Superconducting Sr$_2$RuO$_4$ Thin Films without Out-of-Phase Boundaries by Higher-Order Ruddlesden–Popper Intergrowth

Jinkwon Kim, Junsk Mun, Carla M. Palomares García, Bongju Kim, Robin S. Perry, Yongcheol Jo, Hyunsik Im, Han Gyeol Lee, Eun Kyo Ko, Seo Hyoung Chang, Suk Bum Chung, Miyoun Kim, Jason W. A. Robinson, Shingo Yonezawa, Yoshiteru Maeno, Lingfei Wang, and Tae Won Noh

ABSTRACT: Ruddlesden–Popper (RP) phases ($A_{n+1}B_nO_{3n+1}$, $n = 1, 2, ...$) have attracted intensive research with diverse functionalities for device applications. However, the realization of a high-quality RP-phase film is hindered by the formation of out-of-phase boundaries (OPBs) that occur at terrace edges, originating from lattice mismatch in the $c$-axis direction with the $A'B'O_3$ ($n = \infty$) substrate. Here, using strontium ruthenate RP-phase Sr$_3$Ru$_2$O$_7$ ($n = 1$) as a model system, an experimental approach for suppressing OPBs was developed. By tuning the growth parameters, the Sr$_3$Ru$_2$O$_7$ ($n = 2$) phase was formed in a controlled manner near the film–substrate interface. This higher-order RP-phase then blocked the subsequent formation of OPBs, resulting in nearly defect-free Sr$_2$RuO$_4$ layer at the upper region of the film. Consequently, the Sr$_2$RuO$_4$ thin films exhibited superconductivity up to 1.15 K, which is the highest among Sr$_2$RuO$_4$ films grown by pulsed laser deposition. This work paves the way for synthesizing pristine RP-phase heterostructures and exploring their unique physical properties.

KEYWORDS: Ruddlesden–Popper phase, out-of-phase boundary, Sr$_2$RuO$_4$ thin films, unconventional superconductivity, pulsed laser deposition

The layered Ruddlesden–Popper (RP) phase ($A_{n+1}B_nO_{3n+1}$, $n = 1, 2, ...$) is a homologous series of perovskite structures, consisting of $n$ layers of $ABO_3$ perovskite and an $AO$ rock-salt monolayer stacked in an alternating order along the $c$-axis direction. Compared to conventional $ABO_3$ ($n = \infty$) perovskite oxides, the RP-phase offers an additional degree of freedom to tune dimensionality and thus stimulate a variety of intriguing physical phenomena and superior functionalities. Examples include the spin–orbital-coupled $J_{eff} = 1/2$ Mott state, hybrid improper ferroelectricity, anisotropic colossal magnetoresistance, and significantly suppressed dielectric loss. These emergent phenomena and functionalities are expected to provide a basis for novel oxide-based electronic and spintronic device applications.

In comparison to simple $ABO_3$ perovskites, synthesizing the pure RP-phase in single-crystal form is more challenging. RP-phases with the same elements and unequal $n$ usually have a similar thermodynamic energy landscape; during the growth of RP-phase crystals, homologous RP structures can easily lead to intergrowth. These obstacles can be overcome by epitaxially growing the RP-phase thin films on $A'B'O_3$ perovskite substrates. Structural constraints from the substrate and precisely monitored growth conditions can effectively suppress secondary phases and stacking faults, thus facilitating a single-crystalline RP structure. However, the difference in lattice structure between the RP-phase film and $ABO_3$ perovskite substrate inevitably induces another spatially extended structural defect, so-called out-of-phase boundaries (OPBs).

