Evidence for indirect band gap in BaSnO₃ using angle-resolved photoemission spectroscopy

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ABSTRACT

Transparent BaSnO₃ thin films have been proposed as an alternative transparent conducting oxide (TCO). Although bulk synthesis and high-quality fabrication of epitaxial films are well established, there are still unsolved aspects about their electronic structure, such as the direct or indirect nature and the size of the band gap. We investigated the electronic structure of epitaxial BaSnO₃ thin films using in situ angle-resolved photoemission spectroscopy. We directly measured an indirect band gap of 3.7 eV, a value compatible with those of previous reports, but we also identified additional in-gap states at −1.6 eV below the conduction band minimum that we attribute to intrinsic defects, mainly oxygen vacancies.

PACS number:

Keywords: BaSnO₃, Indirect band gap, Transparent conducting oxide, ARPES

I. INTRODUCTION

Recently, transparent conducting oxides (TCOs) that exhibit high optical transparency in the visible spectrum range, high electrical conductivity and low electrical resistivity have attracted much attention [1,2] with the viewpoint of multiple uses. Indium tin oxide (ITO), in particular, is the TCO most used in various applications, including solar cells, flat-panel displays, light-emitting diodes, and smart coatings [3–5]. However, with the increasing demand for indium-based TCOs and the rather limited availability of indium, the cost of indium has increased greatly, thus increasing manufacturing costs. As a consequence, there has been much effort to find an alternative TCO, such as F-doped tin oxide, Al-doped zinc oxide, Ag nanowires, graphene, or graphene-wrapped silver nanowires [6–10].

BaSnO₃ (BSO) is a ternary perovskite TCO with the optical and electrical properties desired by the TCO market [11–22]. Because of its perovskite structure, BSO can be epitaxially combined with other perovskites that have interesting properties such as high-transition-temperature superconductivity, ferroelectricity, and ferromagnetism [23]. BSO has a cubic unit cell (UC) and a Sn-O-Sn bonding angle of ~180°. Replacing the Ba or Sn sites with other atoms can modify the electrical properties of BSO. For example, by substituting La for Ba, BSO develops n-type semiconductor properties with a dc conductivity of $\sim 10^4 \Omega^{-1} \text{cm}^{-1}$, electron mobility of up to $320 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, and a carrier concentration of $8 \times 10^{19} \text{ cm}^{-3}$, which is larger than that of any other TCO [12]. This triggered interest in investigating the electronic structure of this promising compound.

Table 1 presents the band gap values for BSO and La/Sr-doped BSO obtained from both theoretical and experimental studies. Various methods, such as local density approximation (LDA) [24], generalized gradient approximation (GGA) [24], the Perdew-

Burke-Ernzerhof (PBE and PBE0) functional [25,26], the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [18,19], and the general potential linearized augmented plane wave (LAPW) method [27] were used to study the BSOs. While the theoretical results range from 0.75 to 3.3 eV, they generally indicate that BSO has an indirect band gap, with the valence band maximum (VBM) and the conduction band minimum (CBM) located at the R and Γ points, respectively. On the other hand, the experimental studies, in which optical spectroscopy [11,25,28–30] and integrated photoemission spectroscopy [17,31] were used, showed band gap values in the range of 3.1 - 3.56 eV but did not confirm the indirect nature of the gap. To directly observe the band gap nature experimentally, many researcher successfully applied angle-resolved photoemission spectroscopy (ARPES) to reveal the direct/indirect band gap properties of various semiconductors, whose electronic states near the Fermi level (E_F) are considered as CBM due to intentional charge filling into intrinsic semiconductors [32–34]. As far as we know, there has been no experimental proof for or against the claim that BSO has an indirect band gap. In this paper, we present our measurements on the direct band structure of epitaxial BSO films. In situ ARPES showed that the CBM is located at the Γ point and the VBM is located at the R point. There was a significant difference between the band gap value estimated using the angle-integrated photoemission spectra and that calculated using the ARPES data. A careful comparison of the different measurements yielded an estimated indirect band gap of 3.7 eV.

