酸化物イオン伝導体 YSZ を用いた $SrCoO_{2.5}$ 薄膜の電気化学的酸化・還元

Electrochemical Redox reaction of $SrCoO_{2.5}$ films using YSZ oxide ion conductor

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$SrCoO_x$ shows kinds of properties depending on the oxygen content x; Brownmillerite (BM) $SrCoO_{2.5}$ (Co^{3+}) is brown colored antiferromagnetic insulator and perovskite (PV) $SrCoO_{3-\delta}$ (Co^{4+}) is black colored ferromagnetic metal. Protonated BM $HSrCoO_{2.5}$ (Co^{2+}) is colorless transparent weak ferromagnetic insulator. There is no report on the reduced $SrCoO_2$ (Co^{2+}). In order to obtain $SrCoO_2$ and clarify the properties, we used an oxide ion conductor YSZ as the solid electrolyte[1]. Here we report first observation of $SrCoO_2$.

We fabricated epitaxial films of $SrCoO_{2.5}$ on 10%-Gd-doped CeO_2 buffered (001) YSZ single crystal substrate by pulsed laser deposition technique. The electrochemical Redox reaction of the resultant films was performed by applying current under ±10 V at 300 °C in air.

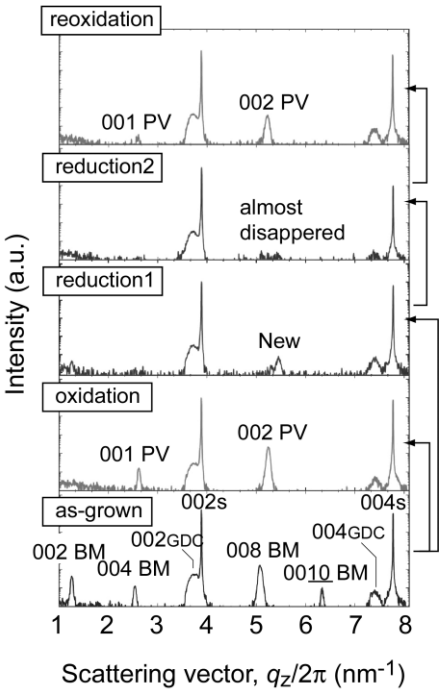

Figure | Out-of-plane XRD patterns of the resultant $SrCoO_x$ films.

Figure shows the out-of-plane XRD patterns of the resultant $SrCoO_x$ films. Only intense diffraction peaks of 00*l* BM $SrCoO_{2.5}$ are observed together with 00*l* GDC and 00*l* YSZ in the as-grown sample. After the electrochemical oxidation, superlattice peaks of 002, 006, and 0010 BM $SrCoO_{2.5}$ disappeared and transformed into PV $SrCoO_{3-\delta}$ completely. The film color changed from brown to black. On the other hand, after the electrochemical reducing treatment, superlattice peaks of 002, 006, and 0010 BM $SrCoO_{2.5}$ disappeared and new diffraction peak appeared around $q_z/2\pi$ ~5.3 nm^{-1}. The film was colorless transparent and electrically insulator. After applying the positive voltage continuously, the new peak almost disappeared. Interestingly, when we applied a current under negative voltage to the reduced sample, intense diffraction peaks of PV $SrCoO_{3-\delta}$ appeared again that demonstrate reversible electrochemical redox reaction of $SrCoO_x$ films.

In order to clarify the valence state of Co ion, we performed the X-ray absorption spectroscopy measurements and confirmed that the oxidation state of Co ion in the reduced sample is +2, clearly indicating that SrCoO2 was successfully obtained for the first time. The present results would be useful to develop memory devices utilizing the multivalent Co ions in $SrCoO_x$ with rich functionalities.

Reference [1] Q. Yang, H. Jeen, H. Ohta *et al.*, *Adv. Mater. Interfaces* **6**, 1901260 (2019).