layer, potentially damaging the underlying structures. This phenomenon results in the degradation of the BSO surface and subsequent deterioration of its conductance properties. Based on these results, mitigating the etching sensitivity of the BSO surface was crucial for ex-situ termination of BSO.

To reduce the excessive reaction of BaO with water, a mixture of acetone and water in a 9:1 ratio was used for treating the BSO surface, taking advantage of the nonreactive nature of acetone with BaO. The result of treating the BSO surface with a 9:1 mixture of acetone and water is shown in **Figure 4.3**. The Figure 4.3 shows a graph showing the conductance of the LIO/BSO film, which was deposited on both STO and MgO substrate, after treatment with a 9:1 mixture of acetone and water. The conductance measurements were taken by depositing LIO on the treated BSO



Figure 4.2 LIO/BSO 2DEG on MgO conductance as a function of water leaching time. a) Schematic illustration of LIO/BSO 2DEG on MgO with water leaching on BSO layer. b) The sheet conductance of LIO/BSO on MgO conductance as a function of water leaching time. The 2DEG conductance was observed with 10-seconds of water treatment, and for shorter or longer durations, the measurement results showed insulating.

film and varying the treatment time. Figure 4.3a shows a schematic of the sample, where a BSO film grown on STO was subjected to chemical treatment before depositing LIO. As seen in Figure 4.3b, the experimental findings revealed that treating the BSO surface with a 9:1 mixture of acetone and water for 90 seconds, followed by the deposition of LIO, resulted in a higher conductance of $2.20 \times 10^{-6} \Omega^{-1}$.

In the previous our research, when LIO was deposited on BSO with in-situ SnO₂ termination on the STO substrate, the conductance was $4.47 \times 10^{-7} \Omega^{-1}$.[21] However, when LIO was deposited on BSO treated ex-situ, the conductance increased by (a) (b)



Figure 4.3 LIO/BSO 2DEG conductance as a function of leaching time. a) Schematic illustration of LIO/BSO 2DEG on STO with ex-situ treatment. b) The sheet conductance of LIO/BSO on STO substrate as a function of leaching time. The 2DEG conductance increases until 90 seconds and beyond that point, it decreases with increasing leaching time. c) Schematic illustration of LIO/BSO 2DEG on MgO with ex-situ treatment. d) The sheet conductance of LIO/BSO on MgO substrate as a function of leaching time. At 40 seconds, the conductance reaches its peak, and if it exceeds that time, it decreases.

approximately 5 times. As shown in Figure 4.3c and Figure 4.3d, an analogous investigation was performed on the MgO substrate. By using the 9:1 acetone-water mixture, stable control over the termination time was achieved. The highest conductance is $8.03 \times 10^{-06} \Omega^{-1}$ and it surpassed the maximum value of $2.56 \times 10^{-06} \Omega^{-1}$ in our previous work using the in-situ method.[21] These results show the effectiveness of the 9:1 acetone and water mixture in achieving a SnO₂-terminated BSO surface compared to the in-situ method.

To investigate the surface terminations, the Angle-Reserved X-Ray Photoelectron Spectroscopy (ARXPS) analysis was conducted. **Figure 4.4** shows the Ba $3d_{5/2}$ and Sn $3d_{5/2}$ concentration from BSO film. The ARXPS data was measured using Kratos' Axis Supra⁺ and each sample, both as-grown and chemically treated, was measured in ultra-high vacuum. Figure 4.4a is a schematic representation of ARXPS. As the take-off angle θ decreases, the measurement becomes more sensitive to the surface. In Figure 4.4b, the Ba to Sn ratio in the as-grown BSO is shown as a function of the angle θ . As θ decreases, the Ba ratio increases, indicating higher surface sensitivity. Figure 4.4c illustrates the Ba to Sn ratio of BSO treated with a 9:1 mixture of acetone and water for 90 seconds. Compared to Figure 4.4b, an increase in Sn content is observed, indicating a change in surface composition after the chemical treatment. The increase in Sn suggests the successful removal or reduction of BaO from the surface, and the preferential exposure of the SnO₂-terminated surface due to the treatment process. **Figure 4.5** shows the ARXPS spectra measurements of Ba $3d_{3/2}$, Ba $3d_{5/2}$, Sn $3d_{3/2}$ and Sn $3d_{5/2}$ for the samples.


