Fabrication of proton conducting thin films of SrZrO$_3$ and SrCeO$_3$ and their fundamental characterization

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Abstract

Proton conducting thin films of SrZrO$_3$ and SrCeO$_3$ were fabricated by the pulsed laser ablation method using ArF excimer laser. The thin films of SrCeO$_3$ and SrZrO$_3$ were grown in the [100] direction on the SrTiO$_3$(100) substrate and in the [211] direction on the MgO(100) substrate and on the Al$_2$O$_3$ substrate. The Raman scattering spectra show that the thin films grown in the low $P_{O_2}$ contain lots of oxygen ion vacancies compared to bulk crystals.

Keywords: Perovskite-type oxides; Pulsed laser ablation; Thin film

Materials: SrZrO$_3$; SrCeO$_3$

1. Introduction

The acceptor-doped perovskite-type oxides are known as high temperature proton conductors, which are promising materials for devices such as fuel cells, hydrogen sensors and so on [1]. It is known that the proton migrates in the interstitial sites around oxygen ions by hopping in crystals of these proton conductor [2–4]. However, the high proton conductivity in the acceptor-doped perovskite-type oxides has not been understood and the proton conduction mechanism is not yet clear. Raman scattering and XAFS studies of single crystals of these proton conductors suggest that the local lattice distortion caused by acceptor doping plays a very important role for the high proton conductivity [5].

The fabrication techniques of perovskite-type oxides thin films are developed for the growth of ferroelectric thin films, such as SrTiO$_3$ or BaTiO$_3$ [6]. The laser ablation technique is known to be suitable for growth of thin films of these ferroelectric oxides or perovskite-type high $T_c$ superconductors. In this study, the pulsed laser ablation technique was used to fabricate the proton conducting thin films. Studies on proton conductors grown on various substrates will give much information to clarify the relation between the lattice distortion and the proton conductivity. In this paper, the fabrication method of these thin films and their characterization are reported.

2. Experiments

The laser ablation system is shown in Fig. 1. An
Fig. 1. Laser ablation system used in this study. This system consists of two chambers: One is the ablation chamber and the other is the preparation chamber. The ablation chamber is equipped with a SiC heater (max. 1300°C), an RHEED system, a radical gun and a quadrupole mass spectrometer. The preparation chamber is equipped with an ion bombardment system and a lamp heater (max. 500°C). The MgF₂ window was used.

ArF excimer laser (wavelength 193 nm) was used as the ablation beam. The repetition rate is 1~4 Hz and the laser power is about 400 mJ at the exit mirror of the excimer laser. The ablation targets were sintered ceramics of undoped and acceptor doped SrZrO₃ and SrCeO₃. Single crystals of SrTiO₃, MgO and Al₂O₃ were used for substrates. The substrates and the targets are listed in Table 1 and Table 2, respectively. The films were grown in O₂ atmospheres of about 0.5~1 Pa and the substrates were heated at about 700~900°C. The substrate-target distance was 30~50 mm and target and substrate were rotated during the ablation. The ablation chamber was evacuated to 10⁻⁷ Pa before the oxygen gas introduction to the chamber. The laser ablation system is equipped with SiC substrate heater (max. 1300°C), radical gun (O radical and H radical), Reflection High Energy Electron Diffraction (RHEED) system and preparation chamber with ion bombardment (RF-sputtering system for substrate cleaning) and lamp heater (max. 500°C).

Total film thickness was about 1000~4000 Å. RHEED image was observed using 20 keV electron beam with diameter about 100 μm. X-ray diffraction (XRD) measurements were performed using the characteristic CuKα line. The Raman scattering study was performed at room temperature using a microscopic-Raman system. The Ar-ion laser (488 nm) was used as an excitation light.

3. Results and discussion

3.1. RHEED

RHEED patterns of SrCeO₃ were observed on the Al₂O₃ substrate and those of SrZrO₃ and SrCeO₃ were observed on the SrTiO₃ substrate. However, no RHEED pattern of SrCeO₃ was observed on the MgO substrate in this study. It is interesting that the RHEED pattern of SrCeO₃ can be observed on the Al₂O₃ and SrTiO₃ substrates but not on the MgO, of which crystal parameter matching for SrCeO₃ is better than that of Al₂O₃.

The RHEED patterns of the SrCe₀.₉₀Yb₀.₀₅O₃ film deposited on the SrTiO₃ (100) substrate are shown in Fig. 2. This pattern changed to (b) about 30 min after
was changed with film thickness. The pattern (a) was observed even at 750°C of substrate heater temperature, but it faded away soon. When the heater temperature was above 850°C, the RHEED pattern was observed till the end of the deposition.

The RHEED pattern observed on the Al₂O₃ substrate was similar to that of (a) in Fig. 2, but no pattern was observed when the deposition was terminated. The Al₂O₃ substrate surface is fairly flat suggested by the RHEED pattern of Al₂O₃ substrate surface. It is supposed that the SrCeO₃ film is well crystallized on the surface of Al₂O₃ up to several layers because of the flatness of the surface, while the crystallinity of the film should be influenced by a strong stress due to large lattice mismatch with the substrate when the film thickness reaches more than several layers.

