

Room Temperature Proton Conduction of (111)-Oriented $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$ Thin Film

Tohru HIGUCHI^{1*}, Daiki NISHIOKA¹, Koji HORIBA² and Hiroshi KUMIGASHIRA^{2,3}

¹ Department of Applied Physics, Tokyo University of Science, Katsushika, Tokyo 125-8585, Japan

² Photon Factory, Institute of Materials Structure Science, High Energy Research Organization, Tsukuba, 305-0801, Japan

³ Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai 980-8577, Japan

The $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$ (SDC) electrolyte thin films with the spacing of the (111) plane (d_{111}) expanded by 2.6% to compensate for lattice mismatch against the Al_2O_3 (0001) substrate were prepared by RF magnetron sputtering. The wet-annealed SDC thin film exhibited surface protonic conduction in the low temperature region below 100°C. The O 1s photoemission spectrum exhibits H₂O and OH⁻ peaks on the SDC surface. These results indicate the presence of physisorbed water layers and the generation of protons on the SDC (111) surface with oxygen vacancies. The protons generated on the SDC surface were conducted through a physisorbed water layer by the Grotthuss mechanism.

1 Introduction

Fluorite-type $\text{CeO}_{2-\delta}$ oxides are good solid electrolyte candidates for solid oxide fuel cells (SOFC) due to their high oxygen ion conductivity in high-temperature (HT) regions above 800°C. In particular, the oxygen ion conduction of $\text{CeO}_{2-\delta}$ bulk crystal can be tuned by substituting trivalent rare earth cations, while small electron conduction also prevails under low-oxygen potential conditions owing to the formation of hopping electrons on cation sites through the propagation of oxygen nonstoichiometry. However, the operating temperature of SOFC is too high and the oxide ion conduction is not practical level.

In this study, in order to reduce the operating temperature, we prepared a preferentially oriented $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$ (SDC) electrolyte thin film on an Al_2O_3 (0001) substrate and investigated its proton conductivity at surface below 100°C.

2 Experiment

The SDC thin films were deposited on Al_2O_3 (0001) substrates by RF magnetron sputtering using a ceramic target. The ceramic target RF power and the Ar gas flow rate were set at 50 W and 30 sccm, respectively. The deposition pressure and the substrate temperature were fixed at 8.0×10^{-3} Torr and 700 °C, respectively.

The crystalline quality of the thin films was characterized by X-ray diffraction (XRD) with $\text{CuK}\alpha$ using a Rigaku Miniflex 600. The electrical conductivities were characterized by the AC impedance method, using a frequency response analyzer (Solartron 1260) and an amplifier (Solartron 1296). The measurement of the electrical conductivity

frequency region was changed from 32 MHz to 100 MHz.

The electronic structures were measured by photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS). The spectroscopic measurements were conducted at the Photon Factory BL-2A MUSASHI undulator beamline. The XAS spectrum were recorded in a total electron yield mode. PES spectra were acquired using a VG-Scienta SES-2002 hemispherical analyzer. The PES and XAS resolutions were set at approximately 100 and 80 meV, respectively.

3 Results and Discussion

Figure 1 shows the XRD patterns of the SDC ceramic, as-deposited and as wet-annealed SDC thin films. The ceramic was polycrystalline and the thin film was preferentially grown along the [111] direction. In this study, we prepared a nanocrystalline ceramic which, while exhibiting admittedly poor crystallinity, did exhibit sufficient proton conductivity to allow us to discuss the differences between the ceramic and thin film. The 111 peak positions of the SDC ceramic and as-deposited thin film are at $\sim 29.02^\circ$ and $\sim 28.31^\circ$, and the calculated spacing of the (111) plane (d_{111}) are 3.070 and 3.151 Å, respectively. The d_{111} of the thin film was expanded by 2.6% from that of the ceramic target, so as to compensate for the lattice mismatch between SDC and Al_2O_3 . In addition, at 3.091 Å, the d_{111} of the wet-annealed thin film was 1.9% less than that of the as-deposited thin film.

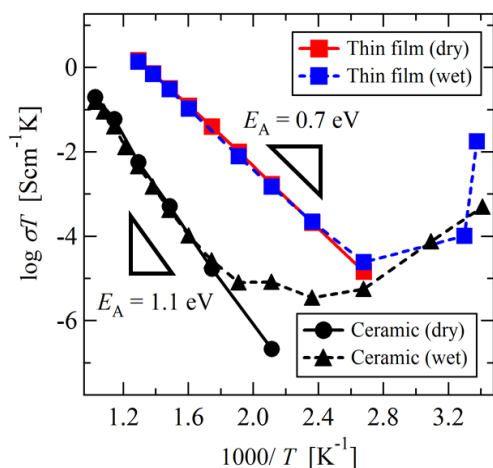


Fig. 1: XRD patterns of the as-deposited, wet-annealed SDC thin films and SDC ceramic.

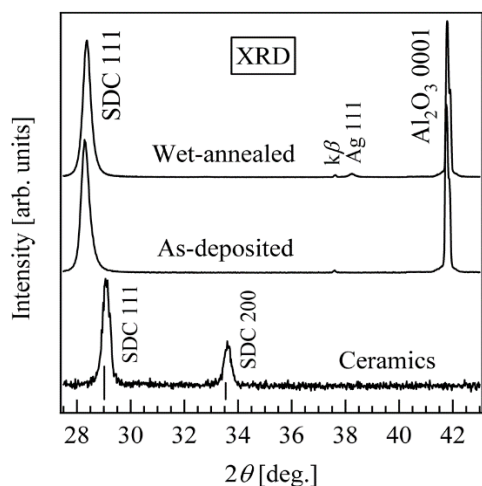


Fig. 2: Arrhenius plots of the electrical conductivities in the in-plane of the SDC thin films and bulk ceramics, measured in dry and wet atmospheres.