Figure 4.4 a) The schematic of principle of ARXPS. As take-off angle θ decreases, measurement is more sensitive to the surface. b) The ratio of Ba and Sn in asgrown BSO as a function of θ . As θ decreases, the Ba ratio increases. c) The Ba to Sn ratio of BSO treated with a 9:1 mixture of acetone and water for 90 seconds. Compared to the as-grown BSO in (b), there is an increase in Sn.



Figure 4.5 ARXPS spectra of as-grown and ex-situ treated BSO. The signal decreases as the photoelectron take-off angle decreases. a) ARXPS image of Ba atoms in as-grown BSO. b) ARXPS image of Sn atoms in as-grown BSO. c) ARXPS image of Ba atoms in BSO treated with a 9:1 mixture of acetone and water. d) ARXPS image of Sn atoms in BSO treated with a 9:1 mixture of acetone and water.

To investigate the selective etched BSO surface by water, the BSO was measured using CAICISS, (Shimadzu, TALIS-9700). We used a Ne⁺ beam in CAICISS measurement. When the Ne⁺ beam is aligned with the BSO [111] direction, only backscattered Ne⁺ ion from the topmost layer's cations is measured, while the cations in the immediately deeper sublayers are completely hidden by the shadow effect. The intensity of the backscattered Ne⁺ beam with respect of the time of flight corresponds to the concentration of the topmost layer.[21,22] In this case, the time of flight of the backscattered Ne⁺ ions is dependent on the cation with which the Ne⁺ ions collided. By measuring its intensity, the ratio of Ba to Sn on the surface can be determined.



Figure 4.6 a) The CAICISS spectrum of BSO measured after annealing at 750 °C in an oxygen atmosphere. Compared to the as-grown BSO in Figure 4.7, the Sn peak significantly decreased. b) RHEED image of BSO after annealing. The RHEED was measured under ultra-high vacuum at room temperature after annealing.



Figure 4.7 a) CAICISS spectrum of the As-grown BSO shows that the intensity of both the Ba and Sn peaks are large.[21] The CAICISS spectrum of BSO treated with DI water for 1 minute shows near perfect SnO₂ termination. b) The RHEED image of as-grown BSO under ultra-high vacuum at room temperature. c) The RHEED image of water leached BSO under ultra-high vacuum at room temperature.

The as-grown BSO sample deposited on MgO showed significant peaks for both Ba and Sn during CAICISS measurements.[21] Additionally, as reported in **Figure 4.6**a, when this BSO sample was annealed at 750 °C and O2 100 mTorr atmosphere, an increase in Ba and a decrease in Sn were observed. The BSO sample was subjected to further analysis with water leaching. Firstly, it was immersed in deionized water within an ultrasonic bath for 1 minute at room temperature. Subsequently, the sample was dried with nitrogen and placed on a hot plate set at approximately 120°C for a few minutes to ensure complete evaporation of any remaining water. **Figure 4.7**a shows the TOF graph measured by CAICISS of the sample processed as above treatment. In Figure 4.7, the BSO sample, after being treated with water, exhibited an intriguing transformation in its surface characteristics, resulting in a near-perfect SnO₂ termination. This indicates a significant reduction of BaO and suggests that water treatment is an effective means of altering the surface composition. Figure 4.7b and Figure 4.7c are reflection high-energy electron diffraction (RHEED) images of as-grown BSO and water-leached BSO, respectively, both taken separately in an ex-situ UHV environment. It is evident that the RHEED images differ in each case. Similarly, in Figure 4.6b, the RHEED image from CAICISS shows differences when the termination is Ba termination.

On the other hand, **Figure 4.8** shows AFM morphology images. Figure 4.8a, Figure 4.8b are 5 μ m and 1 μ m scale images of as-grown BSO, while Figure 4.8c, Figure 4.8d are 5 μ m and 1 μ m images of BSO samples treated with a 9:1 mixture of acetone and water for 90 seconds. Upon comparing these images, there is little noticeable difference between the two sets. The surface morphology of both samples is quite similar, and the results indicate that the chemical treatment did not have a visually significant changes on the surface structure of the BSO samples as observed in the AFM images. However, it is important to note that despite the lack of visible differences in AFM images, there may still be potential changes in electrical properties, ARXPS and CAICISS.



