Optimization of deposition conditions of yttrium doped-SrZrO₃ thin films fabricated by pulsed laser deposition

Hiroki TANAKA¹, Kiyoshi UCHIYAMA², Takao SHIMIZU¹ and Hiroshi FUNAKUBO¹

¹Department of Innovative and Engineered Material, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226–8502, Japan
²Department of Creative Engineering, National Institute of Technology, Tsuruoka College, 104 Inooka Sawada, Tsuruoka, Yamagata 997-8511, Japan

A SrZrO₃ thin film with yttrium (Y) concentration of 20 at % (SZYO) was successfully deposited by the pulsed laser deposition (PLD) technique. The laser power of PLD affected Y-concentration significantly even though it used the same PLD target. On contrary, the laser reputation frequency and the deposition temperature did not significantly affect the composition. The SZYO film deposited at the optimized conditions was well crystallized and showed no secondary phase and showed (111) and (110) orientations when they were deposited on (111)Pt/SiO₂/Si and on (111)Pt/SiO₂/Si substrates, respectively. This SZYO film is expected to use as an electrode of our proposed novel solid oxide fuel cells.

Key-words : Proton conductive, Perovskite oxide, Thin film, Fuel cell

1. Introduction

Proton conductive perovskites were discovered by Ishihara et al.¹ and considered to be one of the candidates for electrolytes to achieve solid oxide fuel cells (SOFCs) operating at an intermediate temperature (IT) (400–600 °C) range, which is so-called as IT-SOFCs.²⁻⁵ Especially, Ito et al. reported excellent SOFC operations as low as 400 °C.⁴ We also reported low temperature operation of an SOFC fabricated at 400 °C on a Pd plated porous stainless steel substrate.⁵⁻⁸

In these perovskite-based proton conductive oxides, proton is transferred between oxygen sites by hopping, which bring higher conductivity than those of oxygen ion conductor at intermediate temperatures. Though a lot of proton conductive materials have been reported, they exhibit relatively low conductivity⁹⁻¹¹ compared to that of oxygen ion conductors at the operating temperatures. Thus, improving proton conductivity is essential to achieve good IT-SOFC performances.

In this study, we used a pulsed layer deposition (PLD) method as a deposition technique because many studies on highly crystallized deposits of oxide thin films have been reported.¹²,¹³ In addition, we choose a 20 at % doped SrZr₁₋ₓYₓO₃ (x = 0.2) disk as a PLD target to obtain higher proton conductivity. Though the yttrium (Y)-concentration (x) in bulk SrZr₁₋ₓYₓO₃ (SZYO) is chosen less than 0.1 in general,¹⁰,¹¹,¹⁴ M. Arab Pour Yazdi et al. reported much higher Y-concentration of x = 0.16¹⁵,¹⁶ in their film deposition by the reactive magnetron sputtering method and we considered that we can also achieve higher Y-concentration in our thin film deposition by optimising the deposition conditions.

In this paper, we report on the optimization of deposition conditions and the highly crystalized SZYO thin films by the PLD method, which can be used in our SOFC fabrication.

2. Experimental procedure

The deposition conditions of the PLD method were optimized in the point of view of the crystallinity, i.e. the intensity and FWHM of the diffraction peaks measured by the X-ray diffraction (XRD) method. The laser used in this PLD was a Kr-F excimer laser with 248 nm wavelength. The oxygen pressure and target-substrate distance were fixed at 50 mTorr and 47 mm, respectively.

A Pt/SiO₂/Si [here-in-after, abbreviated as Pt/Si] substrate, which is a conventional substrate used in oxide thin film technology and whose Pt layer is strongly (111)-oriented, is used in this study. On some of the Pt/Si substrates, SrRuO₃ (SRO) and Pd layers were deposited as electrodes by the sputtering method at 550 °C. The deposited SRO and Pd are highly (111)-orientated because they
have almost the same lattice constant with Pt and have cubic (or pseudo-cubic) crystal structures which is equivalent to that of Pt.\textsuperscript{17)}

The SZYO films were deposited on Pt/Si, SRO/Pt/Si, and Pd/Pt/Si substrates at the various deposition conditions. The examined deposition conditions are summarized in Table 1. The thickness of the deposited SZYO films was varied between 0.37–3.0\textmu m depending on the deposition conditions.

