\[ \sqrt{2} \times \sqrt{2} R 45^\circ \] surface reconstruction and electronic structure of BaSnO\(_3\) film

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We studied surface and electronic structures of barium stannate (BaSnO\(_3\)) thin-film by low energy electron diffraction (LEED), and angle-resolved photoemission spectroscopy (ARPES) techniques. BaSnO\(_3\)/Ba\(_{0.96}\)La\(_{0.04}\)Sn\(_3\)O\(_9\)/SrTiO\(_3\) (10 nm/100 nm/0.5 mm) samples were grown using pulsed-laser deposition (PLD) method and were ex-situ transferred from PLD chamber to ultra-high vacuum (UHV) chambers for annealing, LEED, and ARPES studies. UHV annealing starting from 300°C up to 550°C, followed by LEED and ARPES measurements show 1×1 surfaces with non-dispersive energy-momentum bands. The 1×1 surface reconstructs into a \[ \sqrt{2} \times \sqrt{2} R 45^\circ \] one at the annealing temperature of 700°C where the ARPES data shows clear dispersive bands with valence band maximum located around 3.3 eV below Fermi level. While the \[ \sqrt{2} \times \sqrt{2} R 45^\circ \] surface reconstruction is stable under further UHV annealing, it is reversed to 1×1 surface by annealing the sample in 400 mTorr oxygen at 600°C. Another UHV annealing at 600°C followed by LEED and ARPES measurements, suggests that LEED \[ \sqrt{2} \times \sqrt{2} R 45^\circ \] surface reconstruction and ARPES dispersive bands are reproduced. Our results provide a better picture of electronic structure of BaSnO\(_3\) surface and are suggestive of role of oxygen vacancies in the reversible \[ \sqrt{2} \times \sqrt{2} R 45^\circ \] surface reconstruction.

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I. INTRODUCTION

Barium stannate (BaSnO\(_3\)) has recently been widely studied for its interesting physical and optical properties. As a wide bandgap perovskite oxide, it has simultaneously shown high room-temperature mobility and optical transparency, making it interesting for applications ranging from optoelectronics and solar energy to functional devices\(^1,2\). Its high room temperature mobility suggests for power electronics applications due to its low power consumption\(^3\). The pioneering work of Kim et al\(^4\) in discovering high room temperature mobility of 300 cm\(^2\)V\(^{-1}\)s\(^{-1}\) in La-doped BaSnO\(_3\) (BSO) suggested that it can be a possible transparent conducting oxide (TCO) and ignited even more studies. Being a TCO combining high conductivity with low carrier concentration and optical absorption operating at room temperature with excellent thermal stability, BaSnO\(_3\) (BSO) paves the way for future electronic devices\(^5,6\).

The importance of BSO as an electronic material naturally calls for a need to study its physical properties. Among the physical properties, electronic structure is the most essential one that determines the electronic and optical properties. For that reason, the electronic structure has been investigated by using first principles and tight-binding calculations\(^24,29\text{--}31,34\text{--}40\). As for the experimental determination of the band structure, it has been limited to couple of angle-resolved photoemission spectroscopy (ARPES) studies on BSO\(^7\) and BLSO films\(^8\) which suggest for an indirect band gap\(^7\) and an upward band bending at the vacuum interface\(^3\). However, the study on BSO was performed on a 8 nm thick film on SrTiO\(_3\) (STO) substrate without a buffer layer and possible existence of defects originating from lattice mismatch between BSO film and STO substrate makes it unclear if the results represents the intrinsic property of BSO. On the other hand, exploiting its potential for nanoscale electronic devices requires deeper knowledge of surface structure as can be seen from the numerous surface structure studies of STO. The effect of oxygen vacancy (OV) on surface structure and surface dependent electronic structure is another important aspects of BSO as an electronic material candidate that require study. All these suggest for more surface studies on fully relaxed films by surface-sensitive techniques such as LEED and ARPES.