Figure 4.8 AFM morphology images of (a,b) As-grown BSO and (c,d) after ex-situ treated BSO.

4.3. Mask-heat treatment for SnO₂ termination of BSO and its role in forming 2DEG in LIO/BSO

In previous researches, the formation of a 2DEG in LIO/BSO interface was achieved without intentional termination control.[12,20] This remarkable outcome was made possible by the unintentional termination of BSO. In the chapter 4.3, the main focus was to analyze the termination of the mask-heat treated BSO surface. To do this, we utilized CAICISS measurement and analyzed the electrical characteristics associated with the termination process. through the dusting method. All samples were made using pulsed laser deposition with a KrF excimer laser at a wavelength of 248 nm. The deposition conditions involved depositing layers at 750°C and 100

mTorr of oxygen pressure, followed by cooling in 600 Torr of oxygen. The process of depositing a 2DEG sample with a van der Pauw structure using a stencil mask is demonstrated in **Figure 4.9**. In order to reduce the effect of threading dislocation due to the difference in lattice mismatch between the substrate and the film, BSO buffer was used. In the previously reported 2DEG, it was noted that a thick layer of BSO was deposited on an STO substrate with the use of a buffer. It should also be mentioned that in order to reduce lattice mismatch on an MgO substrate, a BHO



Figure 4.9 Schematic deposition process using a mask in four steps. a) Deposition of BSO buffers on a substrate. b) Use of a stencil mask to deposit lightly BLSO as the channel layer. c) Deposition of heavily doped BLSO (4% La doping) at the four corners. d) Deposition LIO layer on top of the structure.

buffer was used.[20] Additionally, a SrSnO₃ buffer was used on an NdScO₃ substrate.[23]

Figure 4.9 is a schematic diagram of the deposition process using a mask in four steps. The stencil mask was made of Si and was passivated with the corresponding material (The material used for deposition, e.g., BSO) after annealing. In Figure 4.9a, we deposited BSO buffers on a substrate. Then, we used a stencil mask for the channel layer to deposit lightly BLSO on top of the buffer, as shown in Figure 4.9b. As shown in Figure 4.9c, we then deposited heavily doped BLSO (4% La doping) at the four corners, and finally, as shown in Figure 4.9d, we used a stencil mask to deposit LIO on top. Each step involved heating up to 750°C in an oxygen partial pressure of 100 mTorr and cooling in an oxygen partial pressure of 600 Torr. After each step, we take out the sample from the chamber to change the mask.

4.3.1 Electrical properties for LIO/BSO with mask-heat treatment

To thoroughly examine the conductance of the 2DEG as a function of SnO_2 thickness, we employed an ex-situ LIO/BSO 2DEG structure and introduced different termination conditions by depositing additional SnO_2 . As shown **Figure 4.10**a, the process involved depositing SnO_2 with varying thicknesses on each sample, followed by subsequent LIO deposition. This process followed the sequence illustrated in Figure 4.9, with the SnO_2 deposition step occurring after the final step shown in Figure 4.9d. The thickness of SnO_2 was precisely measured using a Stylus Profiler, and the growth rate of SnO_2 was determined to be 0.173 Å per pulse of laser

deposition. This growth rate was influenced by factors such as increased deposition distance and the reduction in opening size caused by the stencil mask.

Considering the lattice parameters of the rutile structure SnO_2 (a = b = 4.74 Å, c = 3.18 Å) with a volume of 71.51 Å3 and a half unit cell of perovskite BSO (34.87 Å3), we calculated that each laser pulse corresponded to an increase in thickness of approximately 0.169 Å.

The conductance measurements revealed intriguing findings, as demonstrated in Figure 4.10b. Notably, the highest conductance was observed when no SnO₂ was deposited (0 nm or 0 shots), reaching a peak value of $5.37 \times 10^{-06} \Omega^{-1}$. However, as SnO₂ deposition increased, the conductance exhibited a gradual decrease. This trend suggested that the presence of SnO₂ led to a reduction in the conductance of the system.



