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Strong conductivity enhancement of La-doped BaSnO₃ transparent films on Al₂O₃ with the assistance of templated epitaxy for electromagnetic shielding in extreme environments

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Abstract

Transparent La-doped BaSnO₃ (BLSO) epitaxial films grown on expensive perovskites show promising conductive properties. However, BLSO films on Al_2O_3 have a higher sheet resistance by two orders of magnitude. In this research, the sheet resistance of BLSO films is recovered to that of the single-crystalline level by growing (111)-oriented BLSO epitaxial films on (0001) Al_2O_3 with the assistance of (111)BaZrO₃/MgO template bilayer. Their intriguing transparent conductive properties, including high electromagnetic shielding effectiveness (~ 13.2 dB at 10 GHz) and high stability at 700 °C, will promote stable optoelectronic applications in extreme environments with economic benefits.

Keywords Transparent conductors, La-doped BaSnO₃, Templated epitaxy, Al₂O₃, Single-crystalline films

Graphical Abstract



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1 Introduction

Transparent conductors (TCs) are key components of modern optoelectronics [1-7]. The discovery of Ladoped BaSnO₃ (BLSO) has rejuvenated interest in TCs [8-11]. BaSnO₃ is a wide-bandgap oxide, whose bandgap of 3.3-4.1 eV is determined by charge transfer from the valence band of the O 2p orbitals to the conduction band of the Sn 5s orbital [8, 9]. Aliovalent cation (e.g., La^{3+}) doping renders Ba²⁺Sn⁴⁺O₃ conductive, analogous to the prototypical wide-bandgap TC Sn^{4+} -doped $In_2^{3+}O_3$. The straight O-Sn-O connectivity and large Sn 5s orbital in the cubic perovskite structure provide a dispersive conduction band with a small effective mass, resulting in a high electron mobility of ~ $250 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in single crystals [8, 9] and ~100 cm² V⁻¹ s⁻¹ in films [9, 10] at room temperature. The thermal stability of BLSO might enable optoelectronic applications in extreme environments [12]. Methylammonium lead iodide-based solar cells fabricated with colloidally prepared BLSO electrodes have achieved a high power conversion efficiency of 21.2% [13]. Irrespective of such merits, BLSO has rarely been examined for the simultaneous attainment of low sheet resistance, high transmittance in the visible region, high electromagnetic shielding effectiveness, and high stability, which have been critical bottlenecks in optoelectronic technology.

The resistivity of BLSO is highly affected by crystallinity, where BLSO single crystals have a much lower resistivity by 2-3 orders of magnitude than polycrystalline specimens [8, 9]. Hence, the majority of studies concerning BLSO films have reported the properties of epitaxial films grown on cubic substrates, e.g., SrTiO₃, KTaO₃, and MgO [14–18]. The similar cubic structure between the BLSO film and substrates enables cube-on-cube epitaxial due to a moderate lattice mismatch growth $(=\frac{a_{\text{substrate}}-a_{\text{film}}}{1.94\%} \times 100)$ between -5.22 and 1.94% along the [100]BLSO || [100] substrate, where $a_{\text{substrate}}$ denotes the lattice parameters of SrTiO₃ (a=b=c=3.905 Å), KTaO₃ (3.99 Å), and MgO (4.20 Å) substrates and a_{film} represents the lattice parameter of BaSnO₃ (4.12 Å) films (see Table 1 for a summary of the crystal structures and lattice parameters of the materials used in this work). However, SrTiO₃ and KTaO₃ are quite expensive, and hygroscopic MgO tends to absorb water molecules from the environment [19]. On the other hand, Al_2O_3 $(a = b = 4.76 \text{ Å}, c = 12.99 \text{ Å}, \gamma = 120^{\circ})$ is low cost, available in large wafer form, chemically, thermally, and mechanically stable, and highly transparent over a wide spectrum. Consequently, it is used as a conventional substrate for optoelectronics. Therefore, it is highly desirable to characterize the electrical and optical properties of BLSO films grown on Al₂O₃.

