Characteristics of LaGaO₃ Based Perovskite Films Prepared by Pulsed Laser Deposition

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A doped lanthanum gallate of $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_{2.8}$ (LSGMCO) is useable as an electrolyte of a solid oxide fuel cell because of its high oxygen ion conductivity. We prepared the LSGMCO films on porous Ni substrates, which is used as an electrode of the SOFC, by KrF excimer pulsed laser deposition technique with a laser energy of 300 mJ and a repetition rate of 10Hz. LSGMCO films were poly-crystallized on Ni porous substrates in the case of a substrate temperature of 800°C. The grain size of the LSGMCO thin film deposited onto the porous Ni substrate for 10min. was 300-600 nm in a diameter when the oxygen pressure was 133 Pa and the substrate temperature was 800°C and grains were also deposited on the side wall of the substrate. We could control the grain size of the film by changing the oxygen pressure without losing its crystallinity. The smooth and dense LSGMCO film was prepared on the porous Ni substrate after 3 hours deposition.

Key words: Solid Oxide Fuel Cell, LSGMCO, Porous Substrate, Pulsed Laser Deposition

1. INTRODUCTION

LaGaO₃ based perovskite materials such as $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ (LSGMO) [1-11] and $La_{1-x}Sr_xGa_{1-y-z}Mg_yCo_zO_{3-(x+y+z)}$ (LSGMCO) [12,13] have a high oxide ion conductivity and are promising candidates for electrolytes of solid oxide fuel cells (SOFCs). Typical SOFCs use bulks or thick membranes of yttria stabilized zirconia as electrolytes and operate at around 1000°C. This high operating temperature causes a high energy conversion efficiency of the SOFCs. However, there is a material limitation as for an interconnect part between cells.

Then, thin film preparation techniques of the electrolyte material on the porous electrode of the SOFC are needed for the low temperature operation in order to increase the lifetime and decrease costs of materials, the fabrication process and the operation of the SOFC. Several techniques such as a tape casting [14], a screen printing and a sputtering [15] have been employed to make a film of the electrolyte in other works.

In this work, we fabricated LSGMCO thin films by pulsed laser deposition (PLD) technique on quartz, LaAlO₃ and porous Ni substrates. The PLD is an available method to prepare thin films with multi-components due to its superior controllability of stoichiometry.

2. EXPERIMENTAL PROCEDURES

A KrF excimer laser (Lambda Physik, COMPex 110, maximum energy=350 mJ, pulsed duration=30 ns, λ=248 nm) was introduced into a stainless chamber (Φ=400 mm) through a lens, mirrors and a quartz window and focused on a $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_{2.8}$ bulk (Φ=30 mm, t=5 mm) target at an incident angle of 45° with a laser energy density of 3J/cm² (laser energy=300 mJ, spot size=5x2 mm²) and a repetition rate of 10 Hz. The LSGMCO target was prepared by mixing powders of La₂O₃, SrCO₃, Ga₂O₃, MgO and CoO in stoichiometric proportions. The influence of stoichiometry of LSGMCO bulk and optical emission of plasma plume ablated from the target were reported in elsewhere [12,16].

Quartz and LaAlO₃ substrates were used to optimize deposition conditions for crystallization of the film. LSGMCO films were deposited on porous Ni (anode electrode of the SOFC) substrates for 10-180 min. Fig.1 shows surface morphology of the porous Ni substrate. There are many holes with the size of several μm.

A substrate temperature and an oxygen pressure during the deposition were varied from R.T. to 800°C and from vacuum (10⁻³Pa) to 133 Pa, respectively. The substrate temperature and the oxygen pressure dependence of the crystallinity, surface morphology and electric property of the LSGMCO films were measured

by following methods. Crystallinity of the LSGMCO thin films was characterized by X-ray diffraction (XRD: Rigaku, RINT2000) with a CuKα line. Surface morphologies were observed by field emission scanning electron microscopy (FESEM: Hitachi, S4500). Secondary ion mass spectroscopy (SIMS: ATOMICA Instruments, Ion Miocroprobe 4100) was used to measure the composition.
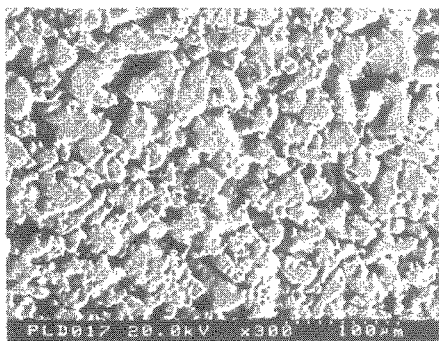

Fig.1   The surface morphology of porous Ni.

3. RESULTS AND DISCUSSION

LSGMCO thin films were prepared on quartz substrates at the various substrate temperature to find an optimal temperature for the crystallization. It was found that a substrate temperature of 800°C was needed to obtain polycrystalline LSGMCO thin film with the same stoichiometry as the target. The LSGMCO thin film exhibited the one order magnitude higher ion conductivity compare to that of the YSZ bulk.

