$SrCoO_{2.5}$ エピタキシャル薄膜の電気化学酸化と電子輸送特性

Electrochemical Oxidation and Electron Transports of $SrCoO_{2.5}$ Epitaxial Films

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Since strontium cobaltite ($SrCoO_x$) can exhibit three different optical, electrical, and magnetic phases, which can be controlled using oxidation/protonation. Therefore, it has excellent potential as the active material for unique electrochemical memory devices.[1-3] Although atomic scale phenomenon of the oxidation of $SrCoO_{2.5}$ into $SrCoO_3$ is known, the macroscopic phenomenon has not been clarified yet thus far. Here, thermopower analysis is used to clarify the electrochemical oxidation macroscopically. A 6-nm-thick GDC (10 mol% Gd-doped CeO_2) film was heteroepitaxially grown on (001) YSZ substrate followed by the growth of ~40-nm-thick $SrCoO_{2.5}$ by pulsed laser deposition. The out-of-plane XRD patterns of the resultant films showed that the $SrCoO_{2.5}$ were heteroepitaxially grown on the GDC/YSZ with the epitaxial relationship of (001)[100] $SrCoO_{2.5}$ ‖ (001)[110] GDC/YSZ. We then deposited Pt electrode on the back side of the YSZ substrate and applied current into the film as schematically shown in Fig. (a) with −5 or −10 V at 300 °C in air. In order to measure the electron transports of the intermediate state, we suspended the electrochemical oxidation several times. From the XRD analyses of the films, we clarified that the conversion rate from $SrCoO_{2.5}$ brownmillerite to $SrCoO_3$ perovskite could be controlled electrochemically. Figure (b) shows the resistivity (upper) and thermopower (lower) of the resultant films at room temperature. Although the resistivity of $SrCoO_{2.5}$ film was high (5.5 Ω cm), the resistivity dropped after slight oxidation due to the parallel electronic circuit composed of very low resistive $SrCoO_3$ (0.35 mΩ cm). Furthermore, the thermopower dropped from 70 μV K^{-1} to ~0 μV K^{-1} after slight oxidation. Steep decrease in both resistivity and the absolute value of thermopower of electrochemically oxidized $SrCoO_x$ epitaxial films indicates the columnar oxidation firstly occurred along the oxidation direction and then spread perpendicular to the oxidation direction. This macroscopic image of the electrochemical oxidation would be useful for developing a functional device utilizing the electrochemical redox reaction of $SrCoO_x$.

References

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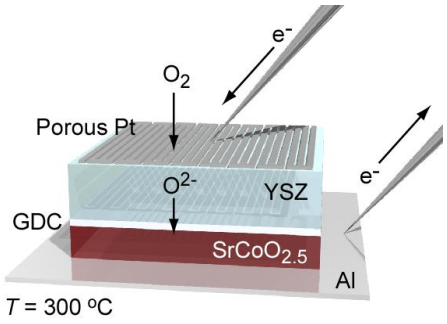
(a)



(b)

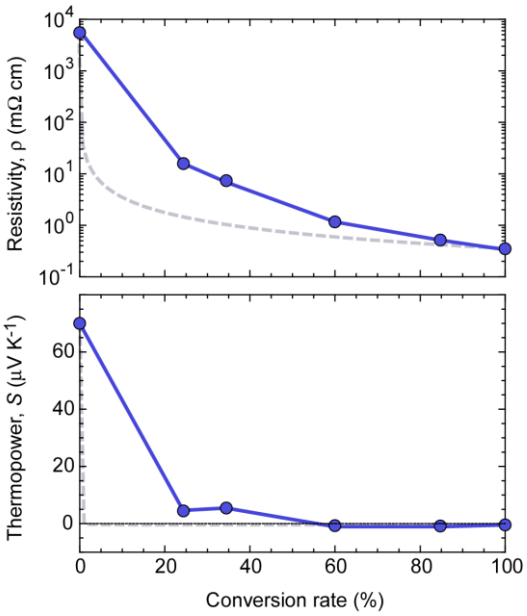


FIG. (a) Schematic illustration of the electrochemical oxidation of $SrCoO_{2.5}$ film grown on GDC-capped YSZ substrate. (b) Electron transport properties of the $SrCoO_x$ as a function of the conversion rate. The as grown sample (0 %) showed the resistivity of 5.5 Ω cm and the thermopower of +70 μV K^{-1}, whereas 100 % converted sample showed 0.3 mΩ cm and −0.5 μV K^{-1}. The dotted lines were calculated by assuming the electrical circuit was parallel.