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Fabrication and ionic conductivity of oriented lanthanum silicate films with apatite-type structure

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ABSTRACT

We have successfully fabricated *c*-axis oriented films of apatite-type lanthanum silicate (LSO) using sputtering technique. Two kinds of thin films, La_2SiO_5 and $La_2Si_2O_7$, were successively deposited on yttria-stabilized zirconia (YSZ) or La-doped $SrTiO_3$ (STO) single crystal substrates by RF magnetron sputtering in pure Ar atmosphere at room temperature. Annealing the films in air at 1100 °C promoted the crystal formation. A surface layer of the obtained specimens were *c*-axis oriented apatite-type LSO, which was confirmed by in-plane and out-of-plane X-ray diffraction patterns. An activation energy of the ionic conductivity of the LSO sample using STO substrate was 0.74 eV, which agrees well with that of polycrystalline $La_{9.33}Si_6O_{26}$ though the conductivity is as low as 2×10^{-5} S cm^{-1} at 600 °C. Using the laminated thin film method, we have accomplished to fabricate *c*-axis oriented apatite-type LSO with shorter time and lower temperature than the bulk diffusion synthesis between La_2SiO_5 and $La_2Si_2O_7$.

1. Introduction

Solid oxide fuel cells (SOFC) shows the highest power generation efficiency among various fuel cells and is used for combined heat and power systems. Nowadays, only yttria-stabilized zirconia (YSZ) is used for the electrolyte material in commercialized SOFCs. Operation temperature of the YSZ system is relatively high, typically 750–1000 °C, and expensive heat-resistant material is necessary for assembling the system. Operation at high temperature also causes the degradation of the product due to heat stress.

Apatite-type lanthanum silicate (LSO) based electrolytes exhibit high ionic conductivity, low activation energy for oxide-ion conduction and high ionic transference number at intermediate temperature (600–800 °C) [1–4]. Therefore, this material is considered to be a good alternatives to YSZ [5]. These characteristics help to increase a range of available material for SOFC products, making the cost and life time more advantageous than the YSZ system which is used commercially.

A unit cell structure of apatite-type LSO is shown in Fig. 1. Oxide ions locate at several sites in the structure and those of the site along the *c*-axis are responsible for the ionic conduction [6–10]. Nakayama et al. reported that the conductivity component parallel to the *c*-axis was higher than the perpendicular component by the ionic conductivity measurements on the apatite-type $La_{9.33}Si_6O_{26}$ single crystal [11]. Thus the *c*-axis oriented apatite-type LSO is expected to be used as a high-output SOFC. Attempts have been made to prepare *c*-axis oriented electrolyte films. Nakayama et al. have used strong magnetic force to order the grains [12]. Fukuda et al. have prepared *c*-axis oriented polycrystalline LSO by heating sandwich-type diffusion couples of La_2SiO_5 and $La_2Si_2O_7$ [13–16]. This work showed that *c*-axis oriented apatite phases can be prepared by contact boundary phase reaction between La_2SiO_5 and $La_2Si_2O_7$. The pellets which combined La_2SiO_5 and $La_2Si_2O_7$ were used as precursor and thickness of the specimen was about 1 mm after heated at 1600 °C for 100 h. If pellets were changed to films, *c*-axis oriented apatite-phase is expected to be prepared with lower temperature and shorter time. Recently, Hori et al. reported that *c*-axis oriented films were successfully prepared by a simple chemical solution deposition method [17]. They obtained *c*-axis oriented LSO thin films by heating spin-coated sol-gel films at 900 °C for 2 h. The obtained films, however, were rather porous and the ionic conductivity was not revealed.

The purpose of our study is to develop a more cost-effective procedure to make thin films of electrolyte which can be used for SOFCs having high power densities at intermediate temperature. We tried to prepare the *c*-axis oriented thin films with apatite phase using RF magnetron sputtering. Here we report fabrication, crystal structure, composition and conductive properties of the thin films. We have demonstrated that *c*-axis oriented thin films with apatite-type LSO can be prepared by annealing the laminated films of La_2SiO_5 and $La_2Si_2O_7$.

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2. Experimental

2.1. Synthesis

Two kinds of LSO compounds were used as target materials for sputtering. La_2SiO_5 and $La_2Si_2O_7$ were prepared by solid-state reactions in air. Well-grind mixtures of La_2O_3 and SiO_2 powders were heated in a Pt crucible at 1600 °C in air for 3 h. La_2O_3 was annealed at 800 °C for 3 h to remove hydroxides before mixing.

Resultant powders were filled in stainless cups for use as sputtering targets. LSO thin films were deposited by RF magnetron sputtering (E-200S, Canon anelva corporation) on single crystal substrates of yttria-stabilized zirconia (YSZ (111)) and La-doped $SrTiO_3$ (STO (100)) in Ar atmosphere. The sizes of YSZ and STO substrates were 10 × 10 × 0.5 mm and ϕ15 mm × 0.5 t mm, respectively. Firstly, La_2SiO_5 was deposited on substrates, La_2SiO_5/substrate, followed by $La_2Si_2O_7$ deposited with the same condition, $La_2Si_2O_7$/La_2SiO_5/substrate. The targets power was 70 W, sputtering time was 3 h or 4 h with one target at a pressure of Ar 0.5 Pa. Subsequent thermal annealing of the samples were carried out at 1100 °C for 1 h in air.