A c-axis oriented LSGMCO thin film was obtained when a LaAlO₃ single crystal was used as the substrate. This result is due to the small lattice mismatch (+2.4%) between the LSGMCO and LaAlO₃ single crystal. The detail study on properties of the LSGMCO thin films prepared on the quartz and LaAlO₃ substrates were reported in elesewhere [17].

In order to obtain an electro-motive force from a SOFC, a dense LSGMCO film without the fuel gas leakage should be deposited on a porous substrate. Therefore, the growth style of the LSGMCO film on the porous substrate, especially the grain size of the film was studied.

The initial stage for the deposition of the LSGMCO thin film on the porous Ni substrate was observed by the FESEM. Fig.2 shows FESEM images for the substrate temperature and the oxygen pressure dependence of the surface morphologies of the LSGMCO thin films deposited on the porous Ni substrates for 10min. The distance between the target and the substrate was constant (45 mm). Because ablated species from the LSGMCO target have less reaction with the atmosphere in vacuum, the deposition rate was very low and grains were not observed clearly in the vacuum pressure of 10⁻³

Pa. The grain size was increased with the increase of the oxygen pressure. However, LSGMCO thin films deposited at the substrate temperature of R.T. and the pressure of vacuum (10^{-3} Pa) – oxygen (133 Pa) were not crystallized and liable to come off due to the low migration energy at the surface of the substrate. On the other hand, LSGMCO thin films prepared at the substrate temperature of 800°C were poly-crystallized (Fig.4). The average grain diameter of the LSGMCO thin film deposited at the oxygen pressure of 20 Pa and 800°C was 60 nm. It is too small compare to the size of porous part to make a dense thin film on the porous substrate. The grain size of the LSGMCO thin film deposited at the oxygen pressure of 133 Pa and 800°C was 300-600 nm, which is several times larger than that of the thin film prepared at the oxygen pressure of 20 Pa. In the case of the oxygen pressure of 1333 Pa and the substrate temperature of 800°C, the deposited film showed the amorphous phase and grain size was the same as that of the film prepared at 133 Pa oxygen pressure. We suppose that higher oxygen pressure resulted in more collisions between ablated species and oxygen gas under the oxygen pressure range of 20 – 133 Pa and relatively large grains were formed in the gas phase and transported onto the substrate.
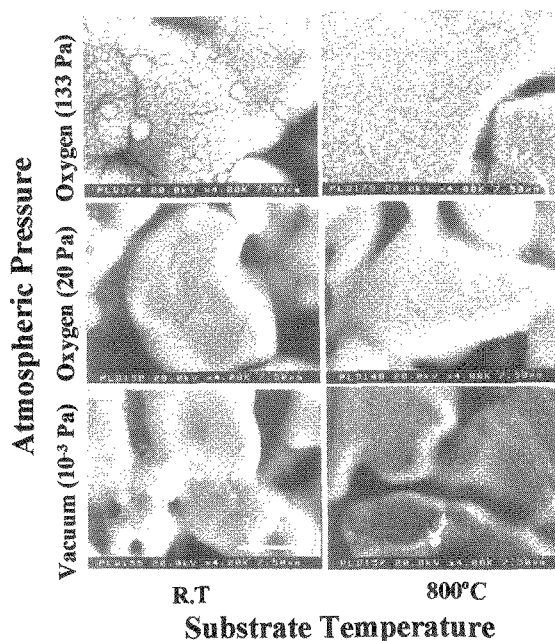

Fig.2   The substrate temperature and oxygen pressure dependence of surface morphologies of LSGMCO thin films deposited on porous Ni substrates for 10min.

Fig.3 shows the FESEM image for the growth of the LSGMCO thin film at the porous part of the substrate

deposited at the substrate temperature of 800°C and the oxygen pressure of 133 Pa for 10min. As can be seen, the grains having the diameter above mentioned were deposited on not only the flat part but also the side wall of the porous part of the porous Ni substrate. This growth style is one of important factors for making electrolyte films with the mechanical strength and without the fuel gas leakage. The long time deposition is needed for covering the porous substrate.

Fig.3   The FESEM image for the porous part of the LSGMCO thin film deposited at the substrate temperature of 800°C and the oxygen pressure of 133 Pa for 10min.

Fig.4   XRD spectra for dependence of the oxygen pressure ((a) Vacuum (10^{-3} Pa), Oxygen of (b) 20 Pa and (C)) during the deposition of LSGMCO thin films on porous Ni substrates at 800°C for 10min.