II. Experimental

High-quality BSO films were epitaxially grown using pulsed laser deposition (PLD) and transferred in situ to the ARPES chamber of the MAESTO (Microscopic and Electronic STRucture Observatory) beamline 7.0.1 at the Advanced Light Source (ALS; Lawrence Berkeley National Laboratory) [35]. A sintered BSO polycrystalline target was ablated at an

O₂ partial pressure of 10^{-4} torr using a KrF excimer laser (248 nm) at a laser fluence of 1.5 J/cm² and 2 Hz repetition. At 550°C, the films showed two-dimensional (2D) growth on Nb-doped SrTiO₃ (STO) (001) substrates. We monitored reflection high-energy electron diffraction (RHEED) to verify the crystallinity of the thin films during PLD growth. In Fig.1(a), clear RHEED oscillations, each one of which corresponds to the growth of one UC, indicate the layer-by-layer growth mode at a growth rate of 0.025 UC/s. The lattice parameter of the BSO UC is about 0.4 nm. Film growth was stopped after 20 oscillations, resulting in a BSO film about 8 nm thick. The insets are RHEED images for the bare STO surface (left) and the deposited BSO film (right), both of which show clear diffraction patterns, i.e., signatures of highly ordered films.

ARPES data were taken at 100 K, with a combined (beamline + electron spectrometer) energy resolution of 35 meV and angular resolution of 0.1° [35]. The photon energy was set at 123 eV for measuring across the Γ point of the BSO film at the surface normal. The position of the Fermi level (E_F) was determined by measuring a Mo foil in electrical contact with the sample.

III. RESULTS AND DISCUSSION

A comparison of the two RHEED images in Fig. 1(a) shows an intensity decrease in the diffraction pattern in the BSO film compared to that of the STO substrate. Figure 1(b) shows lateral line profiles taken from the two RHEED images in Fig. 1(a). The peak separation of the BSO profile is 6.9% narrower than that of the STO profile. Using this value and the STO lattice constant of 3.905 Å, we estimated that the BSO film had an in-plane lattice constant of 4.17 Å, which is ~1.3 - 1.5% greater than the in-plane lattice constant of doped BSO films and undoped BSO bulk [12,36]. This increase in the lattice constant is probably due to the introduction of a high concentration of O vacancies during film growth.

These O vacancies introduce Coulomb repulsion between neighboring cations and expand the lattice volume, as is often observed in BSO (volume change of 2.7%) [36] and similar perovskite oxides, such as STO (1%) [33]. The RHEED measures only the top surface layer; hence, the physical properties of the surface, such as the in-plane lattice parameter, may differ slightly from those of the whole film because of the strain caused by surface truncation [38]. Later we discuss the change in the electronic structure due to the O vacancies, which, as in all other oxides, represent intrinsic electron donors.

The size of the band gap was measured using integrated PES on a spectrum of a BSO film, as shown in Fig. 2. The intensity from -7 to -4 eV was assigned to the O 2p states. Extrapolation by a linear fit of the leading edge found the VBM to be about -3.7 eV below E_F . This value is slightly larger than the reported VBM of 3.1–3.5 eV in 0.1–4 % La-doped BSO films determined by high-energy PES [17,31]. The inset in Fig. 2 is a high magnification of the region near E_F , where there is one electronic states at -2 eV (peak β) and one close to the E_F . The latter originates from the onset of the conduction band. The CBM, estimated at -0.5 eV, is similar to what reported for 0.1–0.15% La-doped BSO films from high-energy PES [31]. As a result, the separation between the VBM and the CBM is found to be ~3.2 eV, which is similar to the minimum optical gap values of 3.1–3.3 eV among the several experimental values in Table 1. However, a deeper insight in the gap region and a more accurate estimate of the gap size can be obtained with momentum resolution.