To have a better picture of surface atomic and electronic structures of BSO film, and to understand how those will react to different annealing conditions, we perform LEED and ARPES experiments on the surface of relaxed BSO thin-films. We combine LEED and ARPES measurements to study the effect of UHV and oxygen annealing on the surface and electronic structures and thermal stability of the film. The results show clear band dispersions which are consistent with those of a first principles calculation\(^39\). Our results not only provide a better understanding of the electronic structure of BSO thin-film but also reveal OV-induced reversible surface reconstruction after in-situ UHV annealing. In addition, energy-momentum dispersion from ARPES measurement suggests that the valence band maximum (VBM) is located at 3.3 eV below Fermi level.

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FIG. 1. (a) Perovskite cubic crystal structure of BaSnO$_3$ at room temperature. (b) Schematic of BaSnO$_3$/Ba$_{0.96}$La$_{0.04}$SnO$_3$/SrTiO$_3$ (10nm/100nm/0.5mm) thin-film grown by PLD method (Figure is not drawn to scale). (c) Reciprocal space mapping data of (103) peaks. (d) X-ray diffraction $2\theta$ scan shows corresponding peaks for BSO thin-film (red triangles) and STO substrate (green squares). The inset shows $\omega$-rocking curve data for the film and the substrate. Full width at half maximum (FWHM) for the film (red) is 0.06 and for the STO substrate (green) is 0.035. Figure 1(e) is an enlargement of the XRD data in the $2\theta$ range of 42 – 45.5°. The peak from the thin film (red triangle) shows clear fringe pattern which is a characteristic of thin-film XRD pattern. From angular distance between fitted fringe peaks in Fig. 1(e), we estimate the thicknesses of BSO top layers $(d_{BSO})$ and BLSO buffer layers $(d_{BLSO})$ to be 11.1 and 98 nm, respectively.

II. METHODS

II.1. Sample growth

Thin-films of BaSnO$_3$ (BSO) were epitaxially grown using pulsed laser deposition (PLD) method from a polycrystalline target with cubic perovskite crystal structure (Fig. 1(a)) on top of a SrTiO$_3$ (STO) (001) surface at 750°C. The base pressure in the PLD chamber was $1.4 \times 10^{-7}$ Torr. The partial oxygen pressure in the PLD chamber during growth was $1 \times 10^{-3}$ Torr. KrF excimer laser (248 nm) with energy density of 1.43 J/cm$^2$ and intensity of 42.2 mJ was used. To grow BSO thin-film, first a 100 nm buffer layer of Ba$_{0.96}$La$_{0.04}$SnO$_3$ (BLSO) was grown on the STO substrate to compensate the lattice mismatch between STO substrate and BSO top layer. Then top-most BSO film was grown with a thickness of 10 nm (Fig. 1(b)).

II.2. X-ray diffraction

To check the epitaxial growth of thin-film we did X-ray diffraction (XRD), reciprocal space mapping (RSM) and rocking curve measurements (Fig. 1(c)-(d)). The X-ray measurement was performed using a D8 Discover high-resolution x-ray diffraction (Bruker) machine at Institute for Basic Science, center for correlated electron systems (IBS-CCES) located at Seoul National University (SNU). Figure 1(c) is the RSM data. Figure 1(d) shows $\theta/2\theta$ wide scan. Peaks from BSO thin-film are shown with red triangles and peaks from STO substrate are shown with green squares. Our calculation shows that the experimental values for out-of-plane lattice constant of BSO thin film is 4.1338 Å. Lattice constant of STO substrate is estimated to be 3.9094 Å. The inset image shows fitted $\omega$ rocking curve data for the film and the substrate. Full width at half maximum (FWHM) for the film (red) is only 0.06 and for the STO substrate (green) is 0.035. Figure 1(e) is an enlargement of the XRD data in the $2\theta$ range of 42 – 45.5°. The peak from the thin film (red triangle) shows clear fringe pattern which is a characteristic of thin-film XRD pattern. From angular distance between fitted fringe peaks in Fig. 1(e), we estimate the thicknesses of BSO top layers $(d_{BSO})$ and BLSO buffer layers $(d_{BLSO})$ to be 11.1 and 98 nm, respectively.

II.3. Surface preparation, LEED and ARPES

BSO film samples were ex-situ transferred from the PLD chamber to the preparation chamber equipped with a SPECS ErLEED instrument. The pressure in the preparation chamber was better than $2 \times 10^{-11}$ Torr. Surface preparation was done using electron-beam (e-beam) heating. The annealing temperature was monitored using a pyrometer with the emissivity of BSO thin-film set to 0.35. We performed series of UHV and oxygen annealing on the sample and take LEED data for each annealing temperature.

