Effect of Threading Dislocations on the Electronic Structure of La-Doped BaSnO$_3$ Thin Films

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Abstract: In spite of great application potential as transparent $n$-type oxides with high transparent electrical mobility at room temperature, threading dislocations (TDs) often found in the (Ba,La)SnO$_3$ (BLSO) films can limit their intrinsic properties so that their role in the physical properties of BLSO films need to be properly understood. The electrical properties and electronic structure of BLSO films grown on SrTiO$_3$ (001) (STO) and BaSnO$_3$ (001) (BSO) substrates are comparatively studied to investigate the effect of the TDs. In the BLSO/STO films with TD density of $\sim1.32 \times 10^{11}$ cm$^{-2}$, $n$-type carrier density $n_e$ and electron mobility are significantly reduced, as compared with the BLSO/BSO films with nearly no TDs. This indicates that TDs play the role of scattering-centers as well as acceptor-centers to reduce $n$-type carriers. Moreover, in the BLSO/STO films, both binding energies of an Sn 3$d$ core level and a valence band maximum are reduced, being qualitatively consistent with the Fermi level shift with the reduced $n$-type carriers. However, the reduced binding energies of the Sn 3$d$ core level and the valence band maximum are clearly different as 0.39 and 0.19 eV, respectively, suggesting that the band gap renormalization preexisting in proportion to $n_e$ is further suppressed to restore the band gap in the BLSO/STO films with the TDs.

Keywords: perovskite oxide; barium stannate (BaSnO$_3$); photoemission spectroscopy; threading dislocation; bandgap renormalization

1. Introduction

In recent years, the perovskite stannate BaSnO$_3$ (BSO) system with donor-doping (e.g., La$^{3+}$) has received considerable attention due to its high electron mobility ($\mu_e$), high electrical conductivity ($\sigma$), high optical transparency, and excellent thermal/chemical stability. Moreover, with the control of La$^{3+}$ doping levels, the BSO system can play versatile roles of either transparent semiconductors or transparent conductors. Various transparent electronic devices employing the La-doped BSO (Ba$_{1-x}$La$_x$SnO$_3$, BLSO) have been demonstrated: active $n$-channel materials in the $p$-$n$ junctions [1] and the field-effect transistors (FETs) [2], sensitive UV photoconductors [3], and electron transport layers in perovskite solar cells [4].

Among the various forms of BLSO, single crystals have so far exhibited the highest $\mu_e \sim 320$ cm$^2$/V·s and the highest $\sigma \sim 2 \times 10^4$ S/cm at room temperature. To find the origin...
of these superior electrical characteristics, the band structure of the BLSO film has been intensively investigated both theoretically and experimentally. The indirect nature of the bandgap ~3.1 eV and conduction band filling of the BLSOs were observed by various experimental procedures such as X-ray photoemission spectroscopy (XPS), optical spectroscopy, and ellipsometry [5–7]. Corroborating the experimental results, several recent calculations on the band structures of BLSO with density functional theory (DFT) combined with the hybrid functions predict that the La-doping into BSO results in a degenerate semiconductor with an indirect bandgap of ~3.1 eV [8–11]. Moreover, typical behavior of the degenerate semiconductor such as the Burstein–Moss shift and band gap renormalization was observed in the BLSO films [6]. Both theoretical and experimental investigations indicate that the superior electrical characteristics mainly stem from two intrinsic physical properties. First, the BSO allows the degenerate-doping of La\(^{3+}\) ions into a highly dispersive conduction band, mainly composed of Sn 5s orbitals, allowing a full activation of donors and a small effective mass of electron carriers. Secondly, a high dielectric constant (~20) of BSO leads to the suppressed ionic dopant scattering, resulting in a high \(\mu_e\) [11].

However, the electrical properties of BLSO films are often inferior to those of single crystals. For example, the BLSO films grown on the SrTiO\(_3\) (STO) (001) substrate, having a lattice mismatch of about \(-0.54\%\), exhibit a typical \(\mu_e\sim10–70\ \text{cm}^2/\text{V} \cdot \text{s}\) [12]. This is mainly due to the additional carrier scattering coming from the various types of defects or dislocations, i.e., oxygen vacancies, Ba/Sn antisites, Ruddlesden–Popper shear faults, and threading dislocations (TDs) [13–18]. To envision further improvement of the \(\mu_e\) of the BLSO films, it is thus essential to control the various types of defects and understand the role of such defects in the physical properties of the films.