Figure 3(a) is an ARPES image plot measured along high symmetry points. The O 2p bands are located from -4 to -11 eV, with several nearly flat bands of various intensities between -4 and -8 eV and a weak and dispersive band between -7 and -11 eV. Both groups of bands are consistent with most theoretical calculations [17–19,25,26]. To explore the nature of the band gap in BSO, we focused on the momentum position of both the CBM and the VBM. The noticeable electronic states at E_F in Fig. 3(b) assign the CBM to the Γ point. On

the other hand, the VBM is clearly not located at the Γ point, directly proving an indirect band gap. Consistent with our results, the result from most previous theoretical calculations show the CBM at the Γ point and the VBM at the R point, as listed in Table 1 [18,24–27]. Ours is the first direct experimental evidence of an indirect band gap in electron-doped BSO films.

To locate the VBM in the ARPES spectra, we analyzed the valence band structure of the BSO film in Fig. 3(a). The top of the valence band, near -4 eV, showed a slight dispersion and the VBM was found at the R point. On the other hand, a more dispersive band was visible from -8 to -12 eV, with the minimum at the R point. Comparison with the theoretical calculations of all the methods in Table 1 also supports the VBM at the R point, which is slightly higher than the M point. More precisely, we extracted energy dispersion curves from the raw data at the high symmetry points, as shown in Fig. 3(d), demonstrating that the VBM is at the R point (-3.88 eV) and the CBM is at the Γ point (-0.15 eV). Therefore, the indirect band gap value is ~3.7 eV, which is 0.2–0.4 eV larger than the values (3.2–3.5 eV) found by all the optical and PES measurements.

To understand the discrepancy in our band gap measurement with previous experimental results, we consider several possible origins, namely, O vacancies, strain, and surface band bending. Recent hard X-ray PES data showed that the band gap shrunk with an increase in La doping [31]. Theory predicts a band gap reduction of 0.35 eV upon a lattice expansion of 1%. Our BSO film is slightly electron-doped, with some native defects (O vacancies or antisite defects), and has an in-plane lattice constant ~1.3–1.5% larger than that of the reported pristine and La-doped BSO films. In addition, a recent ARPES study of In_2O_3 films showed that high surface electron density causes the band gap close to the surface to shrink [39]. All these scenarios cannot explain the difference between our experimentally determined indirect band gap and the other experimental values.

Next, we compared the experimental band gap value with the theoretical calculations, as listed in Table 1. Both LDA and GGA calculations drastically underestimated the band gap, similar to the case of the TCO ZnO [34]. On the other hand, the hybrid functional PBE, HSE, and LAPW yielded significant increases in the band gap. PBE0 and LAPW increased the band gap up to 3.2–3.3 eV, slightly less than the experimental band gap of 3.7 eV. Recent ZnO calculations showed that the hybrid functional calculation along with a suitable correlation energy U could simultaneously correct the band gap value and the d band position for higher binding energy [34]. [This implies that future theoretical calculations should be compared with the experimental valence band structure for tuning the parameters in band structure calculations \[40\].](#)

Finally, we discuss the origin of the in-gap states. The energy of defect states and their effect on the electrical conductivity of wide-band-gap semiconductors such as In_2O_3 , SnO , ZnO , BSO , and ATiO_3 ($A=\text{Sr, Ba}$) [26,38,39,34,41] have been controversial topics for past decades. As shown in both the insets of Fig. 2 and Fig. 3(d), the in-gap state β is present at 1.75 eV below the CBM in the BSO films. [The state \$\beta\$ spreads over wide momentum space without clear dispersion, so that it's hard to consider the states as the valence band but as the localized in-gap states.](#) Such in-gap states are found in other semiconducting oxides, but at different energy levels from that of the BSO, e.g., that for ATiO_3 ($A=\text{Sr, Ba}$) and In_2O_3 is 0.6–1.1 eV and ~1.6 eV below CBM, respectively [39,42,43]. However, there are striking differences between the ATiO_3 and In_2O_3 with respect to the contribution of free electrons from a single O vacancy. For SrTiO_3 , theoretical modelling shows that an O vacancy donates both one free electron and a localized electron as a result of vacancy clustering accompanied by strong electron localization. On the other hand, a recent ARPES study [39] revealed an O vacancy state at 1.6 eV below CBM in slightly doped In_2O_3 films, which is consistent with the doubly occupied O vacancy state found by recent first principle calculations [44]. By comparing the