	Materials	Crystal structures (space group)	Lattice parameters	Epitaxial relationships among BLSO film, template layers, and (0001)Al ₂ O ₃ in-plane lattice mismatches (%)
Film	La-doped BaSnO ₃ (BLSO)	Cubic perovskite ($Pm\overline{3}m$)	a = 4.12 Å for BaSnO ₃	-
Substrate	Al ₂ O ₃	Hexagonal (R3̄c)	a = b = 4.76 Å, c = 12.99 Å $\gamma = 120^{\circ}$	_
Template layer	BaZrO ₃ /MgO	Cubic perovskite ($Pm\overline{3}m$) Cubic halite ($Fm\overline{3}m$)	a=4.19 Å a=4.20 Å	(111)BLSO (111)BaZrO ₃ (111)MgO (001) Al ₂ O ₃ [110]MgO [100]Al ₂ O ₃ , lattice mismatch —19.9% (0.2% for 4:5 MgO:Al ₂ O ₃)
				[110] BaZrO ₃ [[110] MgO, 0.2% [110] BLSO [110] BaZrO ₃ , 1.7%
Template layer	MgO	Cubic halite ($Fm\overline{3}m$)	a=4.20 Å	(111)BLSO (111)MgO (001)Al ₂ O ₃ [110] MgO [100]Al ₂ O ₃ , lattice mismatch —19.9% (0.2% for 4:5 MgO:Al ₂ O ₃)
				[110] BLSO [110] MgO, 1.9%
Template layer	Y-stabilized ZrO ₂ (YSZ)	Cubic fluorite ($Fm\overline{3}m$)	a=5.13 Å	$\begin{array}{l} (011) \text{BLSO} \parallel (111) \text{YSZ} \parallel (001) \text{Al}_2 \text{O}_3 \\ [1\overline{10}] \text{YSZ} \parallel [100] \text{Al}_2 \text{O}_3, \text{lattice mismatch} - 34.4\% \\ (-1.6\% \text{ for } 2:3 \text{ YSZ:Al}_2 \text{O}_3) \end{array}$
				[100]BLSO [110] YSZ, -11.9%
Template layer	Gd-doped CeO ₂ (GDC)	Cubic fluorite ($Fm\overline{3}m$)	a=5.41 Å	(011)BLSO (111)GDC (001)Al ₂ O ₃ [112]GDC [100]Al ₂ O ₃ , 7.7% [011]BLSO [112]GDC, -19.5%

Table 1 Materials, crystal structures, lattice parameters, and epitaxial relationships among the La-doped BaSnO₃ (BLSO) film, template layers, and (0001)-oriented Al₂O₃ substrate, and in-plane lattice mismatches

Here, we found that the sheet resistance of BLSO films grown on Al₂O₂ was much higher by two orders of magnitude than that of single-crystalline films grown on perovskites. These poor properties might be attributed to the hexagonal structure of Al₂O₃ substrates hindering the single-crystalline growth of cubic perovskite BLSO epitaxial films. However, the sheet resistance was recovered to the single-crystalline level by epitaxially growing (111)-oriented BLSO films on (0001)Al₂O₃ with (111) BaZrO₃/MgO template bilayer. Using our BLSO epitaxial films, we could measure the ultraviolet transmittance, electromagnetic shielding effectiveness, and thermal stability, which have rarely been investigated. To understand the origin of the enhanced crystallinity, we carried out X-ray diffraction (XRD) and transmission electron microscopy (TEM). Hereafter, we sometimes use the simpler form BLSO $_{substrate}^{template layers}$, e.g., BLSO $_{(0001)Al_2O_3}^{BaZrO_3/MgO}$, for the BLSO films on (0001)Al₂O₃ with BaZrO₃/MgO template bilayer.

2 Result and discussion

2.1 Epitaxial stabilization of La-doped BaSnO₃ (BLSO) films on (0001)-oriented Al₂O₃ with BaZrO₃/MgO template bilaver

The direct growth of BLSO films on Al_2O_3 resulted in poor crystallinity. The XRD θ - 2θ scans revealed a mixture of (110), (200), (220), and (222) diffraction peaks for BLSO films grown on (0001)-oriented Al_2O_3 (Fig. 1a). Scans of the BLSO films on (1102)-, (1120)-, and (1010) -oriented Al_2O_3 showed weak diffraction peaks corresponding to mixed crystallographic orientations (Additional file 1: Fig. S1). This growth of non-epitaxial films was mainly the result of an incommensurate interface between cubic perovskite BLSO and hexagonal Al_2O_3 . In addition, the difference between the thermal expansions of BLSO and Al_2O_3 could contribute to non-epitaxial growth, as observed between perovskite oxides and Al_2O_3 . [20, 21]



