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Synthesis, structure, and electrochemical properties of epitaxial perovskite $La_{0.8}Sr_{0.2}CoO_3$ film on YSZ substrate

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Abstract

Epitaxial films of the perovskite, $La_{0.8}Sr_{0.2}CoO_3$ (LSC), for SOFCs cathode were deposited on yttria-stabilized zirconia (YSZ) single crystals by pulsed laser deposition method. The films were characterized by thin-film X-ray diffraction measurement, atomic force microscopy (AFM), transmission electron microscope (TEM), and ac impedance spectroscopy. The film orientations depend on the substrate planes. The LSC films on the YSZ (100) and (111) substrates showed the (110) orientation with different twin structures, while those on the YSZ (110) had (100) and (112) orientations. Surface morphology of the films also depends on the substrate orientations. These films showed different electrode properties depending on the orientations. The relationships between the properties, the film orientations, surface morphology, and lattice misfit are discussed.

Keywords: SOFCs; LSC; Pulsed laser deposition; Epitaxial films

1. Introduction

Solid oxide fuel cells (SOFCs) are a promising candidate for future power generation systems because of their simple cell design, high efficiency for energy conversion, and high quality of by-product heat [1,2]. However, high operating temperatures restrict the application fields of the SOFCs; if the operating temperature can be lowered by several hundred degrees, variety of uses will be expected, for example, to small-scale consumer systems and this will reduce the cost of the fabrication.

The perovskite metal-oxides have been proposed for oxygen reduction at the cathodes of SOFCs. For example, the Mn-based perovskite, $La_{1-x}Sr_xMnO_3$ (LSM), is widely used in terms of high electrode activity [3], high chemical stability [4], and consistency of the thermal expansion coefficient with yttria-stabilized zirconia (YSZ) [1]. On the other hand, the Co-based perovskite, $La_{1-x}Sr_xCoO_3$ (LSC) shows higher electronic and ionic conductivities than the LSM, which provides higher catalytic activity and thus electrode properties, although the LSC reacts with YSZ at 1000 °C and forms low conductivity products, $La_2Zr_2O_7$ and $SrZrO_3$ [4]. The LSC should be a good candidate for the cathode of SOFCs with intermediate operating temperatures of 500∼700 °C.

It is well known that the cathode reaction in SOFCs proceeds at the three-phase boundary of oxygen gas, the YSZ electrolyte, and the perovskite electrode. In order to decrease the cathode overvoltage and to reduce the SOFCs operating temperatures, it is necessary to understand the limiting factors that influence the oxygen reduction process. The whole electrode process could be divided into successive single processes, gas adsorption, dissociation, charge transfer, and ion-diffusion across the interface between the electrode and the electrolyte, and this makes easier to estimate the kinetic of the individual process [5,6]. Several approaches have been reported to understand each electrode process quantitatively, and to control the reaction path and the length of three-phase boundary. For these mechanistic studies, several types of electrodes were used: the dense film electrodes [7,8], pattern electrode [9,10], and point electrode [11] with polycrystalline state. However, these electrodes contain grain boundary, surface defects, or even impurity

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phases, and these factors might significantly affect their electrode properties. Furthermore, the catalytic activities are expected to depend on the atomic arrangements of the surface of the perovskite lattice.

In the present study, we tried to clarify the cathode reaction process of SOFCs using ideal electrode reaction fields based on single crystal surface. We successfully grew the epitaxial thin-film electrode of the LSC on the single crystal substrate of the YSZ by pulsed laser deposition (PLD) method. Our system has a simple electrode structure with two-phase boundary. The orientation of the LSC was successfully controlled depending on the substrate orientation. The orientations, crystal structures, microstructures, and surface morphology of the deposited films were determined. The relationship between the film characteristic and electrochemical properties was discussed.

