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Structural and electrical characterization of Y-doped $SrZrO_3$ thin films for solid oxide fuel cells

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Abstract. To achieve intermediate-temperature (400-600°C) operation of the solid oxide fuel cells (SOFCs), we proposed to use a porous stainless-steel plate with a Pd layer as a substrate. Sol-gel deposition of proton conductive oxide thin film, i.e. Y-doped $SrZrO_3$ (SZYO), was successfully deposited on this substrate. The annealing temperature of 700°C was the best to obtain crystallized SZYO with lower leakage at a room temperature. The proton conductivity of this film was about 10^{-6} S/cm at 600°C in a dry condition and showed almost the same value in the wet atmosphere. To achieve good SOFC operations, we are investigating the fabricating method of the SOFC cells with a cathode electrode as well as the improvement of the proton conductivity of the electrolyte. We believe we can solve these issues and obtain good SOFC operations in a near future.

Introduction

Solid oxide fuel cells (SOFCs) are considered to be one of the candidates for future energy sources. In these years, a new SOFC structure using a proton conductive oxide as an electrolyte was proposed [1, 2] for intermediate-temperature (400-600°C) operations, which brings the SOFC cost reduction and ease of start-up. However, it was difficult to fabricate actual SOFCs with proton conductive electrolytes because of the low conductivity (10^{-2}-10^{-4}S/cm) of the electrolytes. To reduce resistivity, Ito et al. proposed to use a thin film of the proton conductive oxide, doped-$BaCeO_3$, as the electrolyte [3] and achieved good SOFC operations as low as 400°C. However, they need to use a thick Pd foil (>40μm) as a substrate to support their SOFC structure mechanically. As a consequence, their SOFC becomes too expensive and not realistic.

Recently, we have successfully deposited a solid proton conductive oxide directly on a porous stainless-steel (PSS) substrate by MOCVD [4]. Using this film, we can fabricate SOFCs with a thin film electrolyte on an inexpensive substrate. We have been working to fabricate SOFCs using this film and considering we would have a good result in a near future. However, using MOCVDs for fabricating SOFCs is not realistic neither because it is one of the expensive

methods as an oxide deposition technique and its deposition conditions for fabricating solid oxide on the PSS is very narrow. Thus, other conventional and inexpensive oxide deposition methods, i.e. sputtering, sol-gel, etc, is preferable for the SOFC fabrications. In order to use these deposition techniques, the surface of the substrate needs to be smooth with no pores. To achieve smooth surface on the PSS, we deposited a solid Pd layer on it. Though we use some amount of Pd in this structure, its thickness is several μm and quite small compared to Ito et al's[3]. Thus, we consider this substrate structure will bring realistic SOFC fabrications with good SOFC operations.

In this paper, we chose a sol-gel spin-coating as an electrolyte deposition method because of its ease of compositional control and lower deposition costs. In addition, we have already achieved high quality epitaxial-growth of $(Pb,La)(Zr,Ti)O_3$ thin films by sol-gel [5,6] and considered it would also effective for high quality deposition of electrolytes. Y-doped $SrZrO_3$ (SZYO) was chosen as an electrolyte because it has a good chemical stability and relatively large proton conductivity with about 10^{-4}S/cm at 300 ^{o}C [7].

Experimental

We use Pt deposited silicon wafers to reveal a sinterability and a leakage current property of the SZYO films and PSS substrates for SOFC cell fabrications. The PSS substrate was fabricated by sintering of stainless steel powders. After the sintering, the surface of the substrate was polished and a solid Pd layer with several-mm in thick was deposited by plating on it.

$SrZr_{0.8}Y_{0.2}O_{3-\delta}$ (SZYO) thin films were deposited on Pt deposited silicon wafers and Pd deposited PSS substrates by a sol-gel method. The sol-gel solution (Mitsubishi Material) with concentration of 5wt% was spin-coated on the substrates, dried at 80^{o}C, and pyrolyzed 300 and 400^{o}C, subsequently. This process was repeated several times until the film thickness reaches at about 300nm. Finally, the deposited film was annealed at 500～800^{o}C in air for 60min. Typical procedure of the sol-gel process was shown in Fig. 1.

The crystal structure was evaluated by the X-Ray Diffraction (XRD). The cross- sectional structure observation was performed by the Scanning Electron Microscopy (SEM). A Pt top electrode was deposited by sputtering to measure electrical leakage of the films at a room temperature.

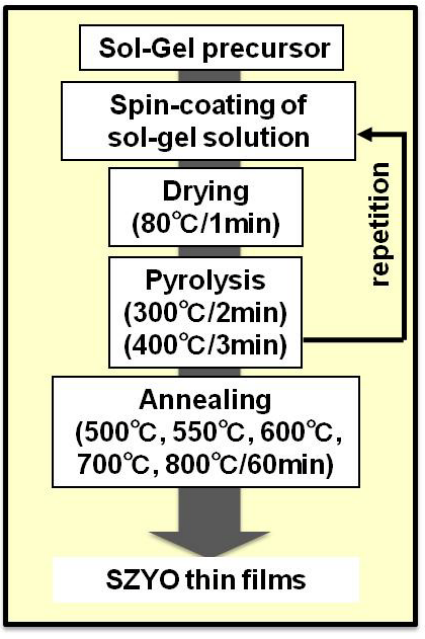

Fig.1 Schematic process of the sol-gel method

Results and Discussion

Figure 2 shows the XRD patterns of the SZYO thin films deposited on the $Pt/SiO_x/Si$ substrate annealed at various temperatures. Below 600^{o}C annealings, the films did not show any diffraction peaks, which means these films were not crystallized. In turn, the films annealed above 600^{o}C showed only diffractions which are belong to those of SZYO. In addition, the intensities of the SZYO peaks do not change seriously when it was annealed above 600^{o}C. Thus, the annealing as low 600^{o}C as is sufficient to obtain crystallized SZYO films.