Figure 4.10 LIO/0.2 % BLSO 2DEG conductance with mask heat-treatment as a function of additional SnO₂ deposition. a) Schematic illustration of the LIO/0.2 % BLSO 2DEG, depicting the step of SnO₂ dusting on the mask heat-treated BSO according to the process in Figure 4.9, just before the final process shown in Figure 4.9d. b) The sheet conductance of LIO/0.2 % BLSO a function of additional SnO₂ dusting increases, the conductance decreases.



Figure 4.11 LIO/0.2% BLSO 2DEG on STO conductance as a function of additional SnO₂. a) Schematic illustration of in situ LIO/0.2%BSO 2DEG on STO with SnO₂ dusting on BSO layer. b) The sheet conductance of LIO/BSO on STO substrate as a function of additional SnO₂ thickness.

Moreover, we investigated the electrical properties of the LIO/0.2% BLSO structure grown in-situ, as illustrated in **Figure 4.11**a. Remarkably, the resulting electrical properties exhibited a similar trend to those observed in Figure 4.11b. Specifically, a peak in conductance was observed at an SnO₂ thickness of 1 Å, which correlated with the findings presented in Chapter 3.3. This implied that the surface had undergone a surface termination process prior to the deposition. Interestingly, considering this observation, it appeared as if a 1 Å layer of SnO₂ had already terminated the BSO surface before the process depicted in Figure 4.9d.

Overall, these detailed investigations provided valuable insights into the influence of SnO_2 thickness on the conductance properties of the LIO/BSO system. The results highlighted the significance of SnO_2 termination and its impact on the overall conductance of the 2DEG structure.

4.3.2 Surface properties of mask-heat treated BSO with CAICISS

In Chapter 3, the surface of the as-grown BSO in Figure 3.8 was determined to have a Ba and Sn composition ratio of 50:50 according to CAICISS. The corresponding electrical data at that point appeared insulating, as observed in Figure 3.4 and Figure 3.5. However, when considering structures like Figure 4.7, the highest 2DEG conductance was observed without additional SnO₂ dusting on BSO, and the 2DEG conductance decreased as excessive SnO₂ dusting was added. This difference prompted the investigation, using the CAICISS method, to determine whether the Ba and Sn composition ratio on the BSO surface actually changed after the stacking of LIO onto BSO in the fabrication process shown in Figure 4.9.

First, the device fabrication process shown in Figure 4.9 was replicated to prepare a sample for CAICISS measurement. The mask in **Figure 4.12** was made of Si and annealed in an oxygen atmosphere at 800 °C, followed by deposition of the



Annealing with Si cap

Blank Si cap

Figure 4.12 CAICISS sample preparation and annealing process. a) Schematic depiction of the preparation for the CAICISS sample, featuring the placement of an Si cap on an as-grown BSO film consisting of an 80 nm BHO buffer layer and a 200 nm BSO film. b) Blank Si cap image



Figure 4.13 CAICISS spectra of two different samples. a) CAICISS spectrum of as-grown BSO, which is identical to the spectrum shown in Figure 3.8a. b) CAICISS spectrum of mask and heat treated BSO, where the intensity of the Ba peak significantly decreased compared to (a).

targeting material on top of it for passivation. The CAICISS sample was prepared by placing an Si cap on top of an as-grown BSO film with an 80 nm BHO buffer and a 200 nm BSO film on an MgO substrate, as shown in Figure 4.12. It has been processed double annealing cycles in a 100 mTorr oxygen atmosphere at 750 °C for 10 minutes each. Cooling was performed in an oxygen environment at 600 Torr. **Figure 4.13** shows the CAICISS spectra of two different samples. In the graph (a), we have the CAICISS spectrum of the as-grown BSO, which is identical to the spectrum shown in Figure 3.8a. On the other hand, the graph (b) shows the CAICISS spectrum of the mask and heat-treated BSO, where the intensity of the Ba peak has significantly decreased compared to the graph (a).



Figure 4.14 Comparison of 2DEG conductance in LIO/BSO: As-grown BSO vs. mask heat treated BSO. Direct LIO deposition on BSO exhibits insulating, while mask heat treated BSO prior to LIO deposition induces a 2DEG conductance.

