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

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The Ce$_{0.9}$Sm$_{0.1}$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$_2$O$_3$ (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 H$_2$O 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 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 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 Ce$_{0.9}$Sm$_{0.1}$O$_{2-\delta}$ (SDC) electrolyte thin film on an Al$_2$O$_3$ (0001) substrate and investigated its proton conductivity at surface below 100°C.

2 Experiment
The SDC thin films were deposited on Al$_2$O$_3$ (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 ºC, respectively.

The crystalline quality of the thin films was characterized by X-ray diffraction (XRD) with 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 ~29.02° and ~28.31°, respectively. 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$_2$O$_3$. 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.
Figure 1 shows the XRD patterns of the as-deposited, wet-annealed SDC thin films and SDC ceramic. The patterns reveal the presence of both the thin film and the ceramic phases.

Figure 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. The activation energies ($E_A$) for the thin film and ceramic are 0.70 and 1.1 eV, respectively. The conductivity of the thin film was two orders of magnitude higher than that of the ceramic, due to the influence of grain boundaries.

In contrast, due to the proton migration, the conductivities of the thin film and the ceramic measured in a wet atmosphere gradually increase as the temperature decreases to below 100°C. In particular, the increase in the conductivity ratio was more marked in the thin film. Single crystals and microporous CeO$_2$ do not exhibit proton conductivity, but since such proton conduction is caused by absorbed protons at the surface, nanoporous crystals and porous CeO$_2$ do exhibit proton conductivity.

In general, the room temperature surface proton conductance of fluorite-type oxides such as CeO$_2$ [1] or YSZ [2] is explained by the Grotthus-mechanism. According to this mechanism, physisorbed H$_2$O forms OH$^-$ and H$_3$O$^+$ ions on the surface at room temperature and the H$_3$O$^+$ proton transfers from one H$_2$O molecule to a neighboring H$_2$O molecule, as in the following reaction:

$$\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}_2\text{O}.$$

Figure 3 shows the O 1s PES spectra of the dry- and wet-annealed thin films. Both exhibited a double-peak structure and a sharp peak at ~529.5 eV, which corresponds to O$^{2-}$ 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 H$_2$O molecules physisorbed at the surface. The peak ratio of physisorbed H$_2$O 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 ~10$^{-4}$ 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 CeO$_2$-δ (111) surface promotes the dissociation of water molecules and the formation OH$^-$ and H$^+$, which contribute to proton conduction. Dissociated protons can migrate through a physically adsorbed water layer by the Grotthus-mechanism. Therefore, the preferentially oriented SDC thin film contributed to such high proton conduction.

References

Research Achievements

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