For each annealing and LEED measurement, the sample was in-situ transferred to the ARPES chamber equipped with a DA30 Scienta Omicron hemispherical electron analyzer for electronic structure measurements. All data were taken at low temperature ($\sim$7-12 K) using a helium discharge lamp with photon energy of 21.2
FIG. 2. 90 eV LEED patterns of BaSnO$_3$ thin-film after annealed at (a) 400°C and 1 atm oxygen with 1×1 surface structure as shown by dashed yellow square, (b), (c), and (d) 300, 400, and 550°C in UHV condition, respectively and (e) 700°C; 1×1 surface reconstructs into a √2×√2R45° surface shown by yellow square. (f) After annealing at 600°C in 400 mTorr oxygen; √2×√2R45° disappears. (g), (h), and (i) 600, 700, and 750°C in UHV condition; √2×√2R45° reconstruction is reproduced as a result of a second UHV annealing.

III. RESULTS

III.1. Surface structure (LEED)

Figure 2(a) shows the LEED data from BSO film after ex-situ post-annealing in a tube furnace in 1 atm oxygen pressure at 400°C. A 1×1 surface structure is visible from LEED diffraction spots as demonstrated by a yellow dashed square in Fig. 2(a). Next, we post-anneal the BSO thin-film in-situ in UHV condition starting from 300°C up to 550°C as shown in Fig. 2(b)-(d). LEED pattern improves and we see sharper diffraction spots as we increase annealing temperature indicating that the surface is getting cleaner under UHV annealing. The 1×1 surface structure is clearly seen (demonstrated by yellow dashed squares). Another UHV annealing at 700°C, shows that new features appear (yellow square) indicating a surface reconstruction (Fig. 2(e)) which will be discussed in details in the Discussion section as a new √2×√2R45° surface reconstruction.

Annealing (in-situ) in 400 mTorr oxygen pressure at 600°C, it is seen that the √2×√2R45° surface reconstruction is reversed to 1×1 surface (Fig. 2(f)). Another series of UHV annealing on the sample reproduces the √2×√2R45° surface reconstruction. The results are shown in Fig. 2(g)-(i). Figure 2(g) shows that after UHV annealing at 600°C the √2×√2R45° surface reconstruction starts to appear again and at 700°C it becomes more clear (Fig. 2(h)), and is stable up to 750°C annealing as shown in Fig. 2(i).

III.2. Electronic structure (ARPES)

In order to have deeper insight into the behavior of BSO surface as far as surface reconstruction is concerned, it is important to have information on the electronic structure. Figure 3 shows our ARPES data from BSO thin-film measured at 12 K after UHV annealing at 750°C. Figures 3(a) and (b) show ARPES data along X-Γ-M and its second derivative, respectively. We can distinguish at least several dispersive bands from the data. From a linear fit of leading edge of integrated EDCs, the valence band maximum (VBM) is estimated to be at 3.3 eV below Fermi level as it is shown in Fig. 3(c). The peak locations of momentum distribution curves (MDC) extracted from ARPES data in Figure 3(a) are shown in Fig. 3(d). Figure 3(e),(f) show the probed momentum points in the BZ with 21.2 eV photons and the cubic BZ of BSO where ARPES data were taken along high symmetry cuts.

IV. DISCUSSION

In this section, we discuss our surface (LEED) and electronic (ARPES) structure data and how they reveal a new type of surface reconstruction for BSO film that
has not been reported so far. We discuss the role of oxygen vacancies in the new surface reconstruction and its impact on stability of BSO surface.

Before we discuss the surface and electronic structures presented in the previous section, we wish to touch upon the robustness of BSO film surface. As already described, PLD grown BSO thin-films were \textit{ex-situ} transferred to UHV chambers for surface studies. Our very first ARPES data of \textit{ex-situ} transferred film without any surface treatment already shows broad spectra as presented in Fig. S.1 (a) (see Supplemental Material). Subsequent UHV annealing at 300°C and 400°C \textit{in-situ} led to better defined electronic structure as shown in Fig. S.1 (b),(c). Non-dispersive bands are clearly seen in the ARPES data. We point out that observation of even non-dispersive bands are surprising for an \textit{ex-situ} transferred oxide system, implying that the surface must be quite stable. As we are more interested in dispersive bands, we did further annealing studies of the film: annealing in 1 atm O$_2$ in a tube furnace and subsequent annealing in UHV chamber. ARPES measurements show clear valence bands as will be discussed below. Therefore, a key observation here is that BSO has rather a stable surface in comparison with other oxides, considering we are able to distinguish individual bands repeatedly for various annealing conditions.