As shown in **Figure 4.14**, it becomes evident that when LIO is simply deposited on top of BSO, the resulting electrical resistance shows insulating. However, an intriguing observation emerges when BSO undergoes mask heat treatment twice prior to the deposition of LIO, resulting in the emergence of a 2DEG conductance. This significant difference in conductivity can be attributed to the increased proportion of Sn termination, as indicated by the CAICISS data. The experiment demonstrated that the treatment of BSO with mask heat, performed twice, plays a crucial role in altering the surface termination and thereby affecting the electrical properties. The higher Sn termination ratio achieved through this process promotes the formation of a 2DEG conductance, in contrast to the insulating behavior observed when LIO is directly deposited on untreated BSO.

4.4. Conclusion

The SnO₂ terminated BSO is crucial for the formation of the 2DEG in LIO/BSO. In addition to the previously established in-situ method, the ex-situ method has also been proven effective in achieving this termination. The in-situ method involves controlling the termination during BSO growth, while the ex-situ method modifies the BSO surface after deposition. Controlling the leaching time when exposed to water was challenging due to the high solubility of BaO. To solve this, the etching time was carefully controlled using a 9:1 mixture of acetone and water, successfully creating SnO₂-terminated BSO surfaces. The SnO₂ terminated of BSO can be accomplished through different methods, including both in-situ and ex-situ approaches. The in-situ method achieves SnO₂ termination during the growth process of BSO itself. On the other hand, the ex-situ method modifies the BSO surface after it has been grown. Interestingly, the ex-situ method has been found to yield significantly higher conductivity enhancement compared to the in-situ method. This indicates the effectiveness of the ex-situ approach in creating a more pronounced SnO2 termination on the BSO surface. It is expected that achieving a perfect SnO2 termination will help increase the mobility of LIO/BSO in the future. Moreover, creating a perfectly SnO₂-terminated BSO through such ex-situ chemical treatment will serve as a guiding principle to enhance the mobility of LIO/BSO 2DEG.

Additionally, previous studies focusing on the formation of LIO/BSO 2DEG have provided insights into the unintentional termination phenomenon. Through thorough CAICISS analysis and electrical characterization, it has been measured that the unintentional termination indeed occurs during the formation of the LIO/BSO 2DEG. These findings not only offer practical methods for creating the desired 2DEG structure but also emphasize the crucial role of termination in determining the overall electrical properties and behavior of the system.

References

- H. L. Störmer, R. Dingle, A. C. Gossard, W. Wiegmann and M. D. Sturge, *Solid State Commun.* 29, 705 (1979).
- [2] T. Mimura, S. Hiyamizu, T. Fujii and K. Nanbu, *Jpn. J. Appl. Phys.* 19, L225 (1980).
- [3] M. Asif Khan, J. N. Kuznia, J. M. Van Hove, N. Pan and J. Carter, *Appl. Phys. Lett.* 60, 3027 (1992).
- [4] A. Tsukazaki, A. Ohtomo, T. Kita, Y. Ohno, H. Ohno and M. Kawasaki, *Science* 315, 1388 (2007).
- [5] K. v. Klitzing, G. Dorda and M. Pepper, Phys. Rev. Lett. 45, 494 (1980).
- [6] K. v. Klitzing, Rev. Mod. Phys. 58, 519 (1986).
- [7] D. C. Tsui, H. L. Stormer and A. C. Gossard, Phys. Rev. Lett. 48, 1559 (1982).
- [8] R. Dingle, H. L. Stormer, A. C. Gossard and W. Wiegmann, *Appl. Phys. Lett.* 33, 665 (1978).
- [9] L. Pfeiffer and K. W. West, *Physica E* 20, 57 (2003).
- [10] A. Ohtomo and H. Y. Hwang, *Nature* **427**,423 (2004).
- [11] N. Nakagawa, H. Y. Hwang and D. A. Muller, Nat. Mater. 5, 204 (2006).
- [12] U. Kim, C. Park, Y. M. Kim, J. Shin and K. Char, APL Mater. 4, 071102 (2016).
- [13] Y. M. Kim, T. Markurt, Y. Kim, M. Zupancic, J. Shin, M. Albrecht and K. Char, *Sci. Rep.* 9, 16202 (2019).
- [14] H. J. Kim, U. Kim, H. M. Kim, T. H. Kim, H. S. Mun, B.-G. Jeon, K. T. Hong,
 W.-J. Lee, C. Ju, K. H. Kim and K. Char, *Appl. Phys. Express* 5, 061102 (2012).
- [15] H. J. Kim, U. Kim, T. H. Kim, J. Kim, H. M. Kim, B.-G. Jeon, W.-J. Lee, H. S. Mun, K. T. Hong, J. Yu, K. Char and K. H. Kim, *Phys. Rev. B* 86, 165205 (2012).