Fig. 4 shows XRD (θ-2θ scan) spectra for the LSGMCO thin films prepared on the porous Ni substrates at 800°C and (a) vacuum (10^{-3} Pa), (b) oxygen pressure of 20 Pa and (c) oxygen pressure of 133 Pa. The detector (2θ) range and angular resolution of the measurement were 20-80° and 0.01°, respectively. The peak identification was based on the JCPDS card of LaGaO$_3$. The thickness of the LSGMCO thin film deposited at the vacuum (10^{-3} Pa) was very thin and the grains were not observed clearly in Fig.2. However, as can be seen in Fig.4 (a), peaks from the poly-crystalline LSGMCO thin film and from the Ni substrate were observed. Peak positions of this XRD spectrum showed good agreement with those of the LSGMCO thin film deposited on the quartz substrate. Since the LSGMCO has oxygen deficiencies in the lattice originally, the thin film is easy to crystallize in the vacuum pressure but the grain size is too small to cover the porous substrate. When the oxygen pressure was 20 – 133 Pa, strong LSGMCO poly-crystalline peaks appeared. We could change the grain size of the LSGMCO thin film with keeping its crystallinity by varying the oxygen pressure during the deposition.
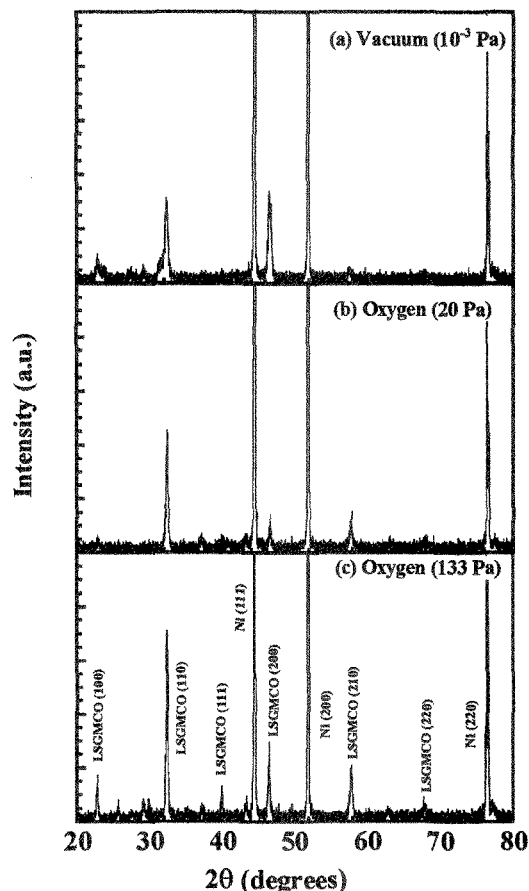
We deposited LSGMCO films for relatively long time at the laser repetition rate of 10 Hz, the substrate temperature of 800°C and the oxygen pressure of 133 Pa to cover the surface of the porous Ni substrate. Surface morphologies of the LSGMCO films after 1 hour and 3 hours deposition are shown in Fig.5 (a) and (b), respectively. As can be seen in Fig.5 (a), the surface of the LSGMCO film after 1 hour deposition was relatively rough and there were holes owing to the influence of the porous part of the substrate. This film may have the fuel gas leakage and is not suitable for the electrolyte film. On the other hand, the dense and smooth surface morphology was observed from the LSGMCO film deposited for 3 hours (Fig.5 (b)).
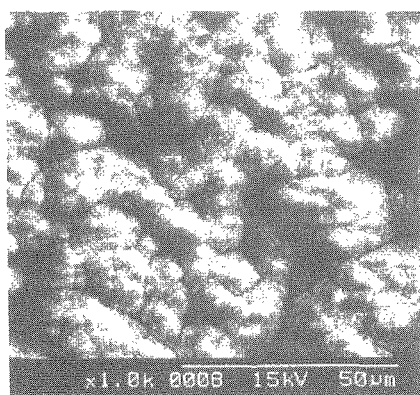
(a) 1 hour deposition

(b) 3 hours deposition

Fig.5 Surface morphologies of the LSGMCO films deposited on porous Ni substrates at the substrate temperature of 800°C and the oxygen pressure of 133 Pa for (a) 1hour and (b) 3 hours.

4. CONCLUSIONS

We prepared films of the LSGMCO which is one of candidates for electrolyte of the SOFCs on the porous Ni substrates by the KrF excimer pulsed laser deposition technique. LSGMCO films were crystallized under the deposition pressure range from vacuum (10^{-3} Pa) to oxygen 133 Pa when the substrate temperature was 800°C. Grains were not confirmed clearly from the LSGMCO thin film deposited at the vacuum (10^{-3} Pa). The grain size of the LSGMCO thin film deposited for 10min. was 300-600 nm in diameter when the oxygen pressure was 133 Pa and grains were deposited on the side wall of the porous Ni substrate. We could control the grain size of the film by changing the oxygen pressure without losing its crystallinity. It was found that holes of the porous substrate had an influence on the surface morphology of the LSGMCO film. However, the smooth and dense LSGMCO film was prepared on the porous Ni substrate after 3 hours deposition.

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