Fig. 1 Epitaxial stabilization of BLSO films on (0001)Al₂O₃ with BaZrO₃/MgO template bilayer. For convenience, the simpler form of BLSO $_{substrate}^{template layers}$ is used. **a** The (110), (200), (220), and (222) diffraction peaks in the X-ray diffraction (XRD) θ -2 θ scan of BLSO $_{(0001)Al_2O_3}^{template layers}$ indicate the formation of mixed-crystalline phases. The asterisks indicate the (003) and (006) diffraction peaks of Al₂O₃. **b** The XRD θ -2 θ scan of BLSO $_{(0001)Al_2O_3}^{teacr_03/MgO}$ shows the (111) and (222) diffraction peaks of BaZrO₃/MgO and BLSO, indicating the formation of (111)-oriented BLSO epitaxial films on (0001)Al₂O₃ with (111) BaZrO₃/MgO template bilayer. **c** The XRD ϕ scans of (110)BLSO, (110)BaZrO₃, and (220)MgO show six diffraction peaks separated by 30° from (012) Al₂O₃, corresponding to three-fold symmetric in-plane matching, as schematically shown in **d**. **e** The full-width at half-maximum in the XRD ω -scans decrease from 1.07° in BLSO $_{(0001)Al_2O_3}^{MgO}$ to 0.39° in BLSO $_{(0001)Al_2O_3}^{BaZrO_3/MgO}$, indicating an improved crystallinity of the BLSO epitaxial films with the use of the BaZrO₃ template layer

Epitaxy with the assistance of template layers, so-called templated epitaxy, is a simple way to grow single-crystalline films when the film and substrate have an incommensurate interface. For example, a Y-stabilized ZrO_2 (YSZ) template layer has been used to integrate epitaxial films (e.g., ferroelectric ${\rm Bi}_{3.25}{\rm La}_{0.75}{\rm Ti}_3{\rm O}_{12}$ and Y-doped HfO_2) on silicon [22, 23]. $TiO_2(B)$ epitaxial films were successfully grown on (001)-oriented SrTiO₂ using the $VO_2(B)$ template layer, while anatase TiO₂ epitaxial films were formed without the template layer [24]. Figure 1b shows an XRD θ -2 θ scan of BLSO films on (0001)Al₂O₃ with BaZrO₃/MgO template bilayer. Different from the direct growth of BLSO films on (0001)Al₂O₃ (Fig. 1a), four strong peaks were observed at 37.2°, 37.8°, 79.1°, and 80.8°, which were due to diffraction from the (111) and (222) planes of BaZrO₃/MgO and BLSO, respectively. (111)BLSO epitaxial films were successfully deposited on (0001)Al₂O₃ with the help of (111)BaZrO₃/MgO epitaxial template bilayer.

XRD ϕ scans were carried out to establish the role of an MgO layer in the epitaxial transformation of BLSO films on (0001)Al₂O₃. These scans provided information on inplane matching between (111)MgO and (0001)Al₂O₃. As shown at the bottom of Fig. 1c, hexagonal Al_2O_3 showed three diffraction peaks corresponding to the (012) plane with a uniform ϕ interval of 120°. The ϕ scan of (220) MgO exhibited six strong diffraction peaks separated by 30° from those of (012)Al₂O₃. This observation indicates the in-plane matching of [110] MgO || [100]Al₂O₃, as schematically shown in Fig. 1d. Considering the lattice parameters of MgO and Al₂O₃, the lattice mismatch along $[1\overline{1}0]$ MgO || [100] Al₂O₃ was -19.9%, and an alternative alignment of a 4:5 lattice ratio of MgO:Al₂O₃ significantly reduced the mismatch to 0.2% [25], which behaviour has been widely observed elsewhere [26]. The six strong diffraction peaks observed in the ϕ scans of (110)BLSO and (110)BaZrO₃ at the same ϕ angles of (220)MgO indicated that the BLSO film and cubic BaZrO₃ (lattice parameters of 4.19 Å) template layer were cube-on-cube aligned on the MgO template layer due to similar lattice parameters. Figure 1e shows the XRD ω scans of (222)BLSO with and without the BaZrO₃ template layer. By inserting a BaZrO₃ layer between the BLSO film and MgO layer, the full-width at half-maximum (FWHM) of peaks in the ω scans decreased from 1.07° to 0.39° since the surfaces of BLSO and BaZrO₃ have a similar atomic arrangement, and the lattice mismatch decreased from 1.9% for BLSO/MgO to 1.7% for BLSO/BaZrO₃. Therefore, while the MgO template layer played a key role in the epitaxial growth of BLSO films on (0001)Al₂O₃, the BaZrO₃ template layer further enhanced the crystallinity of the BLSO films. Table 1 summarizes the epitaxial relationships

among the BLSO film, template layers, and (0001) Al $_2$ O $_3$ substrate and the in-plane lattice mismatches.