- [16] D. K. Gaskill, A. E. Wickenden, K. Doverspike, B. Tadayon and L. B. Rowland, J. Electron. Mater. 24 1525 (1995).
- [17] S. Raghavan, T. Schumann, H. Kim, J. Y. Zhang, T. A. Cain and S. Stemmer, *APL Mater.* 4, 016106 (2016).
- [18] H. Paik, Z. Chen, E. Lochocki, A. Seidner H., A. Verma, N. Tanen, J. Park; M. Uchida, S. Shang; B. Zhou; M. Brützam; R. Uecker; Z. Liu; D. Jena; K. M. Shen; D. A. Muller and D. G. Schlom, *APL Mater*. 5, 116107 (2017).
- [19] D. Pfützenreuter, M. Zupancic, Z. Galazka, R. Schewski, A. Dittmar, K. Irmscher, M. Albrecht and J. Schwarzkopf, *Nanotechnology* **32** 505609 (2021).
- [20] Y. Kim, Y. M. Kim, J. Shin and K. Char, APL Mater. 6, 096104 (2018).
- [21] S. Kim, M. Lippmaa, J. Lee, H. Cho, J. Kim, B. Kim and K. Char, *Adv. Mater*. *Interfaces* 9, 2201781 (2022).
- [22] T. Ohnishi, K. Shibuya and M. Lippmaa, Appl. Phys. Lett. 85, 272 (2004).
- [23] D. Pfützenreuter, S. Kim, H. Cho, O. Bierwagen, M. Zupancic, M. Albrecht, K. Char and J. Schwarzkopf, *Adv. Mater. Interfaces* 9, 2201279 (2022).

Chapter 5. Summary

The formation of the conventional 2DEG has been extensively studied in various semiconductor systems, including AlGaAs/GaAs, AlGaN/GaN, and MgZnO/ZnO, where the formation of a quantum well relies on the conduction band offset between different materials. However, in 2004, a unique type of 2DEG behavior was discovered at the interface of LAO and STO, exhibiting distinct properties and formation mechanisms related to the "polar catastrophe" and charge transfer through the interface. In the case of the LIO/BSO system, the behavior of the 2DEG can be understood through the "interface polarization" model, which involves polar discontinuity near the interface due to the breaking of centrosymmetry. The presence of the SnO₂ terminating layer on the BSO surface plays a crucial role in the formation of the 2DEG at the LIO/BSO interface.

To achieve SnO₂ termination on the BSO surface, different methods have been explored. In-situ methods involve controlling the termination during BSO growth with SnO₂ dusting, while ex-situ methods introduce SnO₂ termination after BSO deposition. Conductance measurements of in-situ grown LIO/BSO heterostructures demonstrate that the 2DEG is only formed when the BSO surface is SnO₂ terminated. Ex-situ methods, such as using a 9:1 mixture of acetone and water, have also proven effective in achieving SnO₂ termination on BSO surfaces. The terminations of the as-grown BSO and the BSO surfaces treated through in-situ and ex-situ methods were confirmed through CAICISS measurement.

The role of the SnO₂ terminating layer in LIO/BSO 2DEG formation is of significant importance. Moreover, the termination has a pronounced impact on the overall electrical properties and behavior of the system. These research findings are

expected to contribute to the development of applications utilizing LIO/BSO 2DEG, including HEMTs, as well as to further explore new physical phenomena.