OPBs are translational boundaries between adjacent crystal regions that are misaligned by a fraction of a unit-cell parameter. As depicted schematically in Figure 1a, when $A'_2B'_4O_6$ ($n = 1$) thin films are grown on $A'B'O_3$ (001) substrates, the one-unit-cell-high terrace edge of the substrate causes a fractional translation of the $A'_2B'_4O_6$ lattice along the $c$-axis. This lattice translation cannot be accommodated in the $A'_2B'_4O_6$ perovskite, resulting in OPBs. Consequently, an array of dislocations nucleates at the terrace edge and propagates through the entire RP-phase film, forming the OPB. Given that a terrace structure is inevitable in atomically flat perovskite substrate surfaces due to the vicinal cut of the substrate, the

Received: December 17, 2020
Revised: April 29, 2021
formation of OPBs is widely observed in RP-phase epitaxial thin film growth.8

As an unavoidable modulation of the film structure, the OPB has a significant impact on the physical properties of RP-phase epitaxial films.12–18 The most representative example is superconductivity in Sr$_2$RuO$_4$ (SRO214) thin films. The superconducting critical temperature ($T_c$) of a bulk SRO214 single crystal is around 1.5 K.19,20 Despite the relatively low $T_c$, SRO214 has been studied intensively and might be a topological superconductor with potential application in quantum computing.21–23 Recently, the debate over the nature of the superconducting symmetry of SRO214 has intensified and new experimental approaches are required to clarify the underlying physics of this material.24–26 High-quality SRO214 thin films with robust superconductivity could lead to the development of Josephson junctions or spin-valve devices with a well-controlled geometry, which is important for detailed studies of the superconducting state.27–30 However, superconducting SRO214 thin film growth is challenging owing to the unconventional nature of the pairing symmetry and the long in-plane superconducting coherence length ($\xi_{ab}\sim\sigma_{nm}$).31,32 In particular, structural defects are considered to be detrimental to the superconductivity of SRO214.33 SRO214 thin films are usually grown on perovskite-structured NdGaO$_3$, or (LaAlO$_3$)$_{0.3}$(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT) substrates in which high-density OPBs or mosaic tilts easily form.34–36 The presence of such planar defects easily destroys the superconductivity,37 and so, achieving reproducible superconductivity in SRO214 thin films remains challenging.38–40

Here, using SRO214 thin films as a model system we designed an experimental approach to suppress OPBs in RP-phase films by pulsed laser deposition (PLD). We intentionally induced a higher-order RP-phase (e.g., the $A'B'O_3$ phase) near the interface between the $ABO_3$ films and $A'B'O_3$ substrate, as depicted schematically in Figure 1b. These higher-order RP stacking faults compensate for the unfavorable lattice translation near the terrace edge, thus suppressing the formation of OPBs. Using this method, we obtained single-crystalline and nearly defect-free SRO214 layers at the upper region of the film. Consequently, the SRO214 thin films exhibited robust superconductivity with a sharp resistive transition ($\Delta T_c\sim0.1$ K). We observed an optimized onset $T_c$ of up to 1.15 K, which is the highest value reported among homogeneous SRO214 thin films grown by PLD. Our work provides an approach to overcoming the formation of OPBs in RP-phase films, thus facilitating exploitation of the intriguing properties of the RP-phase oxides and development of RP-phase-based functional devices.

Epitaxial SRO214 thin films were grown on (001)-oriented LSAT substrates by PLD. We investigated how the substrate temperature ($T_{sub}$) affected the thermodynamic equilibrium of the strontium ruthenate RP-phase (Figure S1 in the Supporting Information), where other growth parameters (oxygen partial pressure, laser fluence, and laser repetition rate) were kept constant (see Methods in the Supporting Information). At $T_{sub} = 840$ and 860 °C, the film structure exhibited mixed SRO214 and Sr$_2$RuO$_3$ (SRO237) phases, while $T_{sub} = 880$ and 900 °C gave SRO214 single phase with epitaxial structure. On the basis of the phase modulation of strontium ruthenate films according to the change in $T_{sub}$ we employed two sets of growth parameters at different $T_{sub}$ values for deposition. For Condition A, we maintained $T_{sub} = 880$ °C over the entire deposition period (Figure 2a, left panel). For Condition B, we gradually increased $T_{sub}$ from 840 to 880 °C during deposition (Figure 2a, right panel).

