Investigation of oxidation states in oxyhydride SrVO$_2$H epitaxial thin films

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1 Introduction
Recently, oxyhydride SrVO$_2$H was synthesized from the parent oxide SrVO$_3$ via topotactic reaction using CaH$_2$ [1]. In SrVO$_2$H, the doped H$^-$ anions occupy the axial position of VO$_2$H$_2$ octahedral units, resulting in a one-dimensional (1D) V-H-V bond network along the c-axis and a 2D VO$_2$ network in the ab-plane. Owing to the 1D-type hydride coordination, SrVO$_2$H has a tetragonal structure with a large a/c lattice ratio ($a = 3.93$, $c = 3.66$ Å). SrVO$_2$H has a V 3$d^2$ configuration, and the occupied $d_{xz}$ and $d_{yz}$ orbitals interact with O 2$p$ orbitals, not H 1$s$ orbitals, because of their orbital symmetry. This V 2D 3$d$–O 2$p$ bonding network leads to strong antiferromagnetic coupling with Néel temperatures above 300 K. A theoretical study predicted that SrVO$_2$H is a quasi-2D Mott insulator.

Topotactic reaction of epitaxial thin films with metal hydrides is an effective way to obtain single crystalline transition metal oxyhydrides [2,3]. Furthermore, the high reactivity of thin film samples enables us to suppress the reaction temperature [4], which is beneficial in reducing unwanted reaction. In this study, we prepared single crystalline SrVO$_2$H films by combining pulsed-laser deposition (PLD) and topotactic hydride doping techniques, and investigated the oxidation states in the fabricated films.

2 Experiment
Perovskite SrVO$_3$ precursor thin films were fabricated on SrTiO$_3$(001) substrates using PLD. The obtained SrVO$_3$ precursor films were subsequently reacted with CaH$_2$ powder at a temperature range ($T_r$) of 450-600°C for 24 h in vacuum sealed quartz glass tubes. Two kinds of the films with different thicknesses, 15 nm and 55 nm, were prepared for characterization. Hydrogen content in the films was determined by dynamic secondary ion mass spectroscopy (SIMS), where H-implanted SrTiO$_3$ samples were used as standard references. X-ray absorption spectroscopy (XAS) measurements were performed at the BL-2A beamline of the Photon Factory, KEK, using the total electron-yield method at 300 K.

3 Results and Discussion
In order to confirm the hydrogen doping in the film, dynamic SIMS measurement was performed. Figure 1(a) shows the SIMS depth profile of hydrogen ion for the 55-nm-thick SrVO$_2$H film on SrTiO$_3$ substrate. Hydrogen ions were doped almost homogeneously throughout the film at a concentration of $\sim 1.9 \times 10^{22}$ atom/cm$^3$. The hydrogen concentration in the film was very similar to that of bulk SrVO$_2$H, $\sim 1.8 \times 10^{22}$ atom/cm$^3$ [1], which also supports the formation of SrVO$_2$H.

Figure 1(b) shows V 2p XAS spectra for the 15-nm-thick SrVO$_3$ and SrVO$_2$H films together with CaVO$_3$ and YVO$_3$ as references of V$^{4+}$ and V$^{3+}$, respectively [5]. The V L$_3$ and L$_2$ peaks were clearly observed in all spectra. The spectra of the SrVO$_3$ and SrVO$_2$H films are highly similar in peak shape and position to those of the CaVO$_3$ and YVO$_3$ references, respectively, demonstrating that the oxidation states of vanadium in the film changed from 4+ to 3+ in the topotactic reaction. From these results, the oxidation state of H in the SrVO$_2$H film can be calculated to be $\sim 1$, that is, the doped H exists as hydride in the film.

References
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