Yttria-stabilized zirconia (YSZ) thin films were deposited on Pt substrates by pulsed laser deposition (PLD). The pinhole free YSZ thin film was deposited on Pt (111) substrate as thin as 600 nm. The electrical conductivity of thin film cell Pt/YSZ/Pt was studied using impedance spectroscopy. X-ray diffraction and electron microscopy results showed that the films were polycrystalline cubic YSZ with a columnar structure. The influence of grain boundaries on the conductivity was not observed. This could be due to the columnar structure of thin film, in which the grain boundary is parallel to the current direction. The conductivity of thin film YSZ was close to that of bulk YSZ.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have been developing rapidly for clean and efficient power generation using a variety of fuels. Most currently developing SOFCs employ YSZ as an electrolyte and require an operating temperature of ~1000°C to minimize ohmic loss (1). Recent focus has been on the advances of SOFCs through the lowering of the operating temperature for using fuel cells in portable devices. One promising approach being pursued is based on the integration of thin-film SOFC materials with silicon technology (2). Hence, a variety of research activities are in progress to develop “micro-SOFCs”, i.e., SOFCs based on silicon substrates with lateral dimensions in the submillimeter range (3,4). However, as the temperature is reduced, the ionic conductivity significantly decreases. This can be overcome by decreasing the thickness of electrolyte. The most promising approach in decreasing electrolyte thickness is to make the electrolyte by a thin-film deposition process (5). Several authors have reported on the conductivity of thin film YSZ. However, there are contradictions among the authors. Kosacki et al. (6), who investigated 8YSZ (8 mol% Y2O3-doped ZrO2) thin films prepared by a polymer precursor process on alumina substrate, reported that the thin film YSZ exhibited two orders of magnitude increase in conductivity compared to polycrystalline bulk materials. On the contrary, Wanzenberg et al. (7) reported that the measured conductivity of thin film was lower than that of the thick YSZ substrate or bulk materials due to the influence of contacting electrodes.

In this study, YSZ thin films were deposited on Pt substrates by pulsed laser deposition (PLD). PLD has become an increasingly important technique for depositing thin films of a variety of materials. Its advantage is its ability to deposit almost any material while preserving the stoichiometry of the multicomponents (8). The electrical conductivity of
thin film cell Pt/YSZ/Pt was studied using impedance spectroscopy. Pt electrodes are convenient because they do not react with YSZ film, and thus the film and substrate interactions can be ignored. On the other hand, for Ni electrodes, Ni oxidation may complicate the study in YSZ film conductivity. In this study, we have grown pinhole-free thin film on two different Pt substrates. The electrical conductivity of thin films was measured and compared with that of the bulk sample.

EXPERIMENTAL

YSZ thin films were deposited on Pt (200), (111) substrates using PLD at oxygen partial pressures of 50 mtorr. The films were deposited on the commercially available Pt(111)/SiO2/Si and Pt(200)/TiO2/SiO2/Si substrates. A stainless steel chamber was evacuated to a base pressure of 5*10^{-6} torr using a turbo molecular pump. Pulsed laser ablation was carried out with a KrF excimer laser (248 nm with 30 ns pulse width) at energy of ~150 mJ and repetition rate of 10 Hz. The laser beam was focused on an 8YSZ (8 mol% Y2O3-doped ZrO2) target that rotated at ~10 rpm. Substrates were positioned parallel to and 5 cm away from the target. This distance allows sufficient interaction between the plasma plume and the background oxygen gas. The substrate temperature was maintained at 770°C. To enhance the crystallization of the film, samples were annealed in oxygen gas at 800°C for 1 hr after deposition. To avoid short-circuiting through pin-hole during electrical measurement, the film on Pt (111) substrate was grown thicker than 600 nm and the film on Pt (200) was grown thicker than 1.5 nm. For electrical measurements, 0.05 cm² Pt electrode was sputtered on the surface of thin film. For comparison, a bulk sample was made by pressing 8YSZ (99.9%, TOSOH, Japan) commercial powder into pellets, followed by cold-isostatic pressing and sintering at 1600°C for 4 hr. Pt paste electrodes were painted on both sides of the disc-shaped specimen. The bulk conductivity of 8YSZ was measured by another group member (O. H. Kwon). Target and conductivity specimens were made using the same procedure.

The impedance spectroscopy was measured in the frequency range 5Hz-13MHz using impedance analyzer (HP4192a, Hewlett Packard, USA). To avoid humidity effects, the conductivity was measured between 300° and 500°C in dry air. The phase of thin film was characterized by x-ray diffraction (XRD) using Cu-Kα radiation (MAC Science, M18XCE, Japan). The microstructure was observed by a field-emission scanning-electron-microscope (FE-SEM). The compositions were also confirmed using an FE-SEM equipped with an energy dispersive X-ray spectroscopy system (EDS). To analyze the impedance patterns, the spectra were fitted using analysis software (ZSimpWin, PerkinElmer Instruments, U.S.A.).

