Columnar grain boundary coherence in ytttria-stabilized zirconia thin film: effects on ionic conductivity

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This study elucidated the effects of coherence of grain boundary of 6 mol % Y2O3-doped ZrO2 (YSZ) thin films on ionic conductivity. The YSZ thin films were deposited with several orientation textures on MgO (100) and Al2O3 (102) substrates using metal–organic chemical vapor deposition (MOCVD). Impedance measurements revealed that the total ionic conductivity of the thin films was restricted by the columnar grain boundary. The orientation degree, defined by the average full width at half maximum (FWHM) of 100 pole of the YSZ thin films, mainly determines the ionic conductivity across the columnar grain boundary because of the degree of the crystallographic coherence. Films with a strongly oriented columnar structure showed ionic conductivity of about 30 times higher than that of nanocrystalline films having random orientation. The activation energy of the ionic conduction across the columnar grain boundaries simply increased concomitantly with decreasing degree of orientation of the columnar grains of the films. HRTEM analyses revealed that the small tilt angle grain boundary with low lattice defect density and with no second phase at grain boundaries showed superior properties. Consequently, a columnar structure with high coherence is preferred for use as a thin film ionic conductor.

Key-words: Zirconia, Columnar structure, Grain boundary, Ionic conduction, Morphology, Orientation, Thin film, Transmission electron microscopy

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1. Introduction

Actually, ZrO2 is well known to have polytypes of cubic, tetragonal, and monoclinic phases under atmospheric pressure depending on the temperature.1–6 These phases can be controlled by doping some oxides including di-, tri-, and tetravalent cations such as MgO, Y2O3, and CeO2.7–9 Among them, doping of MgO or Y2O3 introduces oxygen vacancies in ZrO2 lattices because of charge neutrality. At concentrations of less than about 10 mol % Y2O3, charged oxygen vacancies associate with Zr4+ so that seven-fold local coordination around Zr4+ is stabilized in cubic symmetry.10–14 The oxygen vacancies engender higher mobility of oxygen ions by hopping at elevated temperature, which makes stabilized zirconia a good candidate for use as an electrolyte. Particularly, Y2O3 tends to produce a homogeneous solid solution with ZrO2 at elevated temperatures.17 For doping amounts of 8–10 mol % Y2O3, the cubic phase solid solution stabilizes at room temperature. Yttria-stabilized zirconia (YSZ) shows excellent ionic conductivity of oxide ions at elevated temperatures.15 This property is attractive for oxygen sensors and electrolytes for use in solid-oxide fuel cells (SOFCs).

Most early studies of the ionic conductivity on YSZ have assessed bulk crystals.15–18 However, the operating temperature of YSZ electrolytes generally requires temperatures higher than 700°C. It is important for energy conservation to lower the operating temperature. Decreasing the ohmic loss across the electrolyte can lower the operation temperature of SOFCs and its life cycle. Therefore, thin film electrolytes are attractive for use as next-generation electrolytes operating at lower temperatures.19,20

Generally, the electrical properties of YSZ are affected strongly by the microstructures. The thin films particularly have a characteristic microstructure: a columnar structure. Most epitaxial YSZ thin films tend to grow according to the Stran–Krstanov mode because of the large lattice mismatch between the film and the substrate.21 This growth mode introduces 3D island growth of the film, so that the film shows columnar morphology with high density of grain boundaries and lattice defects such as dislocations. Among the early reports of studies of YSZ, Aoki et al. described that the grain boundary acts as a barrier against the conduction of oxygen ions for polycrystalline YSZ. Kosacki et al. reported that the grain boundary in the nano-crystalline YSZ acts as a rapid diffusion path of oxygen ions.22,23 Otsuka et al. reported that the dislocation line also acts as a rapid diffusion path.24,25 The impurity segregation along grain boundaries also affects the YSZ properties.26,27

