Fabrication and characterization of YSZ thin films for SOFC application

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Yttria stabilized zirconia (YSZ) thin films are deposited on thin Si₃N₄ layer coated Si substrates by RF-sputtering with different substrate temperatures, room temperature (YSZ-RT) and 550°C (YSZ-550). Fine polycrystalline structure is observed for YSZ-RT (thickness = 620 nm), while columnar crystal structure (111) oriented for YSZ-550 (thickness = 660 nm), respectively. The conductivity measurement shows that the activation energies of YSZ-RT and YSZ-550 are 1.34 and 1.58 eV, respectively, indicating that grain boundary conduction is dominant. Shear strengths of the YSZ films are determined by using a micro-blade cutting system to be 150 MPa for YSZ-RT and 200 MPa for YSZ-550, respectively. YSZ-550 is found to be better for solid oxide fuel cell application from mechanical and electrical properties point of view.

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1. Introduction

Solid-oxide fuel cells (SOFCs) have been intensively studied in recent years as a key technology of the future energy sources due to their energy conversion efficiency.^{1)–5)} SOFCs are operated at high temperatures of 700–1000°C, and thus hydrocarbon fuel can directly be applied to the cells with appropriately selected anode materials.^{6)–9)} Thus they are more suitable for a variety of application use, especially for portable devices, automobile and stationary use in the remote area. In order to spread the SOFC systems, lowering the cost of the system is necessary and, many SOFC studies have focused on lowering the operating temperature of the SOFCs for this purpose.^{10)–17)} For example, new electrode and electrolyte materials have been proposed and developed for reducing cell resistance. The other method to reduce the operating temperature is to realize self-standing ultra thin film electrolyte below 100 nm. This category of SOFC is called μ -SOFC or MEMS-SOFC, and typically utilizing Si-substrate and sputtering coating technique^{18)–20)}. For example, Huang et al. showed cell performance of 400 mW cm^{–2} at 400°C using 50 nm thick yttria stabilized zirconia (YSZ) electrolyte fabricated on Si substrate.¹⁸⁾ Tsuchiya, et al., overcame the drawback of μ -SOFC, small cell area, and showed the 4 × 4 cm self-standing 100 nm electrolyte by utilizing thin metal grid on the electrolyte.¹⁹⁾ Understanding the physical and electrochemical properties of sputtered YSZ thin film is thus of importance for further development of μ -SOFC. Especially the mechanical property of the YSZ film strongly relies on the size of active area and the thickness of the film for realizing self-standing electrolyte.²¹⁾ In this study, we report the electrical and mechanical properties of about half micron thick YSZ thin films, rather thicker electrolyte to improve the mechanical property, fabricated using RF sputtering process.

2. Experimental

8 mol% yttria stabilized zirconia (YSZ) thin films were deposited on Si substrates (both surfaces Si₃N₄ coated) by RF-sputtering system (ISP -2000-HC1-S, Ulvac, Japan). Carrier gas of Ar and O₂ in the ratio O₂/Ar = 0.1 was flowed at the flow rate of 40 ml min^{–1}, after the pressure inside the chamber reached 1 × 10^{–3} Pa. The RF-power was fixed to be 200 W for 240 min, which allowed a deposition rate of 2.6–2.8 nm min^{–1}. Two different substrate temperatures were chosen, room temperature (kept by water cooling) and 550°C, namely YSZ-RT and YSZ-550, respectively.

X-ray measurement was carried out using a RINT2500V (Rigaku, Japan) at 20–60° for determining the crystal structure of the films, and SEM measurement was conducted using a JSM-6330F (JOEL, Japan) for determining the thickness of the films.

The electrical conductivity of the thin YSZ film was investigated by using a Reference 600 (Gamry Instruments, USA) that includes potentiostat and impedance analyzer. Au electrodes with 15 mm width were attached by using sputtering method so that the gap between electrodes being 1 mm, followed by Ag wires fixed to the electrodes using Ag paste as shown in **Fig. 1**.

The mechanical property of thin films was obtained by evaluating the interfacial adhesion of the thin films using a micro-blade cutting system [Surface And Interfacial Cutting Analysis System (SAICAS), Daipia Wintes Co., LTD, Japan].²²⁾ **Figure 2** shows the schematic image of the measurement mechanism. SAICAS can provide peeling strength, shear strength of a thin film by slicing the sample with a diamond cutting tool, applying constant vertical and horizontal force. Shear strength, τ , can be given by following equations,

$$\tau = F_H / (2 d W) \cot \phi,$$

$$\phi = \pi/4 - \arctan (F_V / F_H),$$

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Fig. 1. Sample geometry for electrical conductivity measurement.