국문초록

LaInO₃/BaSnO₃ 인터페이스에서 2DEG 상태 형성에 있어서 BaSnO₃ 의 SnO₂ 터미네이션의 역할에 대한 연구

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최근 몇 년 동안 산화물 반도체는 탁월한 전자 및 광학적 특성으로 인해 전자공학, 광전자학 및 에너지 변환 장치 등 다양한 응용 분야에서 주목받고 있다. 인듐 산화물 (In₂O₃), 아연 산화물 (ZnO), 인듐 주석 산화물 (ITO) 등의 전이 금속 산화물로 구성된 산화물 반도체는 효과적인 도핑을 통해 높은 캐리어 이동도와 밀도를 제공하여 실리콘 (Si)이나 갈륨질화물 (GaN)과 같은 전통적인 반도체를 능가하는 장점을 가지고 있어왔다. 또한, 산화물 반도체는 일반적으로 3 eV 이상의 넓은 밴드 갭을 가지고 있어 가시광선을 투과하며 투명한 전도성 산화물 (TCO)로 사용하기에 적합함이 알려져 있다. 이러한 독특한 특성의 조합으로 인해 산화물 반도체는 다양한 전자 및 광전자 응용 분야에서 매우 유용한 재료로 주목받고 있다.

본 논문은 특히 산화물 반도체인 바륨 주석 산화물(BaSnO₃, BSO)과 그 특성에 초점을 맞추었다. BSO 는 넓은 밴드 갭과 높은 전자 이동도로 알려져 있으며, 특히 란타넘 인듐 산화물 (LaInO₃, LIO)과의

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인터페이스에서의 이차원 전자 기체 (2DEG) 형성인 LIO/BSO 2DEG 로 인해 주목을 받고 있다.

전통적인 2DEG 형성은 AlGaAs/GaAs, AlGaN/GaN, MgZnO/ZnO 와 같은 다양한 반도체 시스템에서 광전자 구조물의 생성으로 연구가 진행되어 왔다. 여기서 양자 우물은 다른 재료 간의 전도대역 간격 차이로 형성되며, GaAs 의 경우 모듈레이션 도핑 방법이 사용되고, GaN 및 ZnO 에서는 극성에 의한 캐리어 축적이 발생한다. 그러나 2004 년에 LaAlO₃ 와 SrTiO₃ 의 인터페이스에서는 다른 유형의 2DEG 거동이 발견되어 "폴라 카타스트로피" 및 인터페이스를 통한 전하 이동과 관련된 독특한 특성 및 2DEG 형성 메커니즘을 보여준 바 있다.

LIO/BSO 2DEG 은 "인터페이스 극성" 모델로 설명할 수 있으며, 인터페이스 근처에서 중심대칭의 파괴로 인해 극성의 불연속이 발생한다. 이 모델에 따르면 LIO/BSO 인터페이스에서의 2DEG 형성에 대한 BSO SnO₂ 터미네이션 레이어의 역할이 중요함을 시사하며 본 논문은 이 부분을 중점적으로 조사했다. LIO/BSO 의 전도도 측정 결과, 2DEG 는 BSO 표면이 주로 SnO₂로 터미네이션된 경우에만 형성된다. 터미네이션 레이어는 BSO 표면에 추가적인 SnO₂ 증착에 의해 제어될 수 있으며 SnO₂ 터미네이션을 동축 충돌 이온 산란 분광법 (CAICISS)을 사용하여 확인하였다. 또한, SnO₂ 터미네이션을 위해 아세톤과 물의 9:1 혼합물을 사용하는 ex-situ 방법으로 SnO₂ 터미네이션된 BSO 를 달성할 수 있었다. 더 나아가, 마스크와 열 처리를 통한 LIO/BSO 2DEG 형성에 대한 이전의 보고에서, 자동적인 SnO₂ 터미네이션 달성과 그에 대한 기작을 이해하는 데 새로운 이해를 제안하였다.

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결론적으로, 산화물 반도체는 독특한 전자적 및 광학적 특성을 가지고 다양한 응용 분야에 연구되고 있으며 이 중 BSO 는 높은 전자이동도와 전자밀도를 가진 큰 잠재력을 가진 물질이다. 특히 LIO/BSO 2DEG 인터페이스에서 SnO₂ 터미네이션 레이어가 결정적 역할을 한다. 이러한 발견은 LIO/BSO 2DEG를 활용한 고전자이동도 트랜지스터(HEMTs)와 같은 응용 분야의 개발 및 새로운 물리 현상의 탐구에 기여할 것으로 기대된다.

Keyword : BaSnO₃, LaInO₃, 2DEG, Termination, Interfacial polarization

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