

Investigation of oxidation states in oxyhydride SrVO₂H epitaxial thin filmsAkira Chikamatsu^{1,*}, Tsukasa Katayama¹, Keisuke Yamada¹, Kei Shigematsu², Tomoya Onozuka¹, Makoto Minohara³, Hiroshi Kumigashira³, and T. Hasegawa^{1,2}¹Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan²Kanagawa Academy of Science and Technology, Kawasaki, Kanagawa 213-0012, Japan³Institute of Materials Structure Science, KEK, Tsukuba, Ibaraki 305-0801, Japan

1 Introduction

Recently, oxyhydride SrVO₂H was synthesized from the parent oxide SrVO₃ via topotactic reaction using CaH₂ [1]. In SrVO₂H, the doped H⁻ anions occupy the axial position of VO₄H₂ octahedral units, resulting in a one-dimensional (1D) V-H-V bond network along the *c*-axis and a 2D VO₂ network in the *ab*-plane. Owing to the 1D-type hydride coordination, SrVO₂H has a tetragonal structure with a large *a/c* lattice ratio (*a* = 3.93, *c* = 3.66 Å). SrVO₂H 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 SrVO₂H 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 SrVO₂H films by combining pulsed-laser deposition (PLD) and topotactic hydride doping techniques, and investigated the oxidation states in the fabricated films.

2 Experiment

Perovskite SrVO₃ precursor thin films were fabricated on SrTiO₃(001) substrates using PLD. The obtained SrVO₃ precursor films were subsequently reacted with CaH₂ 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 SrTiO₃ 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 SrVO₂H film on SrTiO₃ substrate. Hydrogen ions were doped almost homogeneously throughout the film at a concentration of $\sim 1.9 \times 10^{22}$ atom/cm³. The hydrogen concentration in the film was very similar to that of bulk SrVO₂H, $\sim 1.8 \times 10^{22}$ atom/cm³ [1], which also supports the formation of SrVO₂H.

Figure 1(b) shows V 2*p* XAS spectra for the 15-nm-thick SrVO₃ and SrVO₂H films together with CaVO₃ and YVO₃ as references of V⁴⁺ and V³⁺, respectively [5]. The V L₃ and L₂ peaks were clearly observed in all spectra. The spectra of the SrVO₃ and SrVO₂H films are highly similar in peak shape and position to those of the CaVO₃ and YVO₃ 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 SrVO₂H film can be calculated to be –1, that is, the doped H exists as hydride in the film.

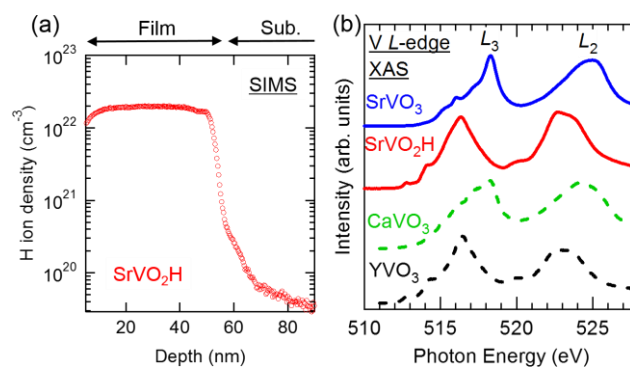


Fig. 1. (a) Dynamic SIMS depth profile of H ions for the SrVO₂H film. (b) V L-edge XAS spectra of the precursor SrVO₃ and SrVO₂H films, and the relevant spectra of CaVO₃ (V⁴⁺) and YVO₃ (V³⁺) [5].

References

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