Figure 3 shows the Arrhenius plots of the electrical conductivities of the SDC thin films and bulk ceramics measured in dry and wet atmospheres. In the dry atmosphere, the SDC thin film and bulk ceramic exhibit Arrhenius-type thermal activation behaviors over the whole temperature range. The activation energies (E_A) of the thin film and bulk ceramic are 0.70 and 1.1 eV, respectively. The conductivity of the polycrystalline SDC ceramic was two orders of magnitude lower than that of the SDC thin film, due to the influence of grain boundaries.

In contrast, due to the proton migration, the conductivities of the thin film and the bulk ceramic measured in a wet atmosphere gradually increase as the temperature decreases to below 100 and 250°C, respectively. In particular, the increase in the conductivity ratio was more marked in the thin film. Single crystals and micropolycrystalline CeO₂ do not exhibit proton conductivity, but since such proton conduction is caused by absorbed protons at the

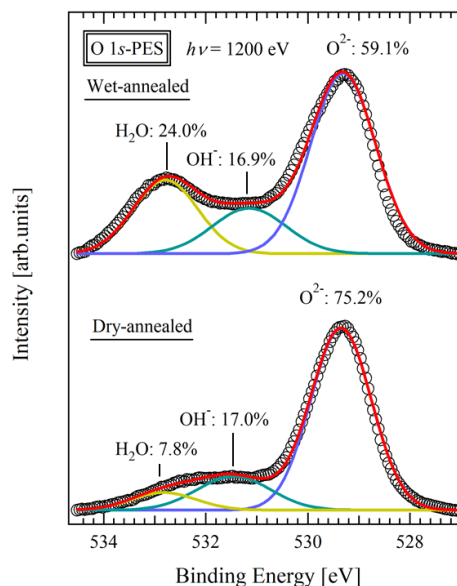


Fig. 3: O 1s core level PES spectra of dry- and wet-annealed thin films. The blue, green and yellow curves are the O²⁻ in the lattice site, and OH⁻ and H₂O on the surface, respectively, obtained from Gaussian fitting.

surface, nanopolycrystals and porous CeO₂ do exhibit proton conductivity.

In general, the room temperature surface proton conduction of fluorine-type oxides such as CeO₂ [1] or YSZ [2] is explained by the Grotthuss-mechanism. According to this mechanism, physisorbed H₂O forms OH⁻ and H₃O⁺ ions on the surface at room temperature and the H₃O⁺ proton transfers from one H₂O molecule to a neighboring H₂O molecule, as in the following reaction:

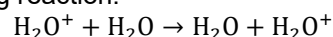


Figure 3 shows the O 1s PES spectra of the dry- and the wet-annealed thin films. Both exhibited a double-peak structure and a sharp peak at ~529.5 eV, which corresponds to O²⁻ in oxygen sites. On the other hand, the positions of the weaker peaks are different, and can be interpreted as follows: (i) the broad peak at ~532 eV in the as-deposited thin film corresponds to the OH⁻ absorbed at the surface created by chemisorbed water.; and (ii) the peak at 533 eV in the wet-annealed thin film corresponds to H₂O molecules physisorbed at the surface. The peak ratio of physisorbed H₂O was increased from 7.8% to 24% by wet-annealing. Thus, the increase in conductivity by wet-annealing reflects an increase in the physically adsorbed water molecules at the SDC surface.

A proton conductivity of 5.98×10^{-5} S/cm was achieved at room temperature in the preferentially oriented thin film, which is two orders of magnitude higher than that of polycrystalline ceramics. Most notable was the $\sim 10^{-2}$ S/cm proton conductivity exhibited in a high humidity atmosphere. Such high

proton conductivity is considered to derive from two features of the preferentially oriented SDC thin film with oxygen vacancy. The first feature is high water adsorbability on the SDC (111) surface. In the O1s PES spectrum, 16.9% of the detected oxygen was attributed to chemically adsorbed water and 24% was attributed to physically adsorbed water. This means that there are layers of physisorbed water on the SDC surface that can act as proton conducting paths. The second feature is the dissociation of adsorbed water at the SDC (111) surface. The reduced $\text{CeO}_{2-\delta}$ (111) surface promotes the dissociation of water molecules and the formation of OH^- and H^+ , which contribute to proton conduction. Dissociated protons can migrate through a physically adsorbed water layer by the Grotthuss-mechanism. Therefore, the preferentially oriented SDC thin film contributed to such high proton conduction.

References

- [1] D. Nishioka *et al.*, *Nanoscale Res. Lett.* **15**, 42 (2020).
- [2] M. Takayanagi *et al.*, *Solid State Ionics* **311**, 46 (2017).

Research Achievements

1. D. Nishioka *et al.*, *Nanoscale Res. Lett.* **15** (2020) 42.
2. M. Takayanagi, *et al.*, *Jpn. J. Appl. Phys.* **58** (2019) SODG08.

* higuchi@rs.tus.ac.jp