RESULTS AND DISCUSSION

Microstructure of Thin Film YSZ

The crystalline phase of YSZ film was determined by using XRD. Figure 1 shows the XRD pattern of YSZ thin films deposited on Pt (111) and Pt (200) substrates. The XRD patterns obtained from the films were consistent with the reference data for single phase YSZ with cubic fluorite structure (JCPDS 30-1468) for both Pt (111) and Pt (200)
Figure 1. XRD 0-20 scans of YSZ thin films deposited on (a) Pt (111) and (b) Pt (200) substrates.

substrates. XRD patterns of Pt(111)/SiO₂/Si and Pt(200)/TiO₂/SiO₂/Si substrates before film deposition showed different peaks, as seen in Figure 1. The polycrystalline nature of the films is apparent in XRD patterns. No tetragonal or monoclinic YSZ phases appeared, and no secondary phases due to film/substrate interaction were detected. It was also found that the crystal orientation changed with substrate. A strongly preferential orientation of (111) planes in the film was obtained on the Pt (200) substrate.

SEM pictures of the thin film deposited on Pt substrate were examined to study the morphology. Figure 2 shows the cross-sectional SEM micrographs of thin film YSZ deposited on (a) Pt (111) and (b) Pt (200) substrates. The columnar growth of the grain is apparent for both films.

This columnar growth may be explained by the high surface energy of YSZ and the large lattice mismatch between YSZ and substrates. Similar phenomena were shown in diamond growth (9). The misfit and the strain energy at the interface may enhance the tendency toward three-dimensional island growth (10).

Figure 2. Cross-sectional SEM micrographs of YSZ thin films grown on (a) Pt (111) and (b) Pt (200) substrate.
To avoid short-circuiting through pinholes during electrical measurement, the film on Pt (111) substrate was grown thicker than 600 nm and that on Pt (200) thicker than 1.5 μm. Figure 3 presents SEM images (top view) of YSZ film deposited on the two Pt substrates. Because these films have columnar structures, the grain size measured from the surface view represents the diameter of the columns. The thin film deposited on Pt (111) substrate shows negligible porosity (Figure 3 a). The electrical conductivity of this film can be measured without short circuit after sputtering of Pt electrode. Nanocrystalline morphology was observed with an average grain size of ~60 nm.

Figure 3 (b) shows the surface morphology of the film deposited on Pt (200) substrate. From the comparison of the film grown with different thickness, it was found that the porosity decreased with increasing film thickness. The apparent grain diameter was also found to increase with increasing film thickness. The pinhole-free YSZ thin film was also obtained on Pt (111) substrate.

Thin-film YSZ had a yttria molar content of ~7.5 mol%, i.e., 7.5 mol% Y₂O₃-doped ZrO₂, determined by EDS. Thus, for the fully oxidized YSZ thin films deposited on Pt (111) and Pt (200) substrates, film composition was ~7.5YSZ, close to the 8YSZ target.

**Figure 3. Surface of thin film YSZ grown on (a) Pt (111) and (b) Pt (200) substrates.**

**Conductivity of the Thin Film YSZ**

The electrical conductivity of thin film and bulk YSZ was investigated by impedance spectroscopy. Figure 4 compares the impedance spectra obtained in dry air at 300°C. The impedance spectrum of thin film consists of a high-frequency semicircle caused by a grain process and a low-frequency inclined line attributed to the interfaces between YSZ film and sputtered Pt electrodes. The spectra were analyzed using equivalent circuits shown in Figure 4. A fitting line was drawn for the film grown on Pt (200), for example. The grain parts of the three spectra nearly coincide. However, the electrode parts are substantially different. To confirm the grain conductivity in the thin film, the relative dielectric permittivity (ε_r) was obtained from the peak of the high frequency semicircle. The value of ε_r at 300°C was ~15, close to the reported values for thin film YSZ (11).

Though for bulk YSZ the small grain boundary contribution was shown at intermediate frequencies, no grain boundary contribution was shown for films. This could be due to
the columnar structure of thin film, in which the grain boundary is parallel to the current direction (12,13). In other words, the highly oriented growth of the thin film YSZ shows that current flow is not limited by grain boundaries in the parallel plate geometry.

Ionic conductivity was calculated from the impedance plots. The resistance of Pt electrode was measured separately and subtracted. Figure 5 shows the grain conductivity of thin films. For comparison, the grain conductivity of bulk 8YSZ is also shown. Grain conductivity in the two films matches quite nicely. Negligible difference in conductivity was shown between films and bulk sample. Thus we may conclude that there is no conductivity enhancement or depression for nanocrystalline YSZ films. The activation energies of YSZ thin films deposited on Pt (111) and Pt (200) and bulk YSZ were 0.93 ± 0.05, 1.02 ± 0.03, and 1.07 ± 0.02 eV, respectively, as indicated by the solid fitting line. Both the ionic conductivity and activation energy of the YSZ thin films were similar to that of bulk YSZ.

Figure 4. Impedance spectra of thin films and bulk YSZ at 300°C and the equivalent circuit used for fitting the data.

Figure 5. Grain conductivity of thin films and bulk YSZ as function of temperature.
CONCLUSIONS

Pinhole-free YSZ thin films were successfully fabricated on Pt substrates using PLD. The thickness of the YSZ thin film deposited on Pt (111) substrate was grown 600 nm, and nanocrystalline morphology was observed with an average grain size of ~60 nm. X-ray diffraction and electron microscopy results showed that the YSZ films were polycrystalline and cubic with a columnar structure. The influence of grain boundaries on the conductivity was not observed. This could be due to the columnar structure of thin film, in which the grain boundary is parallel to the current direction. The ionic conductivity and activation energy of the YSZ thin films were similar to that of bulk YSZ. The thin films may be used as an electrolyte for micro-SOFCs.

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