Toward the end of realizing the films with higher \(\mu_e\), there have been various experimental efforts such as different growth methods, the use of buffer layers and substrates with reduced lattice mismatch, and post-treatment. All of those efforts have so far resulted in the highest achievable \(\mu_e\sim70–183\ \text{cm}^2/\text{V} \cdot \text{s}\) [13–18], which are overall improved but still scattered. As an example relevant to the present study, Mun et al. [19] controlled the growth temperature of Ba\(_{0.96}\)La\(_{0.04}\)SnO\(_3\)/STO (001) films and revealed that \(\mu_e\) is enhanced when TD density (\(N_D\)) is reduced. Furthermore, with the control of the post-annealing condition at Ar and H\(_2\) atmosphere, Yoon et al. [20] similarly observed that the \(\mu_e\) of Ba\(_{1-x}\)La\(_x\)SnO\(_3\)/MgO (001) films, having a lattice mismatch of \(\sim2.2\%\) between \(\delta_{\text{BSO}} = 4.116\ \text{Å}\) and \(\delta_{\text{MgO}} = 4.212\ \text{Å}\), is proportional to \(N_D\). The highest \(\mu_e\) at room temperatures achieved in those studies were \(\sim70\ \text{cm}^2/\text{V} \cdot \text{s}\) \(n_e = 4.0 \times 10^{20}\ \text{cm}^{-3}\) [19] and 120 \(\text{cm}^2/\text{V} \cdot \text{s}\) \(n_e = 1.1 \times 10^{20}\ \text{cm}^{-3}\) [20], respectively. Both studies have thus suggested a critical role of TD in limiting \(\mu_e\). On that account, controlling TD seems to be crucial for improving the \(\mu_e\) of the BLSO films.

The actual \(\mu_e\) should also be affected by other defect sources, which were simultaneously created by either growth temperatures, annealing atmosphere, or the La\(^{3+}\) dopant concentration. For example, Yoon et al. [20] observed from the XPS study of the O 1s core level that extra oxygen vacancies were formed in the BLSO films upon being post-annealed under H\(_2\) gas. Moreover, Cho et al. [21] observed that extra oxygen vacancies were created with increasing La\(^{3+}\) dopant concentration from the XPS study of the O 1s core level. Therefore, understanding the pure effects of the TD only on the transport properties is a challenging task. Moreover, how the electronic structures of BLSO films are affected by the TD has not been fully understood either as the specimens with the TD only are still lacking.

In this regard, the use of a BaSnO\(_3\) (BSO) (001) substrate (with a lattice mismatch < 0.03\%) in the growth should be one of the most effective ways to achieve the BLSO film without TD. In our former study [15], a Ba\(_{0.96}\)La\(_{0.04}\)SnO\(_3\) film grown on BSO (001), subsequently followed by in-situ O\(_2\) annealing, resulted in no TD, \(\mu_e\sim100\ \text{cm}^2/\text{V} \cdot \text{s}\) and \(n_e = 1.3 \times 10^{20}\ \text{cm}^{-3}\) at room temperature. On the other hand, upon the same growth and in-situ annealing conditions being applied, a Ba\(_{0.96}\)La\(_{0.04}\)SnO\(_3\)/STO (001) film showed \(\mu_e\sim25\ \text{cm}^2/\text{V} \cdot \text{s}\) and \(n_e = 5.5 \times 10^{19}\ \text{cm}^{-3}\) [22]. These two BLSO films grown on BSO (001) and STO (001) with the same La\(^{3+}\) dopant concentration and growth/annealing condition are thus expected to be useful for comparing the physical properties of the BLSO films with or without TDs.
In this work, we investigate the role of TD on the electrical properties and electronic band structure of the BLSO films. To have the two kinds of films with or without TDs, the BLSO films with 0.5%, 1%, and 4% La doping are grown under identical growth and annealing conditions on two different substrates, BSO (001) \((a = 4.116 \text{ Å})\) and STO (001) \((a = 3.905 \text{ Å})\). Through the use of the BSO (001) substrate, the BSLO films without TDs are successfully obtained. Therefore, these two sets of BLSO films grown on STO (001) and BSO (001) could be an interesting platform to trace the intrinsic effect of TDs on their transport properties and electronic structures.

2. Materials and Method

2.1. Sample Preparation

Ba\(_{1-x}\)La\(_x\)SnO\(_3\) films with \(x = 0.005, 0.01, \) and 0.04, all of which having a thickness \(t = \sim 80 \text{ nm}\), were grown on the BSO (001) and the STO (001) substrate by the pulsed laser deposition (PLD) method, the growth conditions of which have been reported previously [15]. Stoichiometric dense polycrystalline pellets of Ba\(_{1-x}\)La\(_x\)SnO\(_3\) with \(x = 0.005, 0.01, \) and 0.04 were synthesized to be used as the target material in the PLD process. To minimize the variation of the film quality, the films were grown under the same experimental conditions: a 10 Hz repetition rate by the KrF laser (wavelength 248 nm), laser fluence of 0.7 \(\text{J/cm}^2\), oxygen partial pressure of 100 mTorr, and the substrate temperature of 790 \(\degree\text{C}\).