Growth Conditions A and B produced distinct structural characteristics in the SRO214 thin films. Figure 2b,c shows X-ray diffraction (XRD) $\omega$-$2\theta$ scans of the two SRO214 thin films grown under Conditions A and B (denoted as Samples
Figure 3. Microscopic structure and electrical transport of Sample A1. (a) Large-scale annular bright field-scanning transmission electron microscopy (ABF-STEM) image of Sample A1. The OPBs are indicated by white arrows. (b) An enlarged high-angle annular dark-field STEM (HAADF-STEM) image near a representative OPB. The film–substrate interface is indicated by the dashed line. As indicated by the white arrow, the OPB formed near the terrace edge. The zone axes for all images are [100]. (c) In-plane strain ($\varepsilon_{xx}$) map, derived from (b) by geometrical phase analysis (GPA). The layered structure of the SRO214 thin film is disconnected at the OPB. (d) Temperature-dependent in-plane resistivity [$\rho_{ab}(T)$] curves for Sample set A. The residual resistivity ratio (RRR) values of these samples are provided.

Figure 4. Microscopic structure of Sample B1. (a) Large scale ABF-STEM image of Sample B1. The image does not show any signs of OPBs. However, numerous darker and cloudlike areas of contrast appear near the film–substrate interface. (b) An enlarged HAADF-STEM image of Area 1 (indicated by the solid box in (a)). (c) Atomically resolved ABF-STEM image of Area 2 (indicated by the solid boxes in (a,b)). The ABF-STEM images in (b,c) indicate that the upper region of Sample B1 is composed of a nearly defect-free SRO214 layer. (d) Atomically resolved ABF-STEM image measured from Area 3 (indicated by the solid box in (a)). The film–substrate interface is indicated by the dashed line. A half-unit cell of SRO327 phase accommodates the step-height of the substrate (indicated by a red box). The zone axes for all images are [100]. (e) $\varepsilon_{xx}$ map of Area 3 converted by GPA. (f) Schematic thermodynamic phase diagram for SRO214 growth (adapted from ref 37, licensed under a Creative Commons Attribution (CC BY) license). The lower $T_{sub}$ facilitates the formation of mixed SRO214 and SRO327 phases. Therefore, the linearly increasing $T_{sub}$ during film growth results in SRO327 intergrowth near the interface and pure SRO214 phase at the upper region of the films.
investigated by scanning transmission electron microscopy (marked by white arrows). Figure 3b shows an extended to the OPB emerged at the terrace edges of the substrate and surface topography analysis (Figure S2a,b in the Supporting Information, respectively), conformed a structural gradient along the c-axis direction, and degraded film structure. Figure 2d shows the rocking curves of the SRO214 (006) diffractions for Samples A1 and B1. Sample A1 exhibited a sharp and narrow rocking curve indicating good crystallinity having a full width at half-maximum (fwhm) value of 0.013°, which is comparable to the LSAT substrate (0.010°, Figure S2e in the Supporting Information). Sample B1 also exhibited a sharp rocking curve (fwhm ~0.014°), but it was buried in a broad shoulder. This shoulder had a 10-fold larger fwhm value (~0.144°) than that of Sample A1. We suggest that the broadening observed in the rocking curve of Sample B1 may be attributable to dislocations or mosaicity that disturb the epitaxial structure of Sample A1.

The microscopic structure of the SRO214 films was investigated by scanning transmission electron microscopy (STEM). We first analyzed the annular bright-field (ABF)-STEM image of Sample A1. As shown in Figure 3a, although the XRD measurements indicated a high-quality epitaxial and pseudomorphic structure of Sample A1, the (006) diffraction peak (Figure 2c), RSM and surface topography (Figure S2, Supporting Information) exhibited an asymmetric double-peak feature, implying a structural gradient along the c-axis direction, and degraded film structure. Figure 2d shows the rocking curves of the SRO214 (006) diffractions for Samples A1 and B1. Sample A1 exhibited a sharp and narrow rocking curve indicating good crystallinity having a full width at half-maximum (fwhm) value of 0.013°, which is comparable to the LSAT substrate (0.010°, Figure S2e in the Supporting Information). Sample B1 also exhibited a sharp rocking curve (fwhm ~0.014°), but it was buried in a broad shoulder. This shoulder had a 10-fold larger fwhm value (~0.144°) than that of Sample A1. We suggest that the broadening observed in the rocking curve of Sample B1 may be attributable to dislocations or mosaicity that disturb the epitaxial structure of Sample A1.