The leakage current of the SZYO films were shown in Fig. 3. The films annealed at 500 and

550°C showed lower leakage compared to the others. As shown in Fig. 2, these films is amorphous and this low leakage profile might be originated from their amorphous characteristics. In turn, the film annealed above 600°C shows larger leakage, which might be from the leak passes at the grain boundaries. The reason why the film annealed at 600°C shows the largest leakage is not sure; however, its leakage is larger than almost 2 decades and too large for the electrolyte use. In addition, the annealings above 700°C bring the PSS deformation and oxidation, which is not desirable for the SOFC fabrications. So we consider annealings at 700°C is the best annealing temperature to obtain good electrolyte in our experiment. The conductivity of this film was about 10^{-6} S/cm at 600°C in a wet condition and is a little higher than that of the value measured in the dry atmosphere. We consider this difference in the conductivities is from proton conduction in the SZYO as described in ref. 7. However, the value obtained here is not sufficient for the good SOFC operations. Thus, we need further improvement in the proton conductivity (at least 10^{-4}S/cm) and the optimization of the SZYO fabrication including dopant concentration and the sintering atmosphere is in progress.

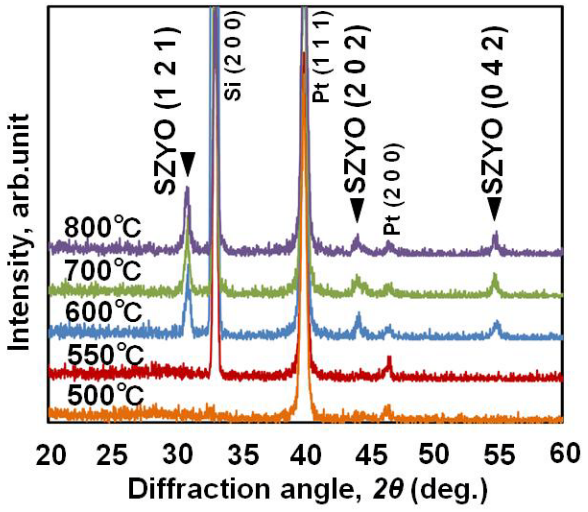

Fig.2 XRD patterns of the SZYO films annealed at various temperatures

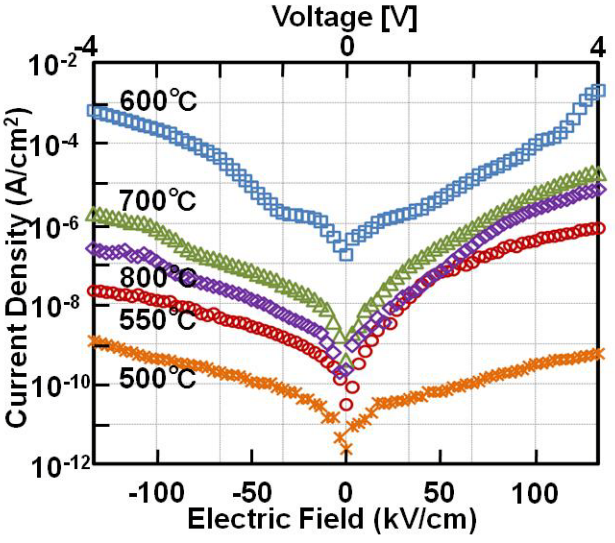

Fig.3 Electrical leakage at a room temperature of the SZYO films annealed at various temperatures

Finally, we deposited SZYO thin films on the PSS substrate with the Pd layer as shown in Fig.4. Solid SZYO thin film was successfully obtained on the substrate by sol-gel method. We are fabricating SOFC cells based on this structure but still suffering the cathode (top electrode) fabrication. Because of the sinterability of cathode materials, we need sintering temperatures of >1000 °C, which causes the deformation of the substrate. We are also investigating sinterable materials as low as 700°C for SOFC cell fabrications and have been trying to use a new material as the cathode. We believe we can solve this issue in a near future.

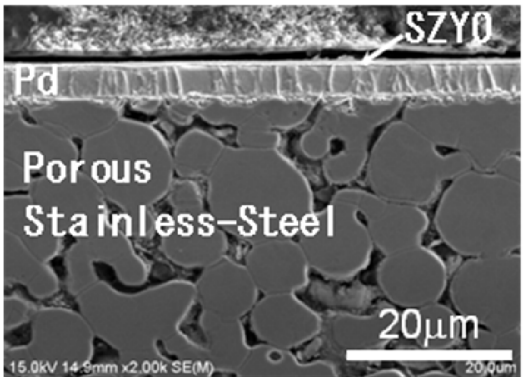

Fig.4 Cross-sectional SEM image of sol-gel derived SZYO deposited on Pd/porous stainless-steel sub.

Summary

The good SZYO thin film fabrications were demonstrated by sol-gel method on the $Pt/SiO_x/Si$ and PSS substrates. Sol-gel-derived films were crystallized above 600°C and the annealing temperature of 700°C was the best to obtain crystallized SZYO with lower leakage. The proton conductivity of this film was about 10^{-6} S/cm at 600°C in a dry condition and showed almost the same value in the wet atmosphere.

To achieve good SOFC operations, we are studying for fabricating SOFC cells with cathode electrode as well as the improvement of the proton conductivity of the electrolyte. We are studying for fabricating SOFC cells with cathode electrode as well as the improvement of the proton conductivity of the electrolyte. However, we have been investigating the optimum fabrication conditions of SZYO and cathode, we consider they would be solved in a near future and will bring good SOFC operations at the intermediate-temperatures.

Acknowledgments

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