

論文の内容の要旨

Anion Control in Transition Metal Oxide Thin Films via Topotactic Reactions

(トポタクティック反応による遷移金属酸化物薄膜のアニオン制御)

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Perovskite transition metal oxides have attracted great attention because of their intriguing properties such as colossal magnetoresistance, ferroelectric, and photocatalysis. The physical properties of the oxides are controllable in a wide range through cation substitution. However, in comparison with cation substitution, anion substitution has scarcely been reported because of the difficulty in synthesizing mixed anion compounds such as oxyhydrides and oxyfluorides. Recently, low-temperature topotactic synthesis was developed to fabricate mixed anion compounds that are not accessible by conventional high-temperature synthesis. Although such topotactic reactions have been studied in various bulk samples, the reactions on thin-film samples is expected to have several advantages over bulk: considerably higher reactivity owing to the larger surface area/volume ratio, stabilization of the perovskite-based framework by epitaxial effect, and modification of physical properties by epitaxial strain. Accordingly, in this study, I performed four types of low-temperature topotactic reactions, i.e., hydridation, fluorination, reduction, and oxidation, on perovskite transition metal oxide films, and investigated the properties of the thus obtained mixed anion films.

For topotactic hydridation, I successfully fabricated perovskite SrCoO_xH_y and SrVO_2H oxyhydride thin films from precursor $\text{SrCoO}_{2.5}$ and SrVO_3 films, respectively, by using CaH_2 . The new Co oxyhydride phase, SrCoO_xH_y film, was epitaxially stabilized by substrate and possessed novel two-dimensional Co-H-Co networks in the perovskite structure, in contrast to previously reported perovskite oxyhydrides, $\text{SrMO}_{3-x}\text{H}_x$ ($M = \text{Cr}, \text{Ti}, \text{V}$). The SrCoO_xH_y thin film exhibited insulating behavior with a much wider band gap than the precursor $\text{SrCoO}_{2.5}$, deriving from the large structure distortion. On the other hand, the single-crystalline SrVO_2H film possessed one-dimensional V-H-V bonds along the out-of-plane direction. With the H^- substitution, binding energy shift of Sr and metal-insulator transition were observed. Furthermore, the synthesis temperature of SrVO_2H film could be lowered by reducing the film thickness.

For topotactic fluorination, I fabricated perovskite $\text{SrFeO}_{3-x}\text{F}_x$ oxyfluoride epitaxial thin films from $\text{SrFeO}_{3-\delta}$ ($\delta \sim 0, 0.5, 1$) precursor films using polyvinylidene fluoride (PVDF). The $\text{SrFeO}_{3-x}\text{F}_x$ films were obtained by fluorination at 150–270 °C, which is substantially lower than the reaction temperature for polycrystalline bulk samples prepared with PVDF. Furthermore, the fluorine content (x) of the $\text{SrFeO}_{3-x}\text{F}_x$ film was widely varied by

controlling the PVDF-treatment temperature and/or the amount of oxygen vacancies in the precursor film, in contrast to bulk SrFeO₂F. The optical bandgap of the SrFeO_{3-x}F_x films was expanded with respect to the fluorine doping and the SrFeO₂F film showed a wider bandgap than perovskite LaFeO₃. The density functional theory (DFT)-based calculations suggested that majority of the FeO₄F₂ octahedra in the SrFeO₂F film had *cis* configurations and that the enlarged bandgap mainly originated from bond bending in the O-Fe-O chains. In addition, I also succeeded in fabricating SrCoO_xF_y epitaxial thin film via topotactic fluorination of SrCoO_{2.5} film using PVDF. The Co valence state of the SrCoO_xF_y film was a mixture of 2+ and 3+, which was smaller than that of the SrCoO_{2.5} precursor film, indicating that PVDF acted as a reductive fluorinating agent, in sharp contrast to oxidative F₂ gas. This compound is the first example of perovskite-related Co oxyfluoride with Co^{2+/3+}.

For topotactic reduction, I fabricated single-crystalline SrFeO₂ epitaxial thin films from SrFeO_{3-δ} films using CaH₂. The highly crystalline SrFeO₂ films prepared on lattice-matched KTaO₃ substrate exhibited metallic conduction, while those grown on SrTiO₃ and DyScO₃ substrates were insulating, in analogy to bulk SrFeO₂. From Hall measurements on the metallic SrFeO₂ films, the conduction carriers were determined to be *n*-type (i.e., electrons) with a carrier density of $3.1 \times 10^{18} \text{ cm}^{-3}$ and mobility of $10.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K. The electron carriers are supplied by oxygen vacancies or hydrogen ions in the metallic SrFeO₂ films. I also found that Sm substitution could enhance the conductivity of SrFeO₂ films.

Finally, I performed topotactic oxidation and reduction on *A*-site cation-ordered perovskite YBaCo₂O_{*x*} epitaxial thin films using NaClO and CaH₂, respectively. The *x* values of the YBaCo₂O_{*x*} films were successfully controlled in a range of 4.5–6, which was wider than the previous reports, 4.5–5.5, manifesting the high reactivity of the films. The resistivity (ρ) of the films changed depending on *x*; the *x* ~ 4.5 film was insulating with $\rho = 5.5 \text{ } \Omega\text{cm}$ at 300 K due to the distortion of the CoO_{*x*} layers, while the new phase (*x* ~ 6) showed metallic behavior with $\rho = 3.5 \times 10^{-4} \text{ } \Omega\text{cm}$ at 300 K due to hole doping. The new YBaCo₂O₆ thin film exhibited ferromagnetic metallic behavior with T_C of 130 K deriving from the double exchange mechanism between Co³⁺ and Co⁴⁺. Furthermore, I found large crystal magnetic anisotropy and negative magnetoresistance in the YBaCo₂O₆ film.

These results proved that topotactic anion doping into transition metal oxide thin films is a promising way of synthesizing new mixed anion compounds.