A commercial STO (001) (MTI Corp., Richmond, VA, USA, \(t = 0.5 \text{ mm}\)) and a custom-made BSO (001) single crystal were used as the substrates. The BSO single crystal was grown by the flux method using the mixture of CuO and CuO\(_2\) as a flux, as described in our previous report [15]. Then, the (001) surface of the as-grown BSO crystal was polished using a commercial polishing machine (Allied #70-1218) with polishing cloths and colloidal silica suspension to achieve a smooth surface. The polished BSO (001) substrate exhibited excellent crystallinity as indicated by the full width at half maximum (FWHM) of 0.022 \(\degree\) in the \(\omega\)-rocking curve of the (002) peak. Moreover, the root-mean-square roughness of 0.09 nm was achieved after polishing to prove an atomically smooth surface [15].

2.2. Structure and Electrical Properties Analysis

The structural properties of the BLSO films were investigated by the reciprocal space mapping (RSM) using high-power X-ray diffractometers (Empyrean\textsuperscript{TM}, PANalytical, Malvern, UK). All the RSM data in this study were measured near the BLSO (103) peak. To visualize the TD, transmission electron microscope (TEM) images (JEM-3000F, JEOL, Tokyo, Japan) were obtained in the two Ba\(_{0.96}\)La\(_{0.04}\)SnO\(_3\) films grown on STO (001) and BSO (001). Electronic properties including resistivity (\(\rho\)), \(n_e\), and \(\mu_e\) were investigated by the Hall effect measurement system (HL5500PC, Bio-Rad, Bend, OR, USA) with Van der Pauw contacts at room temperature. To ensure ohmic contact, Ti (thickness \(t = 5 \text{ nm}\)) and Au (\(t = 50 \text{ nm}\)) electrodes were sequentially deposited by a custom-made thermal evaporator.

2.3. Photoemission Spectroscopy Measurement

To investigate the electronic structure of BLSO films, ultraviolet photoemission spectroscopy (UPS) and XPS based on the synchrotron radiation source were performed at the Pohang Accelerator Laboratory (PLS-II4D, photoemission beamline). Each sample was electrically connected to the ground by using a carbon tape to prevent the surface charging effects. Inside the chamber with the ultra-high-vacuum condition, each sample was then etched with Ar plasma for \(\sim 30 \text{ s}\) to remove surface contamination. Before XPS and UPS measurements, to achieve accurate electron binding energy (\(E_B\)), the work function of the spectrometer was calibrated using the Au reference. Photon energies used for XPS and UPS were 650 eV and 90 eV, respectively.

3. Result and Discussion

In our previous study [15], it was established that Ba\(_{1-x}\)La\(_x\)SnO\(_3\) (\(x = 0.00-0.04\)) films with \(t = -90 \text{ nm}\) could be epitaxially grown on the BSO (001) substrate without any
dislocation and with minimized strain development. On the other hand, those grown on STO films with \( t = \sim 100 \text{ nm} \) have exhibited many TDs with fully relaxed strains [19]. Here, with nearly the same growth conditions, including the same oxygen partial pressure and temperatures, we have grown the Ba\(_{1-x}\)La\(_x\)SnO\(_3\) \((x = 0.005, 0.01, \text{and } 0.04)\) films on the two kinds of substrates, STO (001) and BSO (001). Moreover, we have also fixed \( t = 80 \text{ nm} \) in both sets of films as the transport properties are known to be also varied by thickness [23] via, e.g., strain. In this way, we presume that the transport and the electronic structure can be most affected by the TD, and the influences by other defects or strains can be minimized.

Figure 1 presents the RSM data measured in the Ba\(_{1-x}\)La\(_x\)SnO\(_3\) \((x = 0.005, 0.01, \text{and } 0.04)\) films grown on STO (001) and BSO (001). The RSM data in Figure 1a–c show that the BLSO (103) peak is well separated from the STO (103) peak, which directly supports the fully relaxed strains across the BLSO/STO films, regardless of the La doping ratio. On the other hand, as found in Figure 1d–f, the BLSO (103) peaks of the BLSO/BSO films are located at almost the same reciprocal positions with the corresponding peaks of BLSO/STO films. Moreover, they overlapped well with the BSO (103) peak so that they are not even distinguishable from the BSO (103) peak. Note that the BLSO/BSO (103) peaks are slightly elongated along the \( Q_z \) direction as the La doping ratio \( x \) increases. However, such a small strain variation within \( t = 80 \text{ nm} \) is not likely to affect the transport properties significantly. All these observations in the RSM data thus support the conclusion that the nearly perfect in-plane lattice match resulted in the BLSO/BSO films with minimal effect of strain variation, and their lattice constants are similar to those of BLSO/STO films.