Here, we specifically examine the effects of a columnar-structure in YSZ thin films on the ionic conductivity. The typical width of columnar grains is in several tens of nanometers. The interface behavior is important because the ratio of the columnar grain boundary increases more than in thin films comprising larger grains, as in bulk crystals. Most studies have examined polycrystalline films with random orientation. A few studies
have investigated the ionic conductivity of epitaxial YSZ thin film\(^{29}\) and the columnar grain boundary structure of YSZ thin films.\(^{29}\)

This study elucidated the effects of the orientation, morphology, and grain boundary structure, particularly the coherence of the grain boundary, on ionic conductivity in YSZ thin films with columnar morphologies.

2. Experimental procedures

\(\text{Y}_2\text{O}_3\)-doped \(\text{ZrO}_2\) thin films were prepared using metal–organic chemical vapor deposition (MOCVD) with the vertical cold-wall-type reactor. \(\text{Zr(O·t-C}_4\text{H}_9)_4\), \(\text{Y(C}_1\text{1H}_1\text{9O}_2)_3\), and \(\text{O}_2\) were deposited on \(\text{MgO}(100)\) and \(\text{Al}_2\text{O}_3(102)\) substrates at deposition temperatures of 400–600°C. Details of the thin film deposition were published in a separate paper.\(^{30}\) The \(\text{Y}_2\text{O}_3\) concentrations in \(\text{YSZ}\) thin films were measured using energy dispersive X-ray spectroscopy (EDX, DX95; EDAX Inc.). Films of 6 mol \% \(\text{Y}_2\text{O}_3\) concentration were selected for examination in this study. Only 6 mol \% \(\text{YSZ}\) shows various orientation degrees on \(\text{MgO}\) and \(\text{Al}_2\text{O}_3\) substrates. Then, 6 mol \% \(\text{YSZ}\) was selected for this study to fix the \(\text{Y}_2\text{O}_3\) composition. Impedance spectroscopy of \(\text{YSZ}\) thin films was conducted using an impedance analyzer (4192A; Agilent Corp.) at temperatures of 600–900°C in the electrical furnace in air shown in Fig. 1. A two-probe technique was used for measurement of the impedance spectra because of the adequately high impedance of \(\text{YSZ}\). Pt wires with Pt paste were attached to the bilateral terminal of the samples and were sintered at 800°C in air. The frequency range of the measurement was 10 MHz to 10 Hz. The impedance and the ionic conductivity of the films were obtained from the fitting of measured impedance spectra (Nyquist plots). The activation energy of the conduction obtained was from the slope of the Arrhenius plot \(\log(\sigmaT)\) versus \(1/T\), where \(\sigma\) represents ionic conductivity.

The phase and orientation of the prepared films were measured using XRD (X’pert-MPD PW3050; Philips Co.) and an X-ray pole figure (X’pert-OEC PW3050; Philips Co.), using Cu-K\(\alpha\) line operating at 40 kV and 40 mA. The X-ray pole figures of 100 poles of YSZ with [101] projection were measured. To evaluate the orientation degree, the average FWHM of (100) pole was measured. Figure 2 is a schematic diagram of the W-factor, the average FWHM of (100) pole with [101] projection.