3.2. X-ray diffraction

The X-ray diffraction spectra of the thin films deposited on the SrTiO₃ (100) substrates are shown in Fig. 3. The thin films were deposited at heater temperatures of 730°C–950°C and the substrate temperatures were about 100–150°C lower. The thin films of SrZrO₃ and SrCeO₃ were grown in the [100] direction of the SrTiO₃ substrate as shown in the figure. For SrCe₀.₉₅Yb₀.₀₅O₃ films, two unknown lines of 2.74 Å and 1.37 Å were observed. These

Fig. 3. XRD spectra of SrZrO₃ and SrCe₀.₉₅Yb₀.₀₅O₃ deposited on SrTiO₃ (100). Values in boxes are substrate heater temperatures. These films were grown in the [100] direction. However, the lines at the d-spacings of 2.74 Å and 1.37 Å correspond to the CeO₃ (200) and (400).
lines correspond to the (200) and (400) lines of CeO$_2$. It is interesting that the lattice parameter was 0.08 larger in the Sc-doped film than in the undoped film in SrZrO$_3$ films. This difference is often attributed to the large ionic radius of the acceptor ion. However, this lattice parameter enhancement due to the acceptor ion was not observed in SrCeO$_3$ films on the SrTiO$_3$ substrate.

The X-ray diffraction patterns of the thin films deposited on the MgO (100) substrates are shown in Fig. 4. The thin films of SrZrO$_3$ and SrCeO$_3$ were grown in the [211] direction as shown in this figure. The (211) line in undoped SrCeO$_3$ splits into three lines. These lines correspond to (002), (211) and (020) lines of SrCeO$_3$. The line splitting was not observed in the Yb-doped SrCeO$_3$ films.

The crystal structure matching for the SrZrO$_3$ and SrCeO$_3$ should be better on the SrTiO$_3$ substrate, which has the perovskite-type crystal structure similar to SrZrO$_3$ and SrCeO$_3$, than on the MgO substrate, while the lattice constant matching should be better on the MgO substrate. Thin films of SrCeO$_3$–SrZrO$_3$ solid solution were also grown in the [211] direction on the MgO substrate and the lattice parameter of these thin films was enlarged as the SrCeO$_3$ ratio increases.

The samples (a) and (b) of SrCeO$_3$ and SrCe$_{0.95}$Yb$_{0.05}$O$_3$ were grown under similar conditions. However, the spectra are different from each other. In samples (b), the CeO$_2$ peaks were observed and the lattice parameter were slightly enhanced compared with the samples (a). The reason for these differences is not clear.

The [100] direction of SrZrO$_3$ and SrCeO$_3$ corresponds to the [100] direction of cubic perovskite structure such as SrTiO$_3$, while the [211] direction of those corresponds to the [110] direction of SrTiO$_3$. Thin films of SrZrO$_3$ and SrCeO$_3$ grow in the same direction as SrTiO$_3$ on the SrTiO$_3$ substrate, while they grow in the [110] direction on the MgO and the Al$_2$O$_3$ substrates. The X-ray diffraction results suggest that the growth direction of the thin films depends on the arrangement of atoms of substrate but not on its lattice parameter.

3.3. Raman scattering

Raman scattering spectra of proton conducting thin films and single crystals are shown in Fig. 5. The Raman spectra of the thin films and the single crystals resemble each other. However, in the thin film of SrCe$_{0.95}$Yb$_{0.05}$O$_3$, the high frequency modes above 500 cm$^{-1}$ and the Raman band at about 350 cm$^{-1}$ shift to higher frequency compared to those in single crystals. The Raman bands around 300–375 cm$^{-1}$ correspond to the CeO$_2$ stretching modes on the analogy of those in BaCeO$_3$ [7]. It is suggested that the Raman structure around 500–700 cm$^{-1}$ is

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Fig. 4. XRD spectra of SrZrO$_3$, SrCeO$_3$, and their solid solutions (SrZrO$_3$–SrCeO$_3$) deposited on MgO (100). Arrows at the bottom of this graph indicate the (211) and (422) of SrZrO$_3$ and SrCeO$_3$. The impurity line marked with `X` is the CeO$_2$ (200) line.
connected with distortion due to oxygen ion vacancies [7]. It is recognized that the oxygen vacancy concentration in this thin film is larger than in the bulk single crystals.

On the other hand for SrCe$_{0.95}$Yb$_{0.05}$O$_3$ thin films which were grown under high oxygen gas pressure or under O-radical irradiation, those frequency shifts were not observed and the intensity of the high frequency modes above 500 cm$^{-1}$ is not so different from that in the single crystal of SrCe$_{0.95}$Y$_{0.05}$O$_3$. The impurity structure at 455 cm$^{-1}$ corresponds to the Raman band of CeO$_2$, which is consistent with the result of X-ray diffraction.

4. Summary

Proton conducting thin films of SrZrO$_3$, SrCeO$_3$, and SrCeO$_3$–SrZrO$_3$ solid solution were fabricated by the pulsed laser ablation method. The films were grown in a certain direction depending on the substrates. The synthesized thin films contain high concentrations of oxygen ion vacancies when deposited in 0.5 Pa O$_2$, decreasing when O-radicals were irradiated or in higher oxygen gas pressure, as indicated by the Raman scattering study. The X-ray and Raman experiments showed that the SrCeO$_3$ thin films are contaminated by CeO$_2$, which is a serious problem for fabrication of proton conducting thin films of good quality.

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References