energy level of the in-gap state, we can conclude that BSO is likely to have the doubly occupied O vacancy. Indeed, a recent PBE0 calculation showed that the doubly occupied O vacancy is the most probable in-gap state, but its energy level is 0.37 eV below the CBM [26]. It has been thought that the donor level, such as the O vacancy, is too deep to be ionized and generate free electrons at room temperature, although the ionization energy of the defect is largely suppressed for O vacancies at the surface [44]. Because the BSO film has an expanded lattice volume and an electron-doped electronic structure, it is very likely that the high concentration of O vacancies induces the peak β within the band gap and the resulting donated free electrons play an important role in the applications that use BSO, such as a chemical sensor [45] and buffer layer [46]. Therefore, to study the energy of the in-gap state, the nature of the intrinsic defects in the newly emerging TCO candidate BSO must be understood. To characterize the intrinsic vacancy or antisite defects, extensive studies on their possible origins, such as cation stoichiometry, O vacancy, and surface state formation upon UV irradiation or vacuum annealing, should be conducted [39,41,47].

IV. CONCLUSION

The electronic band structure of BaSnO_3 was directly measured by using in situ ARPES on the epitaxial films. We not only determined the band gap value of 3.7 eV but also showed the existence of an indirect band gap with a CBM at the Γ point and a VBM at the R point. The experimental band gap was significantly larger than that found by theoretical calculations, which had a maximum of 3.3 eV. Furthermore, the intrinsic defect-induced in-gap state is at 1.75 eV below E_F , which is a deeper binding energy than other TCOs.

ACKNOWLEDGEMENT

The authors are grateful to E. Choi for helpful discussion. This work was supported by by the National Research Foundation of Korea (NRF) grant funded by the Korea government (NRF-2015R1D1A1A01060381) for Beom Soo Joo and Moonsup Han. This work was supported by the 2016 Research Fund of the University of Seoul for Young Jun Chang. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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Method (Theory)	E _g (eV)	VBM	CBM	Method (Exp.)	E _g (eV)
LDA [24]	1.51	R	Γ	OS* [30]	3.56
GGA [24]	0.74	R	Γ	OS [29]	3.3
PBE [25]	2.83	R	Γ	OS [25]	3.5
PBE0 [26]	3.22	R	Γ	OS [28]	3.49
HSE1 [18]	2.48	R	Γ	OS [11]	3.1
HSE2 [19]	3.0	R	Γ	HAXPES* [17]	3.48
LAPW [27]	3.3	-	-	HAXPES [31]	3.4
ARPES [This work]	3.7	R	Γ		

Table 1. Band gap values and VBM/CBM locations in k-space predicted from theoretical and experimental methods. All of the theoretical results commonly show the indirect band gap structure. *(OS: Optical spectroscopy, HAXPES: Hard x-ray photoemission spectroscopy)

Figure 1. (a) RHEED intensity oscillation during the film growth. Inset figures show the RHEED images before and after the film growth. (b) Horizontal line profiles along the central peaks on the STO surface (black) and the BSO film surface (red), taken from the inset figures in (a). Shrinkage of peak spacing in BSO compared to the STO indicates in-plane lattice elongation of 6.9%.

Figure 2. *In situ* angle-integrated photoemission spectra of the BSO thin film. VBM and CBM are estimated to be -3.7 eV and -0.5 eV from a linear fit of the leading edges, respectively. The inset shows CBM and in-gap state β in the expanded low energy range.

Figure 3. (a) Raw ARPES spectra of the BSO film along high-symmetry path, as indicated as cuts c_1 , c_2 , and c_3 in (c). The top valence band near -4 eV has small dip at near Γ point. (b) Zoom spectra with different contrast scale shows significant conduction band signal near E_F , indicating CBM at Γ point and therefore indirect band gap character. (c) Brillouin zone of cubic structure with cuts c_1 , c_2 , and c_3 . (d) Energy distribution curves at the high-symmetry points to determine VBM of -3.88 eV at R point. Inset shows the zoomed low energy region, in which only Γ point shows CBM peak at -0.15 eV.