3. Results

3.1 Quantifying the degree of film orientation

First, the orientation degree of the \(\text{YSZ}\) thin films was evaluated using the \(W\)-factor obtained from the X-ray pole figure. Figure 3 shows (100) pole figures of typical \(\text{YSZ}\) thin films with [101] projection. The orientation degree was controlled by varying the substrate species and the deposition temperatures as follows: (a) \(\text{MgO}\) substrate at 600°C, and (b) \(\text{Al}_2\text{O}_3\) substrate at 600°C, (c) \(\text{Al}_2\text{O}_3\) substrate at 500°C, and (d) \(\text{Al}_2\text{O}_3\) substrate at 400°C, respectively. The \(W\)-factors in Fig. 3 are, respectively, (a) 4.2°, (b) 6.8°, (c) 20.3°, and (d) 73.5°. The orientation degree is larger, with higher deposition temperatures of films on the same substrate. The orientation degree of the film on the \(\text{MgO}\) substrate is higher than that on the \(\text{Al}_2\text{O}_3\) substrate under conditions of the same deposition temperature. Consequently, the \(\text{YSZ}\) thin film on \(\text{MgO}\) and \(\text{Al}_2\text{O}_3\) substrate deposited at 600°C has epitaxial like orientation. That on \(\text{Al}_2\text{O}_3\) substrate at 500°C has uniaxial
Fig. 4. Cross-sectional TEM images of columnar YSZ thin films on (a) MgO and (b) Al2O3 substrates, and (c) that of nano-crystalline YSZ thin film on Al2O3 substrates.

Fig. 5. Cross-sectional HRTEM image across a columnar grain boundary in YSZ films on (a) MgO and (b) Al2O3 substrates. (c) and (d) are magnified images of (a) and (b), respectively.

3.2 Morphology and coherence of grain boundaries of YSZ thin films

Morphology and coherence of grain boundaries of YSZ thin films were investigated using transmission electron microscopy. Particularly, we assessed the relation between the W-factor and the morphology and the coherence of grain boundary. Figure 4 shows cross-sectional bright field images of YSZ thin films on (a) MgO substrate with \( W = 4.2^\circ \), (b) Al2O3 substrate with \( W = 6.8^\circ \), and (c) Al2O3 substrate with \( W = 73.5^\circ \). These images show that both columnar YSZ thin films (a) and (b) have columnar morphology with each grain of 20–80 nm width. The dark contrast shows that the grains are close to a Bragg condition. The variation in the diffraction contrast among grains means that the orientation of the columnar grains is not complete, i.e. each grain might slightly rotate in the film plane. This result corresponds to non-zero \( W \)-factor. However, most of the columnar grains orient in the [001] direction because of the uniform contrast along each columnar grain. However, Fig. 4(c) shows markedly different morphology. A polycrystalline YSZ thin film (c) has no columnar structure and does not orientate toward such the definite direction.

Figure 5 shows cross-sectional HRTEM images along a columnar grain boundary of the YSZ film on (a) MgO substrate with \( W = 4.2^\circ \), (b) Al2O3 substrate with \( W = 6.8^\circ \). Figures 5(c) and 5(d) respectively portray enlarged images around a grain boundary presented in Figs. 5(a) and 5(b). A YSZ thin film on MgO substrate shows a small angle tilt grain boundary. Each columnar grain tilts by 3° to each other. Almost no dislocation occurs along the grain boundary. It shows the lattice fringes corresponding to the {200} and {111} lattice planes. The electron beam direction of incidence is parallel to the (011) zone axis. The columnar grain boundary is in a linear manner for the YSZ thin film on MgO substrate, but it is in a stepwise deflection for that on Al2O3 substrate. The latter is a typical structure for a small tilt boundary with high-density array of edge dislocations. These images show that a smaller \( W \)-factor is correlated well with a smaller tilt angle, which indicates a correlation between rotation in the in-plane and out-of plane directions of the YSZ thin films. The difference of the film morphology can be ascribed to the substrate. The YSZ film growth is affected by the crystallinity of the substrate and the lattice matching at the film/substrate interface. In fact, MgO has cubic lattice, whereas \( \alpha \)-Al2O3 has a rhombohedral lattice. The MgO substrate shows better lattice matching with YSZ, which has a cubic lattice. Moreover, YSZ/MgO film has less rotation and tilt than YSZ/Al2O3 has. However, in general, the commercially available MgO substrate shows a mosaic structure. The mosaicity of MgO substrate increases the tilt of YSZ columnar grains.