Figure 2 (a)-(d) show surface structure results after 1 atm O$_2$ annealing and UHV annealing at 300°C, 400°C, and 550°C, respectively. Data show a 1×1 surface (yellow square) suggesting that 1×1 surface of BSO is stable under UHV annealing up to 550°C. The ARPES data taken after each annealing (Fig. S.1 (d)-(h)) shows gradual change towards dispersive bands.

The most interesting observation starts to appear when we increase the UHV annealing temperature to 700°C. The LEED data suggest that the previous 1×1 surface is now reconstructed into a $\sqrt{2} \times \sqrt{2} \times 4$ surface. The relevant reconstructed surface unit cell is shown in Fig. 2(e) by the solid yellow square compared to the underlying 1×1 unreconstructed lattice unit cell (shown by dashed yellow square). This is the first evidence for such a surface reconstruction on BSO surface. As for the electronic structure, ARPES data taken right after LEED show that non- or weakly-dispersive energy bands from 1×1 are now changed into dispersive bands for $\sqrt{2} \times \sqrt{2} \times 45^\circ$ surface (Fig 3 (a), and Fig. S.1 (i)).

A natural question to ask is what is the origin of the new surface reconstruction is. To answer this question, we should notice that it appeared as a result of consecutive UHV annealing and exposure to incident light from photon source. This observation suggests that oxygen vacancies can be the culprit for the surface reconstruction. To test this claim, sample was transferred to a chamber and heated in 400 mTorr O$_2$ at 600°C for 1 hour. Then, it was cooled down to room temperature and then \textit{in-situ} transferred to the UHV chamber where LEED experiment was performed. The result is presented in Fig. 2(f), showing the $\sqrt{2} \times \sqrt{2} \times 45^\circ$ being reversed to a 1×1 surface after oxygen annealing. This suggests oxygen vacancies induced by UHV annealing as the driving force for $\sqrt{2} \times \sqrt{2} \times 45^\circ$ surface reconstruction in the surface of BSO thin-film. As for the electronic structure,
ARPES data show that the dispersive bands become non-dispersive again (Fig. S1 (j)). To support the role of oxygen vacancies in $\sqrt{2} \times \sqrt{2}R45^\circ$ surface reconstruction even further, we performed another round of UHV annealing (to induce oxygen vacancies again), LEED and ARPES measurements starting from 600°C. The idea is to see the effect of UHV annealing and consequent oxygen vacancies on the surface, and also to see if the newly discovered surface reconstruction is reproduced by UHV annealing (after it had been oxygen annealed) or not. The result is presented in Fig. 2(g) which shows that the $\sqrt{2} \times \sqrt{2}R45^\circ$ surface reappears. Increasing the annealing temperature to 700°C and 750°C leads to even more clear $\sqrt{2} \times \sqrt{2}R45^\circ$ spots. As for the relevant ARPES data, the dispersive bands reappear too (Fig. S1 (k)). The emergence of new $\sqrt{2} \times \sqrt{2}R45^\circ$ surface reconstruction on BSO after UHV annealing, its reversal to 1×1 after O₂ annealing, and its recovery after another UHV annealing provide conclusive evidences for oxygen vacancy driven $\sqrt{2} \times \sqrt{2}R45^\circ$ surface reconstruction in BSO thin-film.