To visualize the possible TD and estimate its areal density \( N_D \), a cross-sectional TEM study was performed, particularly in the Ba\(_{0.96}\)La\(_{0.04}\)SnO\(_3\) films grown on STO (001) and BSO (001) substrates (Figure 2a,b). The TDs can be easily identified as dark lines in the TEM image of the BLSO/STO (Figure 2a, red arrows). To extract \( N_D \), we have counted the number of TDs with more than 50 % thickness in a wide range TEM image (Figure S1). The number is then divided by a lateral dimension of the image to calculate the line density, of which square was used to estimate the areal density \( N_D \) as \( \sim 1.32 \times 10^{11} \text{ cm}^{-2} \). Note that \( N_D \) is, in principle, expected to be varied with the lattice constant variation of the film. However, as the lattice constants of the three BLSO films \((x = 0.005, 0.01, \text{and } 0.04)\) are nearly the same within 0.03%, which is also obvious in the RSM data in Figure 1a–c, the \( N_D \) values of the other \( \text{Ba}_{1-x}\text{La}_x\text{SnO}_3/\text{STO} \) films \((x = 0.005 \text{ and } 0.01)\) are likely similar to that of the \( \text{Ba}_{0.96}\text{La}_{0.04}\text{SnO}_3/\text{STO} \) film.

In sharp contrast to the Ba\(_{0.96}\)La\(_{0.04}\)SnO\(_3/\text{STO} \) films, no TDs can be found in the Ba\(_{0.96}\)La\(_{0.04}\)SnO\(_3/\text{BSO} \) film, as is evident in Figure 2b. This is understood to be due to the nearly perfect in-plane lattice match between the film and the substrate. Therefore, a comparison of physical properties in the two sets of BLSO films grown on BSO and STO substrates with \( t = 80 \text{ nm} \) can be suitable to understand the effect of TD with a relatively low strain effect involved. We emphasize again that in all the RSM data of Figure 1, the center position of each BLSO/BSO (103) peak is very close to the corresponding center position of the BLSO/STO (103) peak. This indicates that the physical properties within the BLSO grains at least could be similar to each other, regardless of the substrate used.
Figure 1. The reciprocal space mapping (RSM) data of Ba$_{1-x}$La$_x$SnO$_3$ (x = 0.005, 0.01, 0.04) films grown on (a–c) STO (001) and (d–f) BSO (001) substrates, all of which were taken near the (103) peaks.

Figure 2. Transmission electron microscope (TEM) images of Ba$_{0.96}$La$_{0.04}$SnO$_3$ film deposited on (a) STO (001) and (b) BSO (001) substrates. Red arrows in (a) indicate the TDs.

Figure 3 compares the electrical properties of the BLSO films with various La doping ratios (x = 0.005, 0.01, and 0.04), grown on both STO (001) and BSO (001) substrates. Note that the electrical properties of the Ba$_{0.995}$La$_{0.005}$SnO$_3$/STO film could not be measured due to its high resistivity. In Figure 3, two major systematic behaviors can be identified. For
all \( x \), BLSO/STO films exhibit lower \( n_e \) and \( \mu_e \) as compared with BLSO/BSO films. These experimental findings indicate that the electrical properties of BLSO films are affected by the TDs in two ways. First, TDs act as acceptor-centers and thus reduce \( n_e \). Secondly, TDs provide extra scattering centers and thus reduce \( \mu_e \). A similar reduction of \( \mu_e \) limited by the dislocation was also reported in the other BLSO films (\( \mu_e \sim N_D^{-1} \)) [20] and binary semiconductors such as GaN and GaAs [24].

![Figure 3](image_url)

**Figure 3.** (a) Electron concentration \( (n_e) \), (b) electron mobility \( (\mu_e) \), and (c) resistivity \( (\rho) \) of the \( \text{Ba}_{1-x}\text{La}_x\text{SnO}_3 \) films grown on BSO (001) (red solid symbols) and STO (001) (blue solid symbols) substrates. A green dotted line in (a) indicates a nominal dopant concentration \( (n_{\text{dop}}) \) expected from the fully activated La\(^{3+} \) dopant.