For additional insight into high-quality BLSO epitaxial films, cross-sectional images of ${}_{BLSO_{(0001)Al_2O_3}}^{BaZrO_3/MgO}$ were acquired by TEM (Fig. 2a). The BLSO film, BaZrO₃ layer, MgO layer, and Al₂O₃ substrate are distinguished by dark and bright regions arising from their different atomic numbers. The surface of (111)-oriented BLSO films exhibited triangular characteristics with {100} facets since most perovskite phases have the lowest energy surfaces among the {001} surfaces [27]. However, the surface atomic force microscopy image of the 350-nm-thick BLSO films revealed flatness over a $1 \times 1 \text{-}\mu\text{m}^2$ area with a low roughness of 2.3 ± 0.5 nm (Additional file 1: Fig. S2). Fast Fourier transformation of high-resolution TEM images also indicated the (111)-oriented epitaxial growth of the BLSO film and BaZrO₃ template layer (Fig. 2b). Energy-dispersive X-ray spectroscopy indicated uniform distributions of Sn (blue), Zr (red), Mg (green), and Al (yellow) atoms over the entire area, indicating minimal atomic intermixing among the film, template layers, and substrate.

2.2 Sheet resistance decreased by ~ 50 times in BLSO epitaxial films on (0001)Al₂O₃

Figure 3a presents the temperature dependence of the sheet resistances of ${\rm BLSO}_{(0001)Al_2O_3}^{BaZrO_3/MgO}$ and $BLSO_{(0001)Al_2O_3}.$ These data were compared with the sheet resistances of single-crystalline BLSO epitaxial films grown on cubic KTaO₃, SrTiO₃, and MgO substrates to emphasize the affirmative effect of templated epitaxy (see Additional file 1: Fig. S3–S5a for the corresponding XRD θ –2 θ scans, ω scans, and resistivities). First, it should be noted that BLSO_{(0001)Al₂O₃} exhibited a much higher sheet resistance of 19,000 Ω \Box ⁻¹ at room temperature when compared with 210–290 Ω \Box^{-1} for BLSO_{(001)KTaO3}, BLSO_{(001)SrTiO3}, and BLSO_{(001)MgO}. The sheet resistance of insulating BLSO_{(0001)Al₂O₃ decreased with increasing} temperature; this is clearly indicated by the normalized resistivity $\rho/\rho_{400\,\mathrm{K}}$ ($\rho_{400\,\,\mathrm{K}}$: resistivity at 400 K) shown in the inset. The high sheet resistance of BLSO_{(0001)Al₂O₃ is} equivalent to a resistivity of ~1 Ω cm, which is similar to the 1–10 Ω cm resistivity of polycrystals [8].

The BaZrO₃/MgO template bilayer significantly recovered the conductive properties of BLSO epitaxial films on (0001)Al₂O₃ to the single-crystalline level. The sheet resistance of $\text{BLSO}_{(0001)Al_2O_3}^{\text{BaZrO}_3/\text{MgO}}$ was 370 Ω^{-1} at room temperature, which was significantly lower by ~50 times than that of BLSO_{(0001)Al_2O_3} and comparable to those of single-crystalline BLSO_{(001)KTaO_3}, BLSO_{(001)SrTiO_3}, and BLSO_{(001)MgO}. Figure 3a and the corresponding inset show that the sheet resistance and normalized resistivity



Fig. 2 Nanoscopic investigation of the crystal structure of $BLSO_{(0001)Al_2O_3}^{BaZrO_3/MgO}$. **a** The cross-sectional image obtained by transmission electron microscopy clearly shows the BLSO film, BaZrO_3/MgO template bilayer, and Al_2O_3 substrate. **b** The fast Fourier transformation images at selected areas indicate the (111)-oriented epitaxial growth of the BLSO film and BaZrO_3 template layer. **c** Energy-dispersive X-ray spectroscopy shows the negligible intermixing of Sn (blue colour), Zr (red), Mg (green), and Al (yellow) atoms between the layers

of BLSO $_{(0001)Al_2O_3}^{BaZrO_3/MgO}$ increased with increasing temperature, indicating metallic behaviour near room temperature. Insulating behaviour below 150 K was also observed for BLSO epitaxial films grown on cubic substrates. Hall measurements (Additional file 1: Fig. S5b) established that the carrier density and mobility of BLSO $_{(0001)Al_2O_3}^{BaZrO_3/MgO}$ were 8.7×10^{20} cm⁻³ and 0.14 cm² V⁻¹ s⁻¹, respectively, compared with 2.8–4.1 × 10²⁰ cm⁻³ and 1.5–3.3 cm² V⁻¹ s⁻¹ for single-crystalline BLSO_{(001)KTaO_3}, BLSO_{(001)SrTiO_3}, and BLSO_{(001)MgO} (Additional file 1: Table S1).