To understand how OPBs affect superconductivity in SRO214 thin films, we measured the temperature-dependence of the in-plane resistivity [\(\rho_{ab}(T)\)] for three SRO214 thin films grown under Condition A (denoted as Samples A1–A3). As shown in Figure 3d, Samples A1–A3 exhibited low residual resistivities at 2 K [\(\rho_{ab}(2 \text{ K})\)] of 3.0, 4.6, and 4.9 \(\mu\Omega\cdot\text{cm}\), respectively, with high residual resistivity ratios [\(\Delta R/R = \rho_{ab}(300 \text{ K})/\rho_{ab}(2 \text{ K})\)] of 46, 31, and 26. The thicknesses of Samples A1–A3 were 58.0, 54.0, and 94.9 nm, respectively. Note that the \(\rho_{ab}\) of Sample set A was proportional to \(T^2\), which is indicative of SRO214. Nevertheless, we only observed a plateau or slight drop in \(\rho_{ab}\) down to 0.4 K (inset), indicating the absence of superconductivity or possibly incipient superconductivity, at best. Given that Sample set A exhibited no evidence of Ru deficiency according to Raman spectroscopy measurements (Figure S3 in the Supporting Information), we suggest that the high-density of OPBs is responsible for the absence of superconductivity in Sample set A.

In contrast to the high-density OPBs in Sample set A, Sample B1 exhibited distinct structural defects. The ABF-STEM image of Sample B1 did not show OPB-like contrast or mosaic tilt (Figure 4a). Instead, the image exhibited a nearly defect-free region at the upper region of the film. The enlarged HAADF- and ABF-STEM images (Figure 4b,c, respectively) confirm that region labeled as Areas 1 and 2 was nearly a perfect single-crystalline SRO214 layer. This high-quality SRO214 region spanned over 500 nm, which is an order of magnitude larger than \(\xi_{ab}\). In addition, Figure 4a shows numerous dark-patches near the interface region. These patches were shown to be the SRO327 phase on atomic-resolution ABF-STEM images (Figure S4 in the Supporting Information). Figure 4d shows the atomic-resolution ABF-STEM image of Area 3, at the film–substrate interface of Sample B1. A half-unit cell of SRO327 phase formed at the down step region of the terrace edge (indicated by the red box), while the SRO214 phase was grown on the upper step region. The SRO327 phase accommodated the stepped-height of the LSAT substrate (~4 Å). Above the SRO327 phase, smooth boundaries were formed and defect-free SRO214 layers could be grown through the whole region, as depicted schematically in Figure 1b. Figure 4e shows an \(\varepsilon_{ab}\) map of Area 3, converted by GPA; hence, the accumulation of a pure SRO214 phase at the upper region of the film. The SRO327 intergrowth observed in the film–substrate interface plays a crucial role in the suppression of OPB formation. The SRO327 intergrowth observed in the STEM images was consistent with the XRD results shown in Figure 2. The disarranged stacking sequence derived from SRO327 intergrowth created a structural gradient in Sample B, inducing asymmetric and double-peak features of (006) diffraction in the \(\omega-2\theta\) scan and a diffusive background in the rocking curve. The defect-free SRO214 layers contributed to the sharp peak in the rocking curve.

We now consider the origin of SRO327 intergrowth in Condition B. The thermodynamic phase diagram of the strontium ruthenate RP-phase is plotted schematically in Figure 4f. For Condition B, we initiated the deposition at a relatively low \(T_{\text{sub}}\) of 840 °C, which may have facilitated the formation of a mixed SRO214 and SRO327 phase. As \(T_{\text{sub}}\) increased, the pure SRO214 phase became more energetically favorable (Figure S1 in the Supporting Information). Hence, the gradual increase in \(T_{\text{sub}}\) during deposition could promote the formation of a pure SRO214 phase at the upper region of the film. The self-organized SRO327 phases interrupted the periodic arrangement of layered structure, breaking the continuous propagation of OPBs and allowing to the growth of defect-free SRO214 layers above the intergrowth layer.