The reduced \( n_e \) and \( \mu_e \) in the BLSO/STO films can be explained by the role of dangling bonds existing at TDs. The periodic lattice structure of the BLSO film is expected to be discontinued at the TDs, which can naturally lead to the dangling bonds in the atoms located at the dislocation sites. These dangling bonds can then attract free electrons near the TDs and trap them into their bonding sites, thus resulting in much reduced \( n_e \) as compared with that of the BLSO/BSO films (Figure 3a). From the TEM image in Figure 2a, one can assume that each TD can be approximately modeled as a square rod with a height of 80 nm and width of 10 nm, which results in \( \sim 1.89 \times 10^{20} \) dangling bonds per one TD if each unit cell contains one dangling bond. With the observed \( N_D = 1.32 \times 10^{11} \text{ cm}^{-2} \), a maximum reduced \( n_e \) of \( 3.12 \times 10^{20} \text{ cm}^{-3} \) is then expected for the \( \text{Ba}_{0.96}\text{La}_{0.04}\text{SnO}_3/\text{STO} \) film (see Supplementary Information for details). Note that the experimental value of the reduced \( n_e \) in Figure 3a is \( 2.29 \times 10^{20} \text{ cm}^{-3} \) for the La 4\% specimen, which is roughly consistent with the estimated value. Furthermore, upon the free electrons’ being trapped, the TD sites should become negatively charged. Due to repulsive interaction between negatively charged dislocation sites and free electrons, extra ionic scattering is expected to occur in the electron transport process, thereby resulting in the decrease of \( \mu_e \) as observed in the BLSO/STO films (Figure 3b).

It should be noted that, as presented in Figure 3a, BLSO/BSO films have nearly similar carrier concentrations with a nominal dopant concentration \( (n_{\text{dop}}) \) (green dashed line). \( n_{\text{dop}} \)
is the expected carrier concentration when the donors were fully activated by substitution of \( \text{La}^{3+} \) for \( \text{Ba}^{2+} \) ions. This observation supports the good overall stoichiometry of our films, producing nearly expected carrier concentrations as the target materials. Though, a slightly lower \( n_c \) could indicate that another source of acceptor-centers other than TDs might exist in the BLSO/BSO films. Paik et al. suggested that the Ruddlesden–Popper crystallographic shear faults might also act as acceptor-centers [16].

To investigate the electronic structure of the BLSO films, both UPS and XPS were employed. The UPS and XPS spectra represent the filled electronic density of states (DOS) as a function of energy below the Fermi energy level (\( E_F \)). Due to a low photon energy, \( \sim 90 \, \text{eV} \), the UPS is an ideal probe to investigate the DOS of the valence band near the \( E_F \). Figure 4a presents the UPS spectra as a function of \( E_B \), showing the valence bands of \( \text{Ba}_{0.96}\text{La}_{0.04}\text{SnO}_3/\text{BSO} \) and \( \text{Ba}_{0.96}\text{La}_{0.04}\text{SnO}_3/\text{STO} \) films comparatively. It is worth noticing in Figure 4a that the valence band of \( \text{Ba}_{0.96}\text{La}_{0.04}\text{SnO}_3/\text{STO} \) is shifted to the lower \( E_B \) as compared to that of \( \text{Ba}_{0.96}\text{La}_{0.04}\text{SnO}_3/\text{BSO} \). To quantify the valence band shift, the valence band maximum (VBM) was determined as the intercept of the \( E_B \) axis with a linearly extrapolated line on the steeply increasing valence band tails (dashed lines in Figure 4a). The VBM determined by this method represents the \( E_B \) at the valence band edge of the BLSO films. Therefore, the \( E_B \) of VBM should decrease/increase when the valence band is shifted toward/away from the \( E_F \).

**Figure 4.** (a) The UPS spectra of \( \text{Ba}_{0.96}\text{La}_{0.04}\text{SnO}_3 \) films grown on STO (001) (blue lines) and BSO (001) (red lines) substrates. The inset shows the same UPS spectrum enlarged near the tail. (b) A summary of \( E_B \)’s of the valence band maximum (VBM) estimated from the UPS spectra of BLSO films grown on both STO (blue) and BSO (red) substrates. The inset shows the VBM difference between the BLSO films grown on BSO (001) and STO (001) substrates (c,d) XPS spectra near the Sn 3d core level in \( \text{Ba}_{0.96}\text{La}_{0.04}\text{SnO}_3 \) films grown on STO (001) (blue) and BSO (001) (red). Scattered symbols represent the measured data, and the solid lines are the fitted curves by the Voigt profile. Dashed lines in (c,d) indicate the peak positions of each spectrum.
As a degenerate semiconductor, the $E_F$ of the BLSO should be located well inside the conduction band, which is known to be mainly composed of Sn 5s orbitals. However, in our UPS study, the filled states from the conduction band structure of the BLSO films could not be identified (see the expanded spectra in the inset of Figure 4a). On the other hand, photoemission spectra corresponding to the filled states from the conduction band of the BLSO films were observed experimentally at $E_B$ ~0.5 eV in several hard X-ray photoemission spectroscopy (HAXPES) studies [6,7]. In general, the ratio of photoionization cross-section between Sn 5s orbital and O 2p orbital decreases exponentially with decreasing photon energy. Considering that the photon energy (~90 eV) used in the UPS measurement is ~10 times lower than that of typical HAXPES measurements, conduction electron states are not likely observable due to the low photoemission intensity of the Sn 5s orbital as compared to the O 2p orbital.