Figure 6 presents cross-sectional HRTEM images along a columnar grain boundary of the YSZ film on Al2O3 substrate with \( W = 73.5^\circ \). The morphology is nano-scale granular polycrystalline. Each grain is only several nanometers in diameter. Each grain is faceted by low-order crystallographic planes, with high density of dislocations distributed along the grain boundary. These results imply that nucleation of the crystallization of YSZ thin film tends to occur at deposition temperatures of about 400°C. However, grain growth tends to occur at the deposition temperature about 600°C. These morphologies agree well with those reported from an earlier study.29

Next, chemical segregation or presence of the second phase will
be investigated. Figure 7(a) depicts EDS spectra of the columnar grain boundary and interior of YSZ thin films on MgO and Al₂O₃ substrates. These spectra were obtained from TEM-EDS measurements under a TEM-probe mode. The measurement conditions are portrayed in Fig. 7(b). The nominal probe diameter was 2 nm. These spectra between the grain boundary and interior are almost identical for Mg, Al, and Y peaks, which illustrates clearly that no segregation of these elements occurs at the columnar grain boundaries, and that the traces of Al and Mg peaks are attributable to redeposition of the sputtered debris of the substrate under the ion-milling process. However, Fig. 5 depicts different diffraction contrasts along the columnar grain boundary, which shows brighter contrast regions A and B. In these regions, the lattice fringes are equivalent to those in the grain interior, which shows darker contrast. Reconsidering Figs. 4(a) and 4(b), the bright contrast attributed to the thinner region where the edge region of columnar grains overlap mid-gaps between columnar grains. The lattice fringes in regions A and B are attributed to the edge of the columnar grain by which each grain partly contacts others. Consequently, these columnar grain boundaries are chemically clean, but are nonetheless physically distorted, i.e. with tilt and rotation.

3.3 Impedance spectra of YSZ thin films

Impedance spectra were measured to evaluate the ionic conductivity and activation energy. Figure 8 depicts impedance spectra measured at 900°C of thin films on Al₂O₃ substrates with different W-factors of 4.2°, 6.8°, and 73.5°. The thin films with smaller W-value simply have smaller impedance, i.e. larger ionic conductivity. Apparently, one semi-circular was measured for all W-values. The ionic conductivity of YSZ is expected to be isotropic. The W-factor dependence of the impedance is expected to be the difference of the grain boundaries. The TEM analyses also support this point. Here, HRTEM images in Fig. 5 show that the coherence of the columnar grain boundary is small, with no second phase or segregation. The deviation of atomic structure along columnar grain boundaries is close to the grain interior. Furthermore, it has been reported that the contribution of the grain boundary on the impedance plot becomes larger, decreasing the grain size to less than 1 μm, and that the semi-circle of grain boundary was overlapped with that of bulk lattice in grains when the grain size was less than 100 nm.25,28,33 Then, each single semi-circle of our results is attributed dominantly to the grain boundary component in the films. These results indicate that the impedance of the columnar grain boundary with the higher coherence is lower than that with the lower orientation.

Here, assuming an equivalent circuit of a parallel connection of a resistance and a capacitance component, the real part and the imaginary part of the impedance were calculated. Typical Arrhenius-type plots of the product of ionic conductivity σ and temperature T for each W-factor, obtained from the measured impedance spectra, are shown in Fig. 9 to calculate the apparent activation energy for the grain boundary conduction. Figure 9 depicts almost all samples as showing linearity and no inflection of the plot for measured temperatures of 600–900°C. In general, the apparent activation energy comprises two components: the migration enthalpy of oxygen ions, and the association enthalpy between oxygen vacancy and Y ion. The association enthalpy is important at temperatures lower than 650°C.28 Reportedly, the oxygen vacancy associates with Zr ion in the YSZ of diluted Y concentration.10–14 In our experiment, at temperatures higher than 600°C, the conduction mechanism should be oxygen ion migration. The ionic conductivity depends on the W-factor. The YSZ thin film with W = 4.2° shows three times higher ionic conductivity.
conductivity than that with $W = 20.3\,^\circ$, and shows 30 times higher ionic conductivity than that with $W = 73.5\,^\circ$. These results demonstrate that the grain boundary acts as a conduction barrier, but the highly coherent columnar grain boundary shows the conduction barrier.