Another aspect of our study is the relation between surface structure and the electronic structure in light of newly discovered $\sqrt{2} \times \sqrt{2}R45^\circ$ surface reconstruction. Surface structure dependent electronic structure is an important aspect of other oxide surfaces such as STO. In order to discuss this issue, we look at the energy-momentum dispersion maps in Fig. 3 more closely. First, we note that, in contrast to previous ARPES results which reported additional in-gap states due to intrinsic defects or oxygen vacancies, no spectral weight in ARPES near Fermi level are observed (the inset in Fig. 3 (c)) as expected from relaxed and defect-free surface of our BSO film grown on a BLSO buffer layer. Our observation that, in contrast to previous ARPES results that reported additional in-gap states due to intrinsic defects or oxygen vacancies, no spectral weight in ARPES near Fermi level are observed (the inset in Fig. 3 (c)) as expected from relaxed and defect-free surface of our BSO film grown on a BLSO buffer layer. Our observation that increased annealing temperature to 700°C and 750°C leads to even more clear $\sqrt{2} \times \sqrt{2}R45^\circ$ spots. As for the relevant ARPES data, the dispersive bands reappear too (Fig. S1 (k)). The emergence of new $\sqrt{2} \times \sqrt{2}R45^\circ$ surface reconstruction on BSO after UHV annealing, its reversal to 1×1 after O₂ annealing, and its recovery after another UHV annealing provide conclusive evidences for oxygen vacancy driven $\sqrt{2} \times \sqrt{2}R45^\circ$ surface reconstruction in BSO thin-film.

In summary, we performed LEED and ARPES experiments on PLD grown thin-films of BaSnO₃ to probe surface and electronic structures. Our data show that UHV annealing up to 550°C gives 1×1 LEED pattern with non-dispersive bands from ARPES data which suggest that BSO surface is stable at this temperature. Annealing at 700°C leads to a new $\sqrt{2} \times \sqrt{2}R45^\circ$ surface reconstruction with dispersive bands from ARPES measurements and valence band edge located at 3.3 eV below the Fermi level. The $\sqrt{2} \times \sqrt{2}R45^\circ$ reconstruction is reversed to 1×1 by annealing at 600°C and 400 mTorr oxygen. This is suggestive of the role of oxygen vacancies in the development of new surface reconstruction. A second UHV annealing starting from 600°C shows that the $\sqrt{2} \times \sqrt{2}R45^\circ$ appears again and remains the same for the annealing temperature range of 600-750°C. Finally, we have summarized all our findings in Table. I

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| T (°C) | t (h) | P               | RC | ARPES |
|-------|------|-----------------|----|-------|
| Pre-annealing | — | UHV             | (1×1) | x     |
| ↓ 300 | 1   | UHV             | (1×1) | x     |
| ↓ 400 | 1   | UHV             | (1×1) | x     |
| → 400 | 1   | 1 atm O₂        | (1×1) | x     |
| ↓ 300 | 1   | UHV             | (1×1) | x     |
| ↓ 400 | 1   | UHV             | (1×1) | x     |
| ↓ 500 | 1   | UHV             | (1×1) | x     |
| ↓ 700 | 1   | UHV $\sqrt{2} \times \sqrt{2}R45^\circ$ | √ |    |
| → 600 | 1   | 400 mTorr O₂    | (1×1) | x     |
| ↓ 600 | 1   | UHV $\sqrt{2} \times \sqrt{2}R45^\circ$ | √ |    |
| ↓ 700 | 1   | UHV $\sqrt{2} \times \sqrt{2}R45^\circ$ | √ |    |
| ↓ 750 | 1   | UHV $\sqrt{2} \times \sqrt{2}R45^\circ$ | √ |    |
Fig. S 1. BSO film is grown in PLD chamber. Then, it is \textit{ex-situ} transferred to a UHV chamber for surface studies (LEED and ARPES); (a), (b), (c) ARPES data before annealing, after UHV annealing at 300°C, and 400°C. Afterwards, sample is \textit{ex-situ} transferred to a tube furnace to be annealed at 400°C and 1 atm flowing oxygen. (d) ARPES data taken after sample is \textit{ex-situ} transferred back from tube furnace to the ARPES chamber. (e)-(i) sample annealed in UHV condition starting from 300°C up to 700°C. ARPES data is taken in low temperature after each annealing step. Then, sample is \textit{ex-situ} transferred to PLD chamber to be annealed at 600°C and 400 mTorr O₂. (j) ARPES data taken after sample was \textit{in-situ} transferred back from PLD chamber to the ARPES chamber. (k) ARPES after annealing at 700°C in UHV. All ARPES data were taken with 21.2 eV photons at low temperature (7-12K).