The enhanced conductivity of BLSO epitaxial films on Al_2O_3 with the assistance of $BaZrO_3/MgO$ template bilayer motivated us to explore other template layers for growing conductive BLSO epitaxial films on Al_2O_3 . The template layer should satisfy two important requirements, i.e., epitaxy and a flat surface, to ensure the growth of epitaxial BLSO films. (111)-Oriented YSZ, Gd-doped CeO₂ (GDC), and MgO (without BaZrO₃ layer) epitaxial films were grown on (0001) Al_2O_3 (Additional file 1: Fig. S6a-c) [20, 25, 28–32]. The MgO, YSZ, and GDC epitaxial films had very flat surfaces with a low roughness of 1.4–1.7 nm, as indicated by the clear X-ray reflectivity fringe patterns (Additional file 1: Fig. S7). While (111)-oriented BLSO films were epitaxially grown on a (111)MgO template layer (Additional file 1: Fig. S8a), (011)-oriented BLSO epitaxial films were grown on (111) YSZ (Additional file 1: Fig. S9a) and (111)GDC template layers (Additional file 1: Fig. S10a). Using XRD θ -2 θ scans and ϕ scans, epitaxial relationships were established for (111)BLSO || (111)MgO || (001)Al₂O₃ and [110] BLSO || [110] MgO || [100]Al₂O₃ for BLSO^{MgO}_{(0001)Al₂O₂} (Additional file 1: Fig. S8b), (011)BLSO || (111)YSZ || (001)Al₂O₃ and [100] BLSO || [110] YSZ || [100]Al₂O₃ for BLSO^{YSZ}_{(0001)Al₂O₃} (Additional file 1: Fig. S9b), and (011)BLSO || (111)GDC || (001)Al₂O₃ and [011] BLSO || [112] GDC || [100]Al_2O_3 for ${}_{\text{BLSO}^{\text{GDC}}_{(0001)\text{Al}_2O_3}}$ (Additional file 1: Fig. S10b). Table 1 also includes details of the crystal structures of the MgO, YSZ, and GDC template layers, lattice parameters, epitaxial relationships among the BLSO film, template layer, and (0001)Al₂O₃ substrate, and in-plane lattice mismatch.

Among the template layers used in this work, the $BaZrO_3/MgO$ template bilayer provided the most conductive BLSO epitaxial films. Figure 3b shows that the



Fig. 3 Single-crystalline-level conductive property of BLSO^{BaZrO3/MgO}_{(0001)Al₂O₃} **a** The sheet resistance of BLSO^{BaZrO3/MgO}_{(0001)Al₂O₃} is ~ 50 times lower than that of BLSO_{(0001)Al₂O₃} and is comparable to those of single-crystalline BLSO epitaxial films grown on KTaO₃, SrTiO₃, and MgO. The inset shows that the resistivities ρ , normalized by the 400 K resistivity $\rho_{400 \text{ K}}$, of BLSO^{BaZrO3/MgO}_{(0001)Al₂O₃}, BLSO_{(001)KTaO3}, BLSO_{(001)KTaO3}, BLSO_{(001)KTaO3}, and BLSO_{(001)MgO} increase above 150 K, indicating metallicity near room temperature. **b** The sheet resistances of BLSO^{BaZrO3/MgO}_{(0001)Al₂O₃} and BLSO^{MgO}_{(0001)Al₂O₃} decrease with increasing template layer thickness and are saturated above 10–20-nm-thick template layers. The dashed line indicates the sheet resistance of BLSO^{BaZrO3/MgO}_{(0001)Al₂O₃} with a thicker BaZrO₃ template layer is attributed to enhanced crystallinity, as evidenced by a smaller full-width at half-maximum. **d** Compared with BLSO_{(0001)Al₂O₃}, there are fewer scattering centres for free electrons in BLSO^{BaZrO3/MgO}_{(0001)Al₂O₃}

sheet resistance of ${}^{BLSO}{}^{BaZrO_3/MgO}_{(0001)Al_2O_3}$ reached 370 Ω \Box^{-1} at room temperature, while ${}^{BLSO}{}^{MgO}_{(0001)Al_2O_3}$, $BLSO^{GDC}_{(0001)Al_2O_3}$, and $BLSO^{YSZ}_{(0001)Al_2O_3}$ had minimum sheet resistances of 1300, 5600, and 24,000 Ω \Box^{-1} , respectively. The lowest sheet resistance of $BLSO^{BaZrO_3/MgO}_{(0001)Al_2O_3}$ was consistent with the smallest FWHM of 0.39°, which is comparable