2.2. Characterization

The thickness of the films was measured using a stylus type step profiler. The phase purity and crystal structure were characterized by X-ray diffraction (XRD; SmartLab, Rigaku corporation). The out-of-plane and in-plane diffraction profiles were collected using a diffractometer with Cu Kα radiation (45 kV, 200 mA) over a 2θ range from 10° to 60° with a step intetrval of 0.01°. In the case of in-plane measurements, the incident angle of X-ray was 0.5° with respect to the surface, whereas out-of-plane measurements were performed with a typical θ-2θ configuration. The elemental compositions of the films were determined by Electron Probe Microanalysis (EPMA; JXA-8230, Jeol Ltd.). Morphology of surface and cross-section of the thin films was examined with a field emission scanning electron microscope (FE-SEM; JSM-7610F, Jeol Ltd.). Prior to the SEM analysis, the observed samples were coated with a thin carbon layer to improve electrical conduction. The elemental depth profiles of the films were investigated by X-ray Photoelectron Spectroscopy (XPS; PHI5000 versa probe II, Ulvac-phi, Inc.) using monochromated Al Kα radiation with an intermittent Ar ion beam etching of 3 kV.

Conductivity measurements were made for the annealed films on STO substrates by an AC impedance analyzer. A two-terminal method was employed to measure conductivity perpendicular to the substrate so that the top face of the film and the back face of the substrate were sputter-coated with Pt—Pd electrodes to make electrical contacts, Pt-Pd/LSO films/STO substrate/Pt-Pd. The measurements were performed at temperatures from room temperature to 600 °C with a step of 50 °C with frequencies ranging from 10 MHz to 0.1 Hz using a Solartron 1260 impedance analyzer. The bulk conductivities were separated from the grain boundary and the electrode contributions by Nyquist plots of the AC impedance data and calculated using the geometric factors [6]. The activation energy was evaluated from a slope in an Arrhenius plot of the bulk conductivity at temperatures from 400 °C to 600 °C.

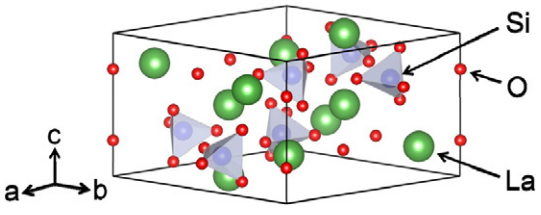

Fig. 1. Crystal structure of apatite-type lanthanum silicate.

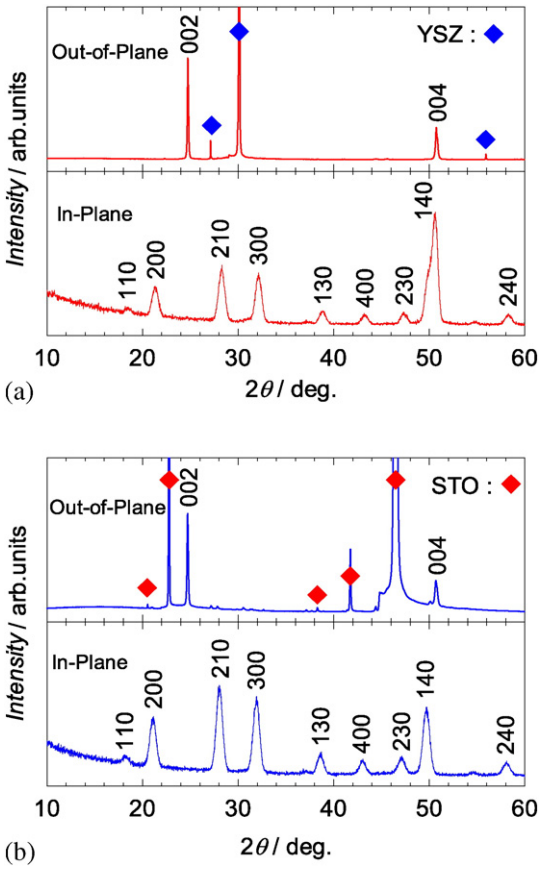

Fig. 2. In-plane and out-of-plane XRD patterns of the La_2SiO_5/$La_2Si_2O_7$ films deposited on a single crystal substrate of (a) YSZ and (b) STO, after annealing for 1 h at 1100 °C. The incident angle of X-ray was 0.5° in the in-plane XRD measurements.

3. Results and discussion

3.1. Characterization of the samples

Total thicknesses of the as sputtered films measured with a step profiler were about 1.5 μm for the LSO film on YSZ substrate and 1.3 μm for the LSO film on STO, respectively, because the sputtering time of the LSO film on YSZ was slightly longer than the LSO film on STO. These thicknesses correspond to the deposition rate of about 200 nm/h.

XRD measurements of all as sputtered films showed broad halos around 25–35° indicating amorphous phase before the annealing. Fig. 2(a) shows out-of-plane and in-plane XRD patterns of the annealed LSO film on YSZ. All the diffraction peaks in the XRD patterns except those of the YSZ substrate could be indexed on the basis of an apatite-type LSO phase. The out-of-plane data only shows 002 and 004 peaks, while in the in-plane data hk0 peaks are observed with 00l peaks unobserved. These two profiles clearly demonstrate that the obtained LSO film on YSZ is *c*-axis oriented. Fig. 2(b) shows X-ray diffraction patterns of the annealed LSO film on STO which also reveal the 002 and 004 peaks are observed in the out-of-plane profile, while the in-plane profile shows a similar behavior as the annealed LSO film on YSZ. These XRD

Table 1
La/Si atomic ratio of the as sputtered sample.

Specimen	La/Si atomic ratio
La_2SiO_5/YSZ	2.86
$La_2Si_2O_7$/YSZ	1.32