In the inset of Figure 4a, the UPS spectrum of Ba$_{0.96}$La$_{0.04}$SnO$_3$/BSO film shows a peak near the tail region around ~2.75 eV. This peak is suspected to represent the DOS of the in-gap state attributable to various defects in the BLSO film (i.e., La$^{3+}$ donor, oxygen vacancies, etc.) [5]. Even though BLSO/BSO films have no TD, other defects such as oxygen vacancy can be a source of such in-gap states. In contrast, there is no clear peak feature attributable to the in-gap state in the UPS spectrum of the Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO film. Since the Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO film has TDs as additional defects, its valence band is shifted toward the $E_F$ so that the edge region of the valence band near 2.75 eV has increased its intensity. Considering the fact that the UPS spectrum of the in-gap state is ~20 times smaller than that of the main valence band region, the in-gap state is expected to be hidden when the in-gap state is located near the valence band edge. Therefore, it is likely that the in-gap state of the Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO film is embedded in the band edge spectra.

We have investigated the UPS spectra of other La dopings as well to compare the shifts of VBM in the two sets of BLSO films (Figure S3) and summarized the results in Figure 4b. The VBM shifts of the BLSO films grown on BSO (001) and STO (001) show three major features. First, the $E_B$ of the VBM in BLSO films generally increases with the increase of $x$. Secondly, BLSO/BSO films exhibit higher $E_B$’s at the VBMs than BLSO/STO films for all the $x$. Thirdly, the difference of the $E_B$’s at the VBM between the BLSO/BSO and BLSO/STO films increases with $x$ (see the inset of Figure 4b). The first and second behaviors can be simply explained by the $E_F$ shift. Since the $E_F$ of the BLSO films increases with $n_d$, the $E_B$ of the VBM of BLSO films supposedly increases with $n_d$. The higher $E_B$’s of the VBMs observed in the BLSO/BSO films compared to the BLSO/STO films are qualitatively consistent with this explanation. Indeed, the Ba$_{0.96}$La$_{0.04}$SnO$_3$/BSO film, which has the highest $n_d$ without TD, exhibits the highest $E_B$ of the VBM ~3.84 eV among the BLSO films investigated in this work. Moreover, the increasing tendency with $x$ observed in the VBM difference between the two film sets (inset of Figure 4b) can also be understood as being due to the $E_F$ shift. Since the $n_d$ difference between the BLSO/BSO films and the BLSO/STO film increases with $x$, as shown in Figure 3a, the VBM difference between the two sets of BLSO films should also increase.

Although the $E_F$ shift can explain the valence band shift of the BLSO films qualitatively, it is questionable whether the $E_F$ shift is sufficient for understanding the effect of TD on the band structure of the BLSO films. To clarify this, we have investigated the core level spectra of Ba$_{0.96}$La$_{0.04}$SnO$_3$ films by XPS. Figure 4c,d shows the Sn 3d core level spectra of Ba$_{0.96}$La$_{0.04}$SnO$_3$/BSO and Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO, respectively. To determine the center positions of the Sn 3d$_{3/2}$ and the Sn 3d$_{5/2}$ peaks, the spectra were fitted by the Voigt function, which contains both Gaussian and Lorentzian terms to represent instrumental broadening and inherent XPS spectrum, respectively. To determine the instrumental broadening, we measured the XPS spectra of Au metal and fitted the Au 4f peak using the Voigt function with a fixed Lorentzian width (FWHM = 0.29 eV) [25]; the instrumental broadening factor was determined as ~1.26 eV. With the known instrumental broadening factor, the Sn 3d$_{3/2}$ and Sn 3d$_{5/2}$ core level spectra were fitted by the Voigt profile; Table 1 summarizes the fit results.
Table 1. The Sn 3d core level of La 4% doped BLSO film deposited on STO and BSO substrates.

|                     | Sn 3d_{3/2} | Sn 3d_{5/2} | FWHM  |
|---------------------|-------------|-------------|-------|
| Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO | 495.10 ± 0.11 eV | 486.69 ± 0.07 eV | 1.77 ± 0.06 eV |
| Ba$_{0.96}$La$_{0.04}$SnO$_3$/BSO | 495.49 ± 0.11 eV | 487.07 ± 0.07 eV | 1.70 ± 0.05 eV |

According to Table 1, it is unambiguously found that both the Sn 3d$_{3/2}$ and Sn 3d$_{5/2}$ core levels of the Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO are found at the lower $E_g$’s by ~0.39 eV and ~0.38 eV, respectively, as compared to those of Ba$_{0.96}$La$_{0.04}$SnO$_3$/BSO. Moreover, the FWHMs estimated in the XPS spectra of Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO and Ba$_{0.96}$La$_{0.04}$SnO$_3$/BSO are 1.77 eV and 1.70 eV, respectively. (Note that the same FWHM is assumed for the Sn 3d$_{3/2}$ and Sn 3d$_{5/2}$ core level spectra.) The FWHM value of the Sn 3d spectra in the BLSO/BSO film is indeed in good agreement with that obtained previously in an indium tin oxide film (~1.70 eV), while the FWHM value in the BLSO/STO film is slightly larger (~1.77 eV) [26].

