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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 楊 倩

学 位 論 文 題 名

Solid-State Electrochemical Protonation / Redox reaction induced Control of Physical Properties of SrCoO_x and SrFeO_x

（固体電気化学的プロトン化/酸化還元反応による SrCoO_x および SrFeO_x の物理的性質の制御）

Transition metal oxides (TMOs) have been widely studied thus far due to their controllable physical properties by controlling the oxygen content. For example, strontium cobalt oxide (SrCoO_x) has been extensively studied because its physical properties are dramatically changed; $\text{SrCoO}_{2.5}$ (Co^{3+}) with brownmillerite (BM) crystal structure is brown colored antiferromagnetic insulator, SrCoO_3 (Co^{4+}) with perovskite structure is black colored ferromagnetic metal, and $\text{H}_x\text{SrCoO}_{2.5}$ (Co^{2+}) ($x = 1, 1.5$, and 2) is colorless-transparent weak ferromagnetic insulator [1,2]. Thus, SrCoO_x would be a good candidate active material of a nonvolatile memory device if the oxygen content is modulated electrically while keeping the solid state.

In 2016, Katase *et al.* reported a solid-state electrochemical redox device based on SrCoO_x [3]. Using NaTaO_3 nanopillar film as the electrolyte, the authors reversibly oxidized/reduced $\text{SrCoO}_{2.5}/\text{SrCoO}_3$ by applying ± 3 V at room temperature. However, the authors did not observe the formation of protonated $\text{H}_x\text{SrCoO}_{2.5}$, probably due to the strong alkalinity of NaTaO_3 nanopillar film. On the other hand, in 2017, Lu *et al.* reported protonation of $\text{SrCoO}_{2.5}$ into $\text{H}_x\text{SrCoO}_{2.5}$ by using residual water in the ionic liquid as the electrolyte [2]. Thus, neutral water would be better to protonate SrCoO_x .

In order to realize the electrochemical protonation of $\text{SrCoO}_{2.5}$ while keeping solid-state, I choose a mesoporous amorphous $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (CAN)[4] film as the solid electrolyte. CAN contains ultrapure water in the mesopores (40 vol.%) and shows the electrical conductivity of $2.2 \times 10^{-9} \text{ S cm}^{-1}$, which is 4% of that of ultrapure water ($5.5 \times 10^{-8} \text{ S cm}^{-1}$)[4] at room temperature. Then, I used an oxide ion conductor yttria-stabilized zirconia (YSZ) single-crystal as the solid electrolyte. I fabricated $\text{SrCoO}_{2.5}$ films on the YSZ substrate and performed the electrochemical redox treatment of $\text{SrCoO}_{2.5}$ film at 300 °C in air. In order to expand this all solid redox method on other materials, finally, I tested SrFeO_x active layer because it also exhibits a clear phase transition like SrCoO_x . This thesis is mainly composed of the following sections:

In chapter 1, the background and purpose of this research are explained.

In chapter 2, experimental methods are introduced.

In chapter 3, I report on unusually large thermopower change from $+330 \mu\text{V K}^{-1}$ to $-185 \mu\text{V K}^{-1}$ of

brownmillerite $\text{SrCoO}_{2.5}$ [5]. I measure the thermopower of $\text{SrCoO}_{2.5}$ epitaxial films grown on several lattice-mismatched substrates at room temperature in the air. Although the differences of the electronic structure and the oxidation states among the samples are extremely small, the thermopower obviously changed from $+330 \mu\text{V K}^{-1}$ to $-185 \mu\text{V K}^{-1}$ with a slight increase of lattice and/or absorbed oxygen in the $\text{SrCoO}_{2.5}$ films, clearly demonstrating the effectiveness of thermopower to analyze the electronic structure and the oxidation states of TMOs.

In chapter 4, I report on solid-state electrochemical protonation of $\text{SrCoO}_{2.5}$ into $\text{H}_x\text{SrCoO}_{2.5}$ ($x = 1, 1.5$ and 2) [6]. I demonstrate a solid-state electrochemical protonation of $\text{SrCoO}_{2.5}$ using mesoporous amorphous CAN film as the solid electrolyte. The crystalline phase discretely changed from $\text{SrCoO}_{2.5}$ to $\text{HSrCoO}_{2.5}$, $\text{H}_{1.5}\text{SrCoO}_{2.5}$, and $\text{H}_2\text{SrCoO}_{2.5}$ through formation of an intermediate phase of $\text{H}_{1.25}\text{SrCoO}_{2.5}$. The $\text{H}_{1.5}\text{SrCoO}_{2.5}$ was colorless-transparent and showed weak ferromagnetism.

In chapter 5, I report on macroscopic visualization of the fast electrochemical reaction of SrCoO_x oxygen sponge [7]. SrCoO_x epitaxial films with various oxidation states were prepared by the electrochemical oxidation of $\text{SrCoO}_{2.5}$ film. Steep decrease of both resistivity and the absolute value of thermopower of electrochemically oxidized SrCoO_x epitaxial films indicated the columnar oxidation firstly occurred along with the oxidation direction and then spread perpendicular to the oxidation direction. Further, I directly visualized the phenomena using the conductive AFM.

In chapter 6, I report on solid-state electrochemical redox control of the optoelectronic properties for SrFeO_x thin films [8]. I fabricated $\text{SrFeO}_{2.5}$ film on the YSZ substrate and modulated the oxygen content by the electrochemical redox treatment. The phase gradually changed from $\text{SrFeO}_{2.5}$ to $\text{SrFeO}_{2.5+x}$, and SrFeO_{3-x} . The color of the film changed from yellowish-transparent to dark brown. Although as-grown $\text{SrFeO}_{2.5}$ film showed high resistivity ($\rho \geq 10^1 \Omega \text{ cm}$), the ρ dramatically decreased ($\sim 10^{-2} \Omega \text{ cm}$) when oxidized. Simultaneously, the thermopower decreased dramatically from $+200 \mu\text{V K}^{-1}$ to $-10 \mu\text{V K}^{-1}$.

In chapter 7, the above researches are summarized.

In a word, the present results of solid-state electrochemical redox treatment of SrCoO_x and SrFeO_x would provide a design concept for future TMOs-based solid-state multifunctional memory devices.

References

- [1] H. Jeon *et al.*, *Nat. Mater.* 12, 1057 (2013).
- [2] N. Lu *et al.*, *Nature* 546, 124 (2017).
- [3] T. Katase *et al.*, *Adv. Electron. Mater.* 2, 1600044 (2016).
- [4] H. Ohta *et al.*, *Nat. Commun.* 1, 118 (2010).
- [5] Q. Yang *et al.*, *ACS Appl. Electron. Matter.* 2, 2250 (2020).

- [6] Q. Yang *et al.*, *ACS Appl. Electron. Mater.* 3, 3296 (2021).
- [7] Q. Yang *et al.*, *Adv. Mater. Interfaces* 6, 1901260 (2019).
- [8] Q. Yang *et al.*, *J. Appl. Phys.* 129, 215303 (2021).