4. Discussion

The results presented above demonstrate the effects of orientation, morphology, and particularly the coherence of grain boundaries, on ionic conductivity in YSZ thin films with columnar morphologies. This section explains the conduction mechanism of the oxygen ions in the YSZ thin films from the viewpoint of the microstructure.

From these analyses, the logarithm of the ionic conductivity and the apparent activation energy are inferred, respectively, as shown in Fig. 10 and Fig. 11. Here, the term “activation energy” denotes the “migration enthalpy of oxygen ions”. Figure 10 shows that the ionic conductivity decreases steeply to less than 10$^{-6}\,\Omega^{-1}\,\text{cm}^{-1}$ at $10^6\,\Omega^{-1}\,\text{cm}^{-1}$ when $W$ decreases to $6\,^\circ$. This behavior is valid for all measurement temperatures of 600–900°C. This result demonstrates that the ionic conductivity of oxygen ions is sensitive to the coherence of columnar grain boundaries. Figure 11 shows that the apparent activation energy is also sensitive to the coherence of columnar grain boundaries. The highest coherence YSZ thin film with $W = 4.2\,^\circ$ shows the apparent activation energy close to $90\,\text{kJ/mol}$. The medium coherence film with $W = 6.8\,^\circ$ shows $103\,\text{kJ/mol}$. Films with larger $W$ values show $110–120\,\text{kJ/mol}$. Here, the $W$-factor is a geometric mean between tilt and rotation angles. The slight difference reflects a large difference of the coherence of the grain boundary and the activation energy. Consequently, the activation energy is strictly affected according to the small deviation of the $W$-factor of less than $10\,^\circ$.

In earlier studies, the reported apparent activation energies for YSZ bulk crystals were $81\,\text{kJ/mol}$, $86\,\text{kJ/mol}$, $87\,\text{kJ/mol}$, $106\,\text{kJ/mol}$ for 10 mol% Y$_2$O$_3$–ZrO$_2$ (10YSZ) single crystals, and $90\,\text{kJ/mol}$ for single-crystal-like epitaxial 10YSZ thin films thicker than 60 nm. The composition of YSZ thin films used for this study was 6YSZ. The concentration of oxygen vacancies as a carrier was less than that reported in the literature cited above. However, YSZ thin films with higher coherence in the columnar grain boundary show apparent activation energy comparable to that of the bulk crystals and epitaxial thin films of 10YSZ. The YSZ thin film is expected to be tetragonal phase because 6 mol% Y$_2$O$_3$ is lower than the cubic–tetragonal phase boundary and because YSZ films are strained bi-axially by the thermal mismatch with substrates. 6YSZ film with $4.2\,^\circ$ of $W$-factor used for this study shows comparable activation energy irrespective of the lower carrier concentration and lower crystallographic symmetry.

Therefore, the effect of the residual stress on the ionic conductivity is considered. Generally, the electrical properties of thin films are affected by the residual stress and the related strain. The sources of the residual stress are the lattice mismatch and the thermal mismatch through the thermal expansion coefficient. Most of the lattice mismatch is relaxed at the deposition temperature introducing misfit dislocations. Then, the thermal mismatch is dominant. The thermal expansion coefficients of YSZ[100], MgO[100], and Al$_2$O$_3$[100] bulk crystals are, respectively, $10.6 \times 10^{-6}$, $13.5 \times 10^{-6}$, $8.1 \times 10^{-6}$, and $8.8 \times 10^{-6}/\text{K}$. Then, in the in-plane direction, 6YSZ films are compressive on the MgO substrates, but tensile on the Al$_2$O$_3$ substrate. Then, 6YSZ films have a tetragonal lattice at room temperature. However, the measurement temperature of the ionic conductivity was close to the film deposition temperature. Figure 4 shows that YSZ thin films have columnar morphology with mid-gaps. Then each columnar grain is locally constrained by the substrate. These facts imply that the residual stress in each columnar grain is slight and that it relaxes through the mid-gaps between columnar grains. Therefore, effects of the residual stress are expected to be negligible.