The constituent phase and the degree of the out-of-plane and in-plane orientation of these films were characterized by a theta (\(\theta\))-2theta (2\(\theta\)) scans and a psi (\(\varphi\))-2\(\varphi\) mappings by the XRD method (PANalytical X’Pert MRD) using a Cu K\(\alpha\) radiation. The composition of the deposited films was also confirmed by the wavelength dispersive X-ray spectrometry (PANalytical PW2404), which was calibrated using a sol–gel derived SZYO thin film. The conductivity was also measured by the cole-cole plot analysis in humidified Ar (10 cc/min., 40 °C humidified).

3. Results and discussion

3.1 Optimization of deposition conditions

Figure 1 shows composition of SZYO vs. PLD laser power density relationship deposited on Pt/Si substrates. The deposition temperature and laser repetition frequency were fixed at 400 °C and at 6 Hz, respectively.

As can be seen in Fig. 1, a strong power dependency on the compositional ratio of Y/(Zr + Y), hereinafter described as Y-concentration, was observed and about 0.53 J/cm\(^2\) of laser power density gives a little high Y composition compared to that of the PLD target. On the contrary, the compositional ratio of A and B sites, which means Sr/(Zr + Y) and hereinafter is described as A/B-ratio, were almost unity in any power density.

Secondary, deposition temperature (T\textsubscript{depo}) dependencies of crystallographic and compositional results deposited on SRO/Pt/Si substrates were investigated. The laser repetition frequency and laser power density were chosen as 6 Hz and 0.53 J/cm\(^2\), respectively in this experiment.

Figure 2 is a XRD patterns of SZYO films deposited on SRO/Pt/Si substrates at various deposition temperature (T\textsubscript{depo}). (Laser repetition: 6 Hz, laser power density: 0.53 J/cm\(^2\))

We also examined the laser repetition frequency to reduce the phase separation of SZYO. Figure 4 shows the

with deposition temperature was observed; however, the Y-composition was about 0.21, which is a little higher than that of the PLD target. We consider this high Y-concentration caused the phase separation of SZYO.

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Table 1. Examined deposition conditions

| Laser power density [J/cm\(^2\)] | 0.53–0.87 |
| Laser repetition frequency [Hz] | 6–10 |
| Depo. Temp. [°C] | 300–500 |

Fig. 1. Compositional ratios of Y/(Zr + Y) and Sr/(Zr + Y) in SZYO vs. laser power density deposited on Pt/Si substrates. (T\textsubscript{depo}: 400 °C, laser repetition: 6 Hz)

Fig. 2. XRD patterns of SZYO films deposited on SRO/Pt/Si substrates at various deposition temperature (T\textsubscript{depo}). (Laser repetition: 6 Hz, laser power density: 0.53 J/cm\(^2\))

Fig. 3. Compositional ratios of Y/(Zr + Y) and Sr/(Zr + Y) in SZYO vs. deposition temperature (T\textsubscript{depo}).
composition of SZYO vs. laser repetition frequency relationships. The deposition was performed at a deposition temperature of 400 °C on SRO/Pt/Si substrates with a fixed laser power density of 0.53 J/cm². According to this result, a slight decrease of Y-concentration with laser repetition frequency was observed though the A/B-ratio is almost constant.

In addition, the change of crystallinity and the secondary phase generation with the laser repetition frequency was detected by the XRD measurement (Fig. 5). The SZYO film deposited at 6 Hz gives Y-concentration which exceeds 0.21 and the secondary phase generation. On the contrary, depositions at 8 and 10 Hz give the Y-concentrations lower than 0.21 and did not show any secondary phase generations. This might be originated from the decrease of Y-concentration and this result indicates that the laser repetition frequencies of 8 and 10 Hz are the optimized ones to obtain single phase of SZYO. In addition, the film deposited with 10 Hz showed (111)- and (110)- diffraction peaks of SZYO, which indicates the film is mixed oriented. On the contrary, the film deposited at 8 Hz repetition frequency showed only (111) diffractions, which means this film is highly (111)-oriented because of the local epitaxial growth between the (111)SRO/Pt/Si substrate and the film. Thus, we adopted the laser repetition frequency of 8 Hz as the best condition because it gives slightly higher Y-concentration without generating the secondary phase in the SZYO deposition.