to 1.09° for $BLSO_{(0001)Al_2O_3}^{MgO}$ (Additional file 1: Fig. S8c), 1.04° for $BLSO_{(0001)Al_2O_3}^{YSZ}$ (Additional file 1: Fig. S9c), and 3.12° for $BLSO_{(0001)Al_2O_3}^{GDC}$ (Additional file 1: Fig. S10c). The other notable feature of Fig. 3b is that the sheet resistance of the BLSO films decreased with increasing template layer thickness (see Additional file 1: Fig. S11 for raw data.). The sheet resistances of the BLSO films on the MgO and BaZrO₃/MgO (10 nm) template layers were saturated when the MgO or BaZrO₃ layers were thicker than 10–20 nm. Figure 3c shows that the resistivity and FWHM for (222)BLSO of BLSO_{(0001)Al₂O₃ tended to decrease with increasing BaZrO₃ template layer thickness. This indicates that the crystallinity of the BLSO epitaxial films was enhanced for thicker template layers due to relaxation of substrate-induced strain. Although the sheet resistances also decreased with increasing YSZ and GDC template layer thickness, this was not further investigated due to the appearance of mixed phases in very thick YSZ (>100 nm) and GDC (>350 nm) films (Additional file 1: Fig. S6d and e).}

We hypothesized that the ~ 50-times-higher conductive BLSO epitaxial films on (0001)Al₂O₃ might be attributed to the enhanced crystallinity promoted by the BaZrO₃/MgO template bilayer. Figure 3d schematically illustrates the correlation between enhanced crystallinity and suppressed electron scattering. The decreased conduction of BLSO_{(0001)Al₂O₃ might be due to electron scattering at the many grain boundaries of the mixed-crystalline films, as reported for polycrystalline specimens [8, 9]. On the other hand, there were few scattering centres in epitaxial BLSO^{BaZrO₃/MgO} films, resulting in free electrons.}

2.3 High transmittance of BLSO epitaxial films on Al₂O₃

The very large bandgap (>6.2 eV) of Al₂O₃ guarantees very high transmittance (~85% at 200-6000 nm) over a wide spectral range; this is not the case for SrTiO₃ and KTaO₃, which have a small bandgap of ~ 3.2 eV ($\sim 75\%$ at 390-5000 nm). Therefore, Al₂O₃ enabled us to investigate the ultraviolet performance of BLSO, which was impossible for SrTiO₃ and KTaO₃. The solid lines in Fig. 4 show the transmittance of BLSO_{(0001)Al₂O₃, BLSO_{(001)SrTiO₃},} and BLSO(001)MgO in the wavelength range of 200–3300 nm. BLSO_{(0001)Al₂O₃} and BLSO(001)MgO showed higher transmittances of ~75% than ~65% of BLSO_{(001)SrTiO3} in the visible wavelength range of 400-1000 nm, consistent with the higher visible transmittances of Al₂O₃ and MgO compared with that of SrTiO₃ (dashed lines). The optical image on top of Fig. 4 emphasized high visible transmittance of $BLSO_{(0001)Al_2O_3}^{BaZrO_3/MgO}$. We could see the clear "DGIST" logo over the film and Al₂O₃ substrate. The oscillating transmittance was likely due to the interference between reflected light from the film and substrate [33], indicating 350-nm-thick BLSO films. The transmittance was typically suppressed at infrared wavelengths (>1000 nm) due to the free electron response. However, the fundamental absorption edges at ultraviolet wavelengths, at which transmittance dropped sharply, depended on the substrate. The BLSO(001)SrTiO3 and



Fig. 4 Transmittance of $BLSO_{(0001)Al_2O_3}^{BaZrO_3/MgO}$. The optical images on top of figure show that we can see a "DGIST" logo over film and bare Al_2O_3 substrate, indicating that the transparency of our $BLSO_{(0001)Al_2O_3}^{BaZrO_3/MgO}$ films is as high as that of the substrate. All BLSO epitaxial films show high transmittances (> 75%) in the visible region and suppressed transmittances in the infrared region. The fundamental absorption edges of $BLSO_{(0001)Al_2O_3}^{BaZrO_3/MgO}$ and $BLSO_{(001)MgO_3}$, at which the transmittance drops sharply at ultraviolet wavelengths, are located at shorter wavelengths than that of $BLSO_{(001)SrTIO_3}$. The dashed lines indicate the transmittances of Al_2O_3 , MgO, and $SrTiO_3$ substrates

SrTiO₃ substrate showed zero transmittance below nearly the same wavelength of ~390 nm, which corresponded to the ~3.2 eV bandgap of SrTiO₃. This observation indicated that the drastic reduction in the ultraviolet transmittance of BLSO_{(001)SrTiO3} was not due to the intrinsic properties of BLSO but possibly to the interband absorption between the O 2*p* and Ti 3*d* orbitals of SrTiO₃. BLSO^{BaZrO3/MgO}_{(0001)Al2O3} and BLSO_{(001)MgO} were transparent at a shorter wavelength of ~300 nm. Since the Al₂O₃ and MgO were transparent below 300 nm, they did not contribute to the absorption edge of BLSO^{BaZrO3/MgO}_{(0001)Al2O3}. Therefore, ~4.1 eV was estimated as the bandgap of the BLSO films, which is similar to that of single crystals [8].