In the ionic conductivity measurement in the in-plane direction of YSZ/MgO or YSZ/Al$_2$O$_3$ thin films, four conduction paths are possible: (1) bulk lattice conduction, (2) grain boundary conduction, (3) surface or film/substrate interface conduction, and (4) substrate conduction. The substrates are a typical insulator with high impedance, which is two–three orders higher than that of the film, even at elevated temperature. Then the path (4) can be ignored. The interface conduction becomes dominant only at less than 60 nm of the film thickness. Then, the path (3) can also be ignored. Regarding the residual paths (1) and (2), the
grain size in the conduction path, i.e. in-plane direction, is less than 100 nm, so the semi-circles in the Nyquist plots attributed to the bulk lattice and the grain boundary cannot be deconvoluted. However, our impedance spectra, the related ionic conductivity and apparent activation energy depend strongly on the coherence of the grain boundary. This result indicates the grain boundary conduction limit of the in-plane ionic conductivity of the columnar thin films. The in-plane conduction path is expected to be bulk-grain boundary-bulk type.

In general, grain boundaries, mid-gaps between columnar grains, and lattice defects such as dislocation disrupt the coherence and continuity of the crystalline lattice. These irregularities are expected to increase the apparent activation energy of the ionic conductivity. The YSZ/\(\text{MgO}\) film shows a flat grain boundary, although the \(\text{YSZ/Al}_2\text{O}_3\) film shows a zig-zag shaped boundary with high dislocation density. Furthermore, \(\text{YSZ/Al}_2\text{O}_3\) film has larger in-plane rotation, which lowers the coherence of the grain boundary. These effects—tilt angle, rotation angle and grain boundary coherence—are responsible for the ionic conductivity of films with a smaller \(W\)-factor. Films with a larger \(W\)-factor have a randomly shaped boundary with lower coherence and numerous dislocations, as shown in Fig. 6(b). They show lower ionic conductivity even at an elevated temperature.

5. Conclusion

This study elucidated the morphology of 6 mol \% \(\text{Y}_2\text{O}_3\) doped \(\text{ZrO}_2\) (6YSZ) thin films prepared using MOCVD on the ionic conductivity, yielding the following conclusions.

1) The YSZ thin films deposited at temperatures above 500°C comprised columnar grains of 20–80 nm width, but those deposited at 400°C comprised nano-scale polycrystalline of several nanometers.

2) The columnar grain boundary quality was estimated quantitatively using the \(W\)-factor, as calculated from the pole figure, for in-plane coherence (rotation), and using cross-sectional HRTEM analysis for out-of-plane coherence (tilt). By lowering the coherence, high-density edge dislocations were observed.

3) The columnar grain boundary is atomically sharp. No second phase or segregation was detected.

4) The impedance measurement revealed that the total ionic conductivity of the thin films was restricted by the columnar grain boundary. The apparent activation energy, the migration enthalpy of the oxygen ions across the grain boundary, of the most coherent grain boundary is 90 kJ/mol, which is comparable to that of the 10YSZ single crystals. Consequently, this columnar structure with high coherence is preferred for use in thin film ionic conductors.

Acknowledgements  This work is partially supported by JSPS KAKENHI Grant Numbers 24656372, 11750584, The Sumitomo Foundation, The Mikiya Science and Technology Foundation, and The Iwatani Naoji Foundation, and The Noguchi Institute. A part of TEM experiments were supported by JEOL Ltd.

References