Since the BLSO films were connected to a common ground in the UPS and XPS measurements, it is natural to align the band structure with respect to $E_F$. Figure 5 shows the schematic band structures of Ba$_{0.96}$La$_{0.04}$SnO$_3$/BSO and Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO aligned with respect to $E_F$. Figure 5a,b shows that both the Sn 3d$_{3/2}$ core level and the valence band in the Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO film are shifted to lower $E_B$ by $\Delta E_{Sn}$ ~0.39 eV and $\Delta E_{VBM}$ ~0.19 eV, respectively. If the $E_F$ shift had only occurred with the TDs, $\Delta E_{Sn}$ and $\Delta E_{VBM}$ would have been nearly the same as described in Figure 5c. Therefore, experimental observation of different $\Delta E_{VBM}$ and $\Delta E_{Sn}$ suggests that the origin of their shift should be explained separately.

![Figure 5. Schematic electronic band structures of (a) Ba$_{0.96}$La$_{0.04}$SnO$_3$/BSO (001), (b) Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO (001) with the $E_F$ shift and the restored band gap ($\Delta E_g$), and (c) Ba$_{0.96}$La$_{0.04}$SnO$_3$/STO (001) with only the $E_F$ shift. These band schematics include the valence band (VB), its maximum (VBM), and a Sn 3d$_{3/2}$ core level (Sn 3d$_{3/2}$).](image)

One of the most probable explanations for different $\Delta E_{VBM}$ and $\Delta E_{Sn}$ is the band gap renormalization effect, which is tied to $n_e$. The band gap renormalization refers to the shrinking of a band gap proportional to $n_e$, which is often observed in degenerate semiconductors like the BLSO system [6]. When free electrons are introduced to degenerate semiconductors, conduction bands/valence bands are shifted to a higher/lower $E_B$, owing to the self-energy effect of added free electrons. Namely, the conduction band is shifted to higher $E_B$ as the self-energy of added free electrons is negative. For the valence band, however, Coulomb interaction between electrons becomes weakened since the Hartree–Fock
exchange is replaced with dynamically screened interaction with added free electrons [27]. As a result, the valence band is shifted to a lower $E_B$. Therefore, upon $n_e$’s being increased, the band gap is reduced due to the band gap renormalization, while upon $n_e$’s being decreased, the bandgap should be restored. In our case, since the TD provides electron trapping sites and clearly reduces $n_e$, the bandgap should be restored to make the valence band move to higher $E_B$ in the BLSO/STO films. Hence, due to the combined effect of the lowered $E_B$ coming from the $E_F$ shift (0.39 eV) and the restored band gap (0.20 eV), the net VBM shift (0.19 eV) is smaller than in the case with the $E_F$ shift only (0.39 eV), which results in different energy level shifts in the VBM and the Sn 3d$_{3/2}$ core levels, as summarized in Figure 5b.

4. Conclusions

The transport, microstructural properties, and electronic band structure of the BLSO films grown on STO (001) and BSO (001) were comparatively investigated to understand the effect of TDs. TDs in the BLSO films play two major roles. First, due to the dangling bonds present in the TDs, they act as electron-traps. Simultaneously, TDs are negatively charged and provide an extra electron scattering center. As a result, TDs make both $\mu_e$ and $n_e$ decrease in the BLSO films.

Decreased carrier density attributed to the TDs affects the overall electronic structure of BLSO/STO films. First, $E_F$ is reduced with reduced $n_e$. As a result, the $E_B$’s of the valence band maximum and Sn 3d core level become reduced. Secondly, the band gap, which is shrunk in proportion to $n_e$, is restored with the reduced $n_e$. This phenomenon is likely to result in the differently valued $E_B$ lowering in the Sn core level and in the valence band spectra, as observed in the $\text{Ba}_{0.96}\text{La}_{0.04}\text{SnO}_3$/STO (001).

