学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

Synthesis and Functionality of Freestanding Perovskite Oxide Sheets Using Amorphous Oxide Protection Layer

（アモルファス酸化物保護層を用いた自立型ペロブスカイト酸化物シートの合成と機能性）

Flexible and functional perovskite oxide sheets with high orientation and crystallization are the next step in the development of next-generation devices. However, perovskite oxides are inherently rigid, necessitating thickness reduction to sub-micrometer levels to achieve flexibility. Recently, a lift-off and transfer method was developed using a water-soluble $Sr_3Al_2O_6$ (SAO) sacrificial layer. (1, 2) In this method, an objective perovskite oxide film is first fabricated in the single-crystal form on SAO-buffered $SrTiO_3$ (STO) single-crystal substrates, after which the film is peeled off from the substrate by dissolving the SAO layer in deionized water. Through this method, highly oriented functional perovskite oxide sheets, such as ferroelectric $BiFeO_3$ (3, 4) and $BaTiO_3$ (BTO), (5-7) ferromagnetic manganite (8, 9) and $SrRuO_3$, (10), and transparent conductive La : $BaSnO_3$ (LBSO) (12), have been obtained thus far.

The synthesis method is facile and applicable to various perovskite oxides, adds flexibility to the oxides, and allows for the reuse of expensive single-crystal substrates. However, one crucial problem, which is the difficulty of suppressing cracks during synthesis, remains unsolved. Indeed, in my study, numerous cracks were generated in La : $SrSnO_3$ (LSSO), LBSO and $Ba_{1-x}Sr_xO_3$ (BST) sheets by performing conventional lift-off and transfer method. Thus, as pointed out by Chiabrera et al., developing a technique for transferring single-crystal oxide sheets with large size, as-grown uniformity, and high quality is a key challenge. (13)

Herein, I report on the significant crack suppression in the as-grown sheet via the deposition of protection oxide layers onto the objective perovskite oxide film prior to lift-off. I systematically investigated the effects of the protection layer thickness, perovskite oxide film thickness, and oxide protection layer type. The results revealed that an amorphous (a-)Al_2O_3 protection layer was effective, owing to the high crack resistance and/or high Young’s modulus of a-Al_2O_3. (15, 16) Through this simple method, a 5×5 mm^2 LSSO sheet, 5×5 mm^2 LBSO sheet, and 5×5 mm^2 BST sheet were obtained without any cracks. This study provides a simple transfer method for obtaining large-size and high-quality single-crystalline sheets on arbitrary substrates.

In chapter 1, the background and purposes of related studies are introduced.

In chapter 2, I report the significantly suppression of crack in LSSO sheet using an amorphous oxide protection layer. The results showed an a-Al_2O_3 is the most effective for crack suppression. Large-size crack-free LSSO sheets (up to 5×5 mm^2) was obtained using this lift-off and transfer method. The sheets could be transferred to various types of substrates, with a selection of the desired layer as the upper or lower side. The LSSO sheet exhibited a wide optical bandgap of 4.4 eV and a high σ value of 1600 S/cm at room temperature. Importantly, the expensive STO single-crystal substrates can be reused.

In chapter 3, I transferred millimeter-size crack-free LBSO sheet by employing the optimized a-Al_2O_3 protection layer despite of the large lattice mismatch. Furthermore, I controlled the shapes of the LBSO sheets such as rolled and flat forms. The rolled sheet had a tubular shape with diameter of 1 mm and length of 5 mm, while the size of the flat sheet was 25 mm^2. The presence of the a-Al_2O_3 protection layer allowed for a significantly large crack-free area. The LBSO sheets exhibited wide optical bandgap of 3.5 eV and high Hall mobility of 80 cm^2 V^{-1} s^{-1}, making it promising for next-generation optoelectronic devices.

In chapter 4, I observed the enhancement of permittivity and tunability in freestanding BST sheets owing to release of substrate-induced strain, while keeping bulk-like ferroelectricity. Millimeter-sized BST epitaxial sheets were also obtained using an a-Al_2O_3 protective layer exceeding 10 nm in thickness. I found that poly-crystalline tin-doped indium oxide (ITO) is a suitable bottom electrode due to its high electrical conductivity and low deposition temperature. The x = 0.25 sheet demonstrated excellent ferroelectric properties, while the x = 0.5 sheet exhibited high permittivity and tunability, attributed to the absent of substrate-induced strain.

In short, I systematically studied on transfer of perovskite freestanding sheet. My research has accelerated the industrialization of single-crystal freestanding sheets and opened up new possibilities for exploring various intriguing properties of the perovskite freestanding single-crystal sheets.

References

1. D. Lu et al., Nat. Mater. 15, 1255 (2016).
2. D. Li et al., Nano Lett. 21, 4454 (2021).
3. D. Ji et al., Nature 570, 87 (2019).
4. R. Guo et al., Nat. Commun. 11, 2571 (2020).
5. Y. Zhao et al., Adv. Funct. Mater. 31, 2009376 (2021).
6. G. Dong et al., Science 366, 475 (2019).
7. M. Lee et al., Adv. Mater. 34, 2204630 (2022).
8. Q. Lu et al., ACS nano 16, 7580 (2022).
9. C. Jin et al., Adv. Sci. 8, 2102178 (2021).
10. P. T. Le et al., Sci. Rep. 11, 12435 (2021).
11. R. Xu et al., Nat. Commun. 11, 1 (2020).
12. P. Singh et al., ACS Appl. Electron. Mater. 1, 1269 (2019).
13. F. M. Chiabrera et al., Ann Phys., 2200084 (2022).
14. K. Gu et al., Adv. Funct. Mater. 30, 2001236 (2020).
15. G. A. Rosales-Sosa et al., Sci. Rep. 6, 1 (2016).
16. N. Claussen, J. Am. Ceram. Soc. 59, 49 (1976).