Though the origins of the compositional variations with the deposition conditions were not certain at this moment, they might come from the differences of the degree of the ablation efficiency of each atom. Taking into account the stoichiometry and the crystallinity of the SZYO film, we set the optimized conditions in our experiments as the laser power density of 0.53 J/cm², laser repetition frequency of 8 Hz, and deposition temperature of 400 °C.

Using the SZYO film deposited at the optimized conditions, the proton conductivity (σ) was measured against measured temperature (T) in a humidified (wet) atmosphere. Figure 6 shows the relationship between σT and 1/T for the SZYO film deposited at the optimized condition in comparison with the data for Y-concentration of 0.16 reported by M. Arab Pour Yazdi et al. We obtained almost the comparable result of M. Arab Pour Yazdi et al.’s and higher conductivity than that in our former report. This improvement might be come from the improvement of the SZYO film crystallinity.

The data shown in Fig. 6 are almost the same values as that in Ref. 16) but our result shows slightly higher value above 400 °C, which might be reflecting the higher Y-concentration of our deposited SZYO. Thus, we can conclude that the SZYO film deposited by the PLD method has the almost the same film crystallinity compared to that of SZYO reported by the reactive magnetron sputtering method in the point of view of the proton conductivity and we consider this film is available for the SOFC fabrication.

3.2 SZYO deposition on Pd film
As we mentioned in the introduction, the SZYO film should be fabricated on the Pd-plated porous stainless steel substrates in our proposed SOFC cell structure. Thus, we examined the SZYO deposition on the Pd electrode to
investigated whether the optimized deposition conditions examined for the SRO/Pt/Si substrates can give almost the same results. The Pd electrode was fabricated on the (111)Pt/Si substrate and showed strong (111)-orientation, which is originated from the local epitaxy of Pd on (111)Pt/Si substrate because the Pt and Pd poses the same crystal structure of fcc with the almost the same lattice constants (Pt: 0.3922 nm, Pd: 0.389 nm). After depositing SZYO on Pd, we also investigated a thermal stability of SZYO by the post-annealing in air for 10 min. at 700 °C.

Figure 7 is the θ-2θ scans of (a) as-deposited and (b) post-annealed SZYO thin films. These SZYO films showed strong (110)-orientation and no (111)-related diffractions though they were deposited under the optimized conditions which gives preferred (111)-orientation on (111)SRO/Pt/Si substrates.

H. H. Kan and J. F. Weaver reported that the epitaxial growth of (101)PdO can be achieved by the surface oxidation of (111)Pd and we reported that this (101)PdO layer works as a seed layer for depositing (110)-orientated perovskite-type oxide films. Almost the same mechanism is occurred unintentionally in the fabrications of as-deposited and annealed SZYO thin films in Fig. 7. Though the PdO diffraction was not detected in the as-deposited sample, the very thin (and undetectable in our XRD measurements) PdO layer might be generated during SZYO deposition, which results in (110)-orientation of as-deposited SZYO film.

To confirm (110)-orientation of the SZYO film, we measured XRD mappings in 2θ and Ψ-directions, which is corresponding to that of a reciprocal space mapping, for as-deposited and post-annealed SZYO films as shown in Figs. 8(a) and 8(b), respectively. As can be seen in these mappings, only (110)-related diffractions of SZYO were observed at about 2θ = 31° with about 60° separated in the Ψ-direction, which suggests that these films are highly (110)-orientated and no secondary phase was generated. Furthermore, the XRD patterns showed no significant change before and after post-annealing, which means the as-deposited SZYO film is well crystallized and the post-annealing did not show noticeable improve for its crystallinity.

In conclusion, the as-deposited SZYO film deposited at 400 °C are well-crystallized with no secondary phase and is stable up to 700 °C under air, which can be used in the SOFC application.

4. Summary

SZYO thin films were successfully deposited by the PLD method. The Y-concentration is strongly affected by the laser power density and the laser repetition frequency but is not affected by the deposition temperature. The SZYO film deposited at the optimized conditions was well-crystallized and showed no secondary phase generation even at the high Y-concentration of 20 at%. This SZYO film is strongly (110)-orientated when they were deposited on (111)Pd/Pt/Si substrates and (110)-oriented when it was deposited on (111)Pd.

This SZYO film can be used as an electrode in our proposed SOFC cells. We have been working to fabricate SOFC cells to demonstrate good IT operations.

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