2.4 High electromagnetic shielding effectiveness of BLSO epitaxial films deposited on (0001)Al₂O₃

The high conductivity of BLSO provided profound electromagnetic shielding capability. We measured



Fig. 5 Total electromagnetic shielding effectiveness (SE) of $BLSO_{(0001)Al_2O_3}^{BaZrO_3/MQO}$. The films have an SE of ~13.2 dB at 10 GHz. SE_A and SE_R represent the transmitted wave through the films and Al₂O₃ substrate and the reflected wave from the BLSO film, respectively. The films have an SE_A of ~12.1 dB, which is larger than the SE_R of ~1.1 dB at 10 GHz

shielding effectiveness (SE) using the coaxial transmission line method. Figure 5 shows the SE of BLSO^{BaZrO3/MgO} in the X-band frequency range, (0001)Al₂O₃ GHz, overlapped with radiowave i.e., 8.5-12.5 $(10^4 - 10^{10} \text{ Hz})$ and microwave $(10^9 - 10^{12} \text{ Hz})$ ranges. The high SE of ~13.2 dB at 10 GHz was comparable to those of metal films, metal meshes, and two-dimensional materials (see Additional file 1: Table S2 for a comparison of resistivity, SE, and infrared transmittance among potential electromagnetic shielding materials) [34-41]. The SE (= SE_A + SE_R) can be divided into SE_A and SE_R , which denote shielding by absorption through $BLSO_{(0001)Al_2O_3}^{BaZrO_3/MgO}$ and reflection from the BLSO film, respectively. The larger SE_A of ~ 12.1 dB at 10 GHz than the SE_{R} of ~1.1 dB indicated that absorption was the dominant mechanism for electromagnetic shielding. Since the SE_A was higher than 10 dB, we ignored shielding by multiple reflections [35]. Thus, $BLSO_{(0001)Al_2O_3}^{BaZrO_3/MgO}$ is promising as a TC material for stealth technology, as also evidenced by its larger absorptivity (>0.7 at 10 GHz) than reflectivity (<0.2) (Additional file 1: Fig. S12). Our BLSO films will attract attention by virtue of having a low sheet resistance, high transmittance, high shielding effectiveness, chemical and mechanical stability, and easy coating fabrication process covering a wide range of applications.



Fig. 6 Thermal stability of $BLSO_{(0001)Al_2O_3}^{BaZrO_3/MgO}$. After annealing in air, even at 700 °C (inset), the **a** XRD θ -2 θ scan and **b** sheet resistance of the as-grown films are persistent

2.5 Thermal stability in air

To test the thermal stability, we increased the temperature at a rate of 50 °C per min, annealed the films at the annealing temperature (T_a) in air for 1 h, and then decreased the temperature by 50 °C per min, as shown in the inset of Fig. 6b. The XRD θ -2 θ scans revealed that the (111) diffraction peaks of BaZrO₃/MgO and BLSO at 2θ = 37.2° and 37.8° were stable during annealing in air, even at 700 °C (Fig. 6a). The sheet resistance of BLSO^{BaZrO₃/MgO} at room temperature also persisted (Fig. 6b) (see Additional file 1: Fig. S13 for raw data of the temperature dependence of sheet resistance). Thus, we found that the BaZrO₃/MgO template bilayers did not deteriorate the thermal stability of BLSO. The thermal stability of BLSO^{BaZrO₃/MgO} is sufficient for most applications below 700 °C.

3 Conclusions

We achieved single-crystalline-level transparent conductive properties of BLSO epitaxial films on $(0001)Al_2O_2$ using BaZrO₃/MgO template bilayer. The epitaxial films had a sheet resistance ~ 50 times lower than that of BLSO films directly grown on Al₂O₃. Using Al₂O₃ substrates guaranteed high ultraviolet transmittance (>75%), which was rarely achieved in most previous studies of epitaxial BLSO films on expensive perovskites. The very conductive property guaranteed a high electromagnetic shielding effectiveness of ~13.2 dB at 10 GHz for the X-band. The phase was stable even at 700 °C in air. Due to their chemical/thermal/mechanical stability and economic benefits, the single-crystalline-level properties of BLSO films on Al₂O₃ would be suitable for applications, such as invisible circuitry, smart windows, and solar-energy harvesting, in extreme environments.