Fig. 2. Schematic image of the measurement mechanism - SAICAS.

where W , F_H , F_V , ϕ , and d are cutting tool width, horizontal force, vertical force, shear angle, cutting depth, respectively. Experimental conditions for SAICAS was constant speed mode of $V_h = 0.02 \mu\text{m/s}$, $V_s = 0.002 \mu\text{m/s}$, respectively.

3. Results and discussion

Figure 3 shows the SEM images of (a) YSZ-RT surface (b) YSZ-550 surface (c) YSZ-RT cross-section (d) YSZ-550 cross-section, respectively. Fine grains of sub-micron order were observed for YSZ-RT while smooth surface for YSZ-550. Columnar crystal structure was observed only for YSZ-550 indicating epitaxial crystal growth. As can be seen, thickness of 620 and 660 nm dense thin films were obtained for YSZ-RT and YSZ-550, respectively.

Figure 4 shows the XRD patterns obtained for YSZ-RT, YSZ-550, and YSZ-RT after post annealed at 550°C for 1 h. As also seen in Figs. 3, YSZ-RT showed poly-crystalline structure, while YSZ-550 showed (111) oriented columnar crystal structure. This could be due to Si_3N_4 layer coated on the Si substrate. For comparison, YSZ-RT was post annealed at 550°C and, showed that it still has poly-crystalline structure. Such difference should affect the physical and chemical properties of YSZ thin films. The deviation of the peaks for three specimens could be caused by the internal stress in the crystal structure, since it has thermal expansion difference in Si substrate and YSZ thin film.

Figure 5 shows the results of conductivity measurements for YSZ-RT and YSZ-550, in addition to that for YSZ bulk specimen. The activation energies for YSZ-RT and YSZ-550 were estimated to be 1.34 and 1.58 eV, respectively. Since the measurement was conducted only at three temperature points, it is considered that the difference in the activation energies for YSZ-RT and YSZ-550 could be in the range of error bar. Nevertheless, these activation energies are relatively higher compared to that of bulk YSZ,

Fig. 3. SEM images of (a) YSZ-RT surface (b) YSZ-550 surface (c) YSZ-RT cross-section (d) YSZ-550 cross-section.

Fig. 4. XRD patterns obtained for YSZ-RT, YSZ-550, and YSZ-RT after post annealed at 550°C.

Fig. 5. Results of conductivity measurements for YSZ-RT and YSZ-550, in addition to that for YSZ bulk specimen.

Fig. 6. Force versus distance profile of (a) YSZ-RT and (b) YSZ-550 obtained using SAICAS.

typically ~ 1 eV, thus, they could represent grain boundary conduction, which is reasonable for low temperature processed YSZ thin films. The conductivity of YSZ-550 at the temperature range of 500–560°C showed similar to that of bulk YSZ, and YSZ-RT showed lower conductivity almost one order of magnitude.

Figures 6 show the force versus distance profile of (a) YSZ-RT and (b) YSZ-550 obtained using SAICAS as explained in Fig. 2. Abnormal curvature in F_H indicates that fracture occurs at the target film. Shear Strengths of the YSZ films were estimated at the point designated in Fig. 6, to be 150 MPa for YSZ-RT and 200 MPa for TSZ-550, respectively. Higher shear strength of YSZ-550 could be correlated to its columnar crystal structure. Obviously from XRD patterns, the crystal size is larger for YSZ-550 and this could provide high shear strength to the YSZ films. It was found that this technique could be effective for designing cell structure and developing thin film electrolyte for SOFC application.

4. Summary

YSZ thin films were deposited on Si substrates by RF-sputtering under the gas ($O_2/Ar = 0.1$) flow rate of 40 ml min^{-1} . With the RF-power of 200 W for 240 min, thickness of 620 and 660 nm dense thin films were obtained for the substrate temperature of room temperature and 550°C, respectively. Fine grains of sub-micron order were observed for YSZ-RT while columnar crystal structure for YSZ-550. These results were also supported by the results of XRD measurement that YSZ-RT and YSZ-550 (111) showed poly-crystalline structure and oriented columnar crystal structure, respectively. The conductivity of YSZ-550 was similar to YSZ bulk specimen with the activation energies of 1.58 eV, indicating that grain boundary conduction could be dominant. Shear strengths of the YSZ films were estimated using SAICAS to be 150 MPa for YSZ-RT and 200 MPa for TSZ-550, respectively. YSZ-550 was found to be better for SOFC application purpose from mechanical and electrical properties point of view.

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