2. Experimental

$La_{0.8}Sr_{0.2}CoO_3$ (LSC) thin films were prepared by PLD method. La_2O_3, $SrCO_3$, and Co_3O_4 used as starting materials were weighed, mixed, pelletized, and calcined at 1000 °C for 12 h. The pellet was crushed and pressed again into a disk with 20 mm in diameter using a cold isostatic press and a pressure of 20 MPa. The pellet was sintered at 1300 °C for 24 h and used as a target for PLD. Single crystals of yttria-stabilized zirconia (YSZ) (Furuuchi Chemical Corporation) with a cubic lattice were used as the substrate. The YSZ substrates with a size of $10\times10\times0.5$ mm and the crystal planes (100), (110), and (111) were used. The deposition was performed for 1 h using KrF excimer laser ($\lambda=248$ nm, Lambra Physik COMPex 102). The laser beam energy was set at 200 mJ/pulse and repetition rate was 10 Hz. The substrates were kept at 600∼800 °C. They were positioned 7.5 cm away from the target and 2 cm off from the center of the plume to avoid direct exposure to the plume. Oxygen gas was flowed into the chamber to show pressure of 0.025 Torr.

Thin-film X-ray diffraction (XRD) was measured with a Rigaku ATX-G diffractometer using monochromatic CuKα1 line generated at 50 kV, 300 mA. The scattering geometry is schematically illustrated in Fig. 1. The out-of-plane and the in-plane measurements gave the orientation and structure normal and parallel to the substrate plane, respectively. The epitaxial growth of the film was confirmed by the ϕ-scan in the substrate plane. The microstructure of the films was observed by a transmission electron microscope (TEM) Hitachi H-9000 with top-entry system. The accelerating voltage was 300 kV and the magnification on the film was 4000 to 300,000 by selected area mode. The thin-film samples for TEM observations were prepared by ion milling method. The surface morphology of the films was also investigated by atomic force microscopy (AFM, Digital Instruments Nanoscope IV).

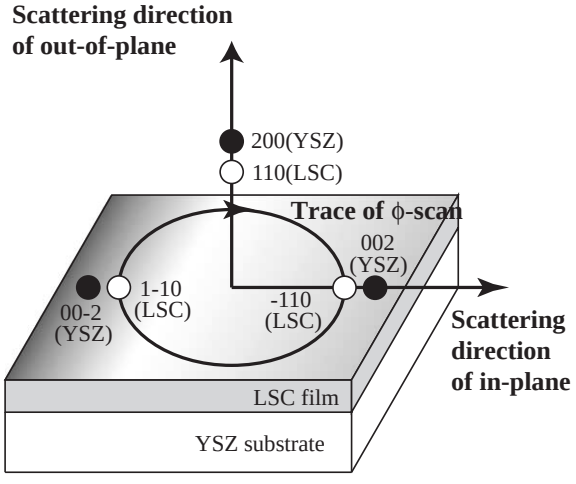

Fig. 1. Schematic illustration of X-ray scattering geometry.

Electrochemical impedance spectra were obtained using Solartron 1260 frequency response analyzer and 1287 potentiostat. The 5 mV alternating current was applied between reference and working electrode in addition to the spontaneous d.c. potential (open circuit potential). The applied frequency ranged from 1 M over 0.1 Hz which could cover both fast process like migration in electrolyte and high capacity process like charge transfer on electrode. The electrochemical measurements were performed at 700 °C under 0.20 atm of oxygen pressure.

3. Results and discussion

3.1. Out-of-plane XRD

Fig. 2 shows the out-of-plane XRD patterns for the LSC films on the different substrate planes, YSZ (100), (110), and (111). The patterns indicate the orientation normal to the substrate plane. The LSC films on the YSZ (100) and (111) planes showed the reflections near 33° and 70° which were indexed as 110 and 220, respectively, based on the cubic perovskite lattice. This indicates the LSC (110) orientation on the YSZ (100) and (111) planes. The lattice parameters varied with the substrate orientation and are calculated to be 3.791 and 3.813 Å for the LSC films on the YSZ (100) and (111), respectively. No reflection was found in the out-of-plane measurements for the LSC on the YSZ (110). It is suggested that this is influenced by lower crystallinity normal to the substrate plane of the LSC on the YSZ (110).

3.2. In-plane XRD, LSC on YSZ (100)

The in-plane XRD was measured for the LSC films on the YSZ (100). The measurements along YSZ [002] direction indicated the −110, −220, 001 and 002 reflections. Fig. 3 shows the ϕ-scan of LSC-110 reflection in the substrate plane. The reflections observed every 90° are indicative of a four-fold symmetry, which contradicts a two-fold symmetry of −110 in the cubic lattice. The LSC film has therefore twin structure with each domain separated by 90°.

3.3. LSC on YSZ (111)

The in-plane orientation was measured for the LSC films on the YSZ (111). The 1-11 reflection of the LSC was observed