4 Experimental section

Templated epitaxy of La-doped BaSnO₃ (BLSO) epitaxial films Using pulsed laser deposition, 350-nm-thick BLSO films were deposited on (0001)-oriented Al_2O_3 with BaZrO₃/MgO template bilayer. To deposit the film and template layers, Ba_{0.8}La_{0.2}SnO₃, BaZrO₃, and MgO pellets were ablated using an excimer laser (IPEX-760; LightMachinery Inc.) with a wavelength of 248 nm, intensity of 1.5 J cm⁻², and repetition rate of 10 Hz. The substrate was heated at 750 °C using a lamp heater. For BLSO and BaZrO₃ deposition, an oxygen partial pressure of 75 mTorr was maintained by a mass flow controller. However, the diffraction peaks of MgO in the XRD θ -2 θ scan disappeared when the MgO films were deposited at 75 mTorr, so 10 mTorr was used for MgO growth. For comparison, BLSO epitaxial films were deposited on various substrates with and without different template layers. The other substrates used in this research were $(1\overline{1}02)$, $(11\overline{2}0)$, and $(10\overline{1}0)$ -oriented Al_2O_3 , (001), (011), and (111)-oriented KTaO₃, SrTiO₃, MgO, and (111)-oriented YSZ. The template layers were MgO (without a BaZrO₃ layer), YSZ, or GDC. YSZ and GDC template layers were deposited by ablating ZrO_2 -Y₂O₃ (8 mol%) and CeO_2 -Gd₂O₃ (10 mol%) pellets, respectively, under the same growth conditions for BLSO and BaZrO₃. Since the electrical properties of BLSO significantly depended on the amount of doped La [8, 9], all films were grown using the same Ba_{0.8}La_{0.2}SnO₃ pellet.

Characterization of structural properties Structural properties were investigated with a four-circle highresolution X-ray diffractometer (Empyrean; PANalytical) that used Cu radiation with a wavelength of 1.54 Å. Cross-sectional images were acquired using a transmission electron microscope (HF-3300; Hitachi) at 300 kV with a lattice resolution of at least 1 Å. Fast Fourier transformation was performed using Digital Micrograph software (Gatan Inc.). Energy-dispersive X-ray spectroscopy was used to study the microstructure and elemental distribution in the film and template layers. An atomic force microscope (XE7; Park Systems) operating in tapping mode was used to obtain surface images and roughness values; the scan area and rate were $1 \times 1 \text{ mm}^2$ and 0.5 Hz, respectively.

Measurement of transparent conductive properties To investigate the transport properties, four Pt pads were deposited on the film surfaces by direct-current magnetron sputtering. Using a physical property measurement system (Quantum Design Inc.), the resistance $(<10 M\Omega)$ was measured under an applied current upon cooling and subsequent heating over the temperature range of 10-400 K. The sheet resistance was calculated by multiplying the measured resistance by the geometric factor (2.5) of the films [42]. Hall measurements in a magnetic field ranging from -4 to 4 T at 300 K were used to determine the carrier density and mobility. To directly measure transmittance, films were grown on double-sided polished substrates. Samples were also examined in the transmission mode of an ultraviolet-visible near-infrared spectrophotometer over the wavelength range of 175-3300 nm (Cary 5000; Agilent Technologies).

Measurement of electromagnetic shielding effectiveness (SE) Using a network analyser (N5222A; Agilent Technologies), we measured SE in a two-coaxial transmission line configuration. For this measurement, we grew the films on double-sided polished (0001)Al₂O₃ substrates (area: $22.8 \times 10.1 \text{ mm}^2$; thickness: 2 mm). The sample was positioned between two waveguides to measure the S parameters (S_{11} and S_{21}) by emitting the electromagnetic wave from port 1. S_{11} was determined from the BLSO films by detecting the reflected wave at port 1. S_{21} was acquired by detecting the transmitted wave at port 2 through the films and Al_2O_3 substrate. The total SE was calculated by summing the contributions from absorption (SE_A = $10\log \frac{1-|S_{11}|^2}{|S_{21}|^2}$) and reflection (SE_R = $10\log \frac{1}{1-|S_{11}|^2}$) [35, 37]. We also calculated reflectivity $R(=|S_{11}|^2)$, transmissivity $T(=|S_{21}|^2)$, and absorptivity A(=1-R-T) [37].

Supplementary Information

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Additional file 1. Additional materials, additional figures S1–S13, additional tables S1, S2.

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Author contributions

YH conducted the experiments and wrote the manuscript under the supervision of SL. Both authors read and approved the final manuscript.

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Availability of data and materials

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

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