Although only TDs are mainly discussed in this work, other defects, such as oxygen vacancies, can also act as additional electron traps. However, the effects of the other defects on the electronic structure of BLSO films have not been fully understood yet. By combining the result of this study and further research on other defects, we expect that understanding the roles of the various defects on the physical properties of the BLSO films could be helpful to achieve higher quality BLSO films comparable to the BLSO single crystals.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/ma15072417/s1, Figure S1: Wide range transition electron microscope (TEM) image. Red arrows represent the threading dislocations counted in the density estimation, Figure S2: (a) Schematic diagram of the threading dislocation and (b) sectional diagram of the threading dislocation. Orange line in (b) represent dangling bonds, Figure S3: Ultraviolet photoemission spectra of $\text{Ba}_{1-x}\text{La}_x\text{SnO}_3$ ($x = 0.005, 0.01, 0.04$) films grown on BSO (001) and STO (001) substrate. Dashed lines indicate linear extrapolation line on the steeply increasing valence band tails.

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References

1. Lee, J.H.; Lee, W.-J.; Kim, T.H.; Lee, T.; Hong, S.; Kim, K.H. Transparent p-Cu/In,SnO$_3$-n Heterojunctions with a High Rectification Ratio. *J. Phys. Condens. Matter.* 2017, 29, 384004. [CrossRef] [PubMed]

2. Park, C.; Kim, U.; Ju, C.J.; Park, J.S.; Kim, Y.M.; Char, K. High Mobility Field Effect Transistor Based on BaSnO$_3$ with Al$_2$O$_3$ Gate Oxide. *Appl. Phys. Lett.* 2014, 105, 203503. [CrossRef]

3. Lee, Y.; Yoon, D.; Yu, S.; Sim, H.; Park, Y.; Nam, Y.-S.; Kim, K.-J.; Choi, S.-Y.; Kang, Y.; Son, J. Reversible Manipulation of Photoconductivity Caused by Surface Oxygen Vacancies in Perovskite Stannates with Ultraviolet Light. *Adv. Mater.* 2021, 34, 2107650. [CrossRef] [PubMed]

4. Shin, S.S.; Yeom, E.J.; Yang, W.S.; Hur, S.; Kim, M.G.; Im, J.; Seo, J.; Noh, J.H.; Seok, S.I. Colloidally Prepared La-Doped BaSnO$_3$ Electrodes for Efficient, Photostable Perovskite Solar Cells. *Science* 2017, 356, 167–171. [CrossRef] [PubMed]

5. Joo, B.S.; Chang, Y.J.; Moreschini, L.; Bostwick, A.; Rotenberg, E.; Han, M. Evidence for Indirect Band Gap in BaSnO$_3$. *Adv. Funct. Mater.* 2018, 28, 1705176. [CrossRef]

6. Lebens-Higgins, Z.; Scanlon, D.O.; Paik, H.; Sallis, S.; Nie, Y.; Uchida, M.; Sterbinsky, G.E.; Arena, D.A.; et al. Direct Observation of Electrostatically Driven Band Gap Renormalization in a Degenerate Perovskite Transparent Conducting Oxide. *Phys. Rev. Lett.* 2016, 116, 101204. [CrossRef]

7. Sallis, S.; Scanlon, D.O.; Chae, S.C.; Quackenbush, N.F.; Fischer, D.A.; Woicik, J.C.; Guo, J.-H.; Cheong, S.W.; Piper, L.F.J. La-Doped BaSnO$_3$ Degenerate Perovskite Transparent Conducting Oxide: Evidence from Synchrotron X-ray Spectroscopy. *Appl. Phys. Lett.* 2013, 103, 042105. [CrossRef]

8. Wang, W.; Liang, S.; Ding, K.; Bi, J.; Yu, J.C.; Wong, P.K.; Wu, L. Microwave Hydrothermal Synthesis of MSnO$_3$ (M$^{2+}$ = Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$): Effect of M$^{2+}$ on Crystal Structure and Photocatalytic Properties. *J. Mater. Sci.* 2014, 49, 1893–1902. [CrossRef]

9. Singh, D.J.; Xu, Q.; Ong, K.P. Strain Effects on the Band Gap and Optical Properties of Perovskite SrSnO$_3$ and BaSnO$_3$. *Appl. Phys. Lett.* 2014, 104, 011910. [CrossRef]

10. Kraut, E.A.; Grant, R.W.; Waldrop, J.R.; Kowalczyk, S.P. Precise Determination of the Valence-Band Edge in X-ray Photoemission Spectra: Application to Measurement of Epitaxial Perovskite Interface Potentials. *Phys. Rev. Lett.* 1980, 44, 1620–1623. [CrossRef]

11. Song, W.; So, S.K.; Cao, L. Angular-Dependent Photoemission Studies of Indium Tin Oxide Surfaces. *Appl. Phys. A* 2001, 72, 361–365. [CrossRef]

12. Berggren, K.-F.; Sernelius, B.E. Band-Gap Narrowing in Heavily Doped Many-Valley Semiconductors. *Phys. Rev. B* 1981, 24, 1971–1986. [CrossRef]