The defect-free SRO214 layers led to robust superconductivity. Figure 5a shows \(\rho_{ab}(T)\) curves of Sample set B (denoted as Samples B1–B7). As shown in Figure 5a,b, Sample set B exhibited \(\rho_{ab}(2 \text{ K})\) from 2.3 to 6.7 \(\mu\Omega\cdot\text{cm}\) with...
The thickness of the defect-free SRO214 layers ($t_{\text{def}}$) was positively correlated with superconductivity (Figure S5 in the Supporting Information). This tendency can be understood as thickness-dependent superconductivity, which is generally observed in superconducting thin films. As the film becomes thinner, the reduced dimension and increased disorder usually degrade the superconductivity. We speculate that the $t_{\text{def}}$ varies from sample to sample, resulting in the observed variations in electrical transport and superconductivity. During the deposition of Sample set B, the microstructure may not be precisely controlled by $T_{\text{sub}}$ engineering due to the similarities in Gibbs formation energies between SRO214 and SRO327 phases. In addition, the high kinetic energy scale of PLD (∼100 eV) provides a dynamic environment in which the intergrowth can be randomly formed during deposition. Despite the difficulties in control, the presence of the SRO327 phase ensures the Ru-rich environment as well as suppression of OPBs, which are both essential for superconductivity in SRO214 thin films. Note that the SRO327 intergrowth at the film−substrate interface was also reported previously for superconducting SRO214 thin films. Therefore, we suggest that SRO327 intergrowth engineering could be effective for achieving superconductivity in SRO214 films, and our thermodynamic method could promote the comprehensive realization of superconducting SRO214 films. Identifying experimental approaches for improved control over SRO327 intergrowth should be a target for future investigations.

In conclusion, we have successfully grown superconducting SRO214 films by inducing SRO327 intergrowth near the film−substrate interface. The intergrowth was controlled by $T_{\text{sub}}$ during growth and interface−intergrowth formation blocks lattice translation at the terrace edges of the substrate, thus suppressing OPB formation. The nearly defect-free SRO214 layers were formed above the intergrowth layers and facilitated homogeneous superconductivity with a transition temperature of 1.15 K and a sharp superconducting transition width of 0.1 K. A synthesis approach to inhibit OPB formation is key for the development of versatile RP-phase-based oxide heterostructures and creates opportunities for the development of novel functional devices.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.0c04963.

Additional characterization data, and spectroscopy data are included (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
Lingfei Wang − Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China; Center for Correlated Electron Systems, Institute for Basic Science (IBS), Seoul 08826, Republic of Korea; Department of Physics and Astronomy, Seoul National University, Seoul 08826, Republic of Korea; orcid.org/0000-0003-1675-0941; Email: wanglf@ustc.edu.cn

Tae Won Noh − Center for Correlated Electron Systems, Institute for Basic Science (IBS), Seoul 08826, Republic of Korea; Department of Physics and Astronomy, Seoul National University, Seoul 08826, Republic of Korea;
Author Contributions
J.K. and J.M. contributed equally to this work.

Acknowledgments
This work was supported by the Research Center Program of IBS (Institute for Basic Science) in Korea (IBS-R009-D1), National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2017R1A2B3011629), the National Key Basic Research Program of China (Grant 2020YFA0309100), the National Natural Science Foundation of China (Grant 12074365), the Fundamental Research Funds for the Central Universities (WK2030000035, WK234000102), EPSRC-JSPS Core-to-Core International Network "Oxide Superspin" (Nos. EP/P026311/1 and JPJSCCA20170002), JSPS KAKENHI Nos. JP15H05852, JP15K21717, and JP17H06136 funded by Japan Society for Promotion of Science (JSPS), and the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2016R1A6A1A03012877, 2020R1A2C1007554, and 2018R1A6A1A06024977). Experiments at PLS-II 3A beamline were supported in part by MSIT and POSTECH. STEM measurement was supported by the National Center for Inter-University Research Facilities (NCIRF) at Seoul National University in Korea. The authors acknowledge Prof. Tae Heon Kim, Dr. Gideok Kim, Dr. Yeong Jae Shin, Dr. Atsutoshi Ikeda, Dr. Mi Kyung Kim, Nahyun Lee, Jeong Rae Kim, Suhan Son, Han Gyeol Park, and Takuto Miyoshi for the technical support and fruitful discussions.

References


