Effect of Pulsed Electrical Field on Deposition of YSZ Thin Films in an Aqueous Solution

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In this study we investigated YSZ thin film deposition from an aqueous solution by applying constant electrical field and the effect of a pulsed electrical field upon the growth condition of films. The precursor was an aqueous solution of Zr(NO$_3$)$_2$-2H$_2$O, Y(NO$_3$)$_3$-6H$_2$O, and 0.5 vol% NH$_3$ (aq). The thin film was deposited on the minus electrode side of the glass substrate, which was placed above the minus electrode with a gap distance of 48–530 μm. By applying the electrical field, the thin film was effectively deposited on glass substrates under an applied voltage of 2.5 V for 300 s at room temperature. The as-deposited film was amorphous, and a crystalline phase with a transparent and smooth surface can be obtained after annealing at 773 K for 3 h in air. When a pulse bias is applied to the electrical field, the film thickness, surface defects, and roughness were changed with the frequency. At 2 Hz, the film was fabricated effectively, and a thick film was obtained, but films with smoother and fewer defect surfaces were obtained in a range of about 10–100 Hz. [doi:10.2320/matertrans.MC200920]

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1. Introduction

Zirconia is critical for electrical property and thermal, mechanical, chemical stability, and its thin films have attracted much attention for such applications as the miniaturization of solid oxide fuel cells (SOFCs), thermal-shield or corrosion-resistant coatings, buffer layers of electric devices, optical coatings, and oxygen sensors. Thin and dense films are needed for these applications. To improve such properties many YSZ films are fabricated by PVD or CVD methods including pulsed laser deposition (PLD), electron-beam physical vapor deposition (EB-PVD), magnetron sputtering, and metal organic chemical vapor deposition (MOCVD). On the other hand, liquid phase deposition (LPD) methods such as spin coating, electrophoresis deposition (EPD), electrochemical deposition (ECD), and mist deposition have also been used for relatively thick films. One fabrication method for zirconia thin films using relatively environment friendly materials is to use aqueous solutions as raw materials. However, application of the LPD method is restricted since eliminating the residual fluorine is difficult when hexafluorozirconate salt is used as the zirconium source. For the self-assembled mono-layer (SAM) technique, a large amount of chlorine or sulfur is generally included in the as-deposited thin films when zirconium sulfate (Zr(SO$_4$)$_2$-4H$_2$O) and HCl are used as raw materials. On the other hand, by using the decomposition reaction of an aqueous peroxozirconium complex solution with a zirconium oxyxinate dihydrate (ZrO(NO$_3$)$_2$-2H$_2$O) as a Zr source, pure amorphous ZrO$_2$ precursor thin film was deposited at room temperature. In our previous work, we reported that YSZ thin film was effectively deposited on the minus electrode gap side of the glass substrate from a zirconium oxyxinate dihydrate solution by applying a constant electrical field.

In this study we investigated the relationship between the gap distance and the thickness of the YSZ thin films from an aqueous solution by applying a constant electrical field. We also investigated the effect of a pulsed electrical field in the aqueous solution on the growth rate of films.

2. Experimental Procedure

Zirconium oxyxinate dihydrate (ZrO(NO$_3$)$_2$-2H$_2$O, 99.99%) and Yttrium nitrate hexahydrate (Y(NO$_3$)$_3$-6H$_2$O, 99.99%) were selected as the Zr and Y sources. The composition and concentration of the precursor aqueous solution were adjusted to 94 mol%ZrO$_2$-6 mol%YO$_1.5$ and 0.073 mol/dm$^3$. Appropriate quantities (0–0.5 vol%) of an ammonia aqueous solution (NH$_3$ (aq), 28%) were added to adjust the acidity and to promote a radical exchange reaction between the ZrO(NO$_3$)$_2$ and NH$_3$OH to produce an intermediate product of ZrO(OH)$_2$. After the mixture was stirred for 1 h in an ice bath, a homogeneous colorless and transparent solution was obtained. Glass substrates (9.0 × 9.0 × 0.15 mm$^3$) were cleaned ultrasonically in an ethanol and glass cleaner (Semico clean 56) and irradiated by UV light for 20 min to improve wettability. Figure 1(a) is a schematic diagram of the cell for thin film deposition. The glass substrate was placed above the minus electrode with a gap distance of 48–530 μm. The YSZ thin film was deposited on the minus electrode side of the glass substrate by applying a constant or a pulsed electrical field for 300 s. In this study, a square type pulsed electrical field was used, whose duty ratio, amplitude, and bias voltage (DC offset) were fixed to 50 : 50, 1.25 V, and 1.25 V, respectively, and its frequency was changed from 0.5 to 1000 Hz. Since as-deposited films were smooth and almost transparent but amorphous, heat treatment was performed at 573, 673, and 773 K for 3 h afterwards to obtain crystallized YSZ.

The crystallization of the films was investigated using an X-ray diffractometer (XRD, 40 kV, 30 mA, CuKα, LabX, Shimadzu). Their chemical composition was analyzed by an X-ray fluorescence spectrometer (PW2400, PANalytical). The film morphology was observed by scanning electron microscope (SEM, S-3500, HITACHI) and optical microscope (BHSM-313MB, OLYMPUS).
3. Results and Discussion

3.1 Film deposition

During the film deposition, a constant voltage of 2.0 to 4.5 V was applied between the electrodes. The current value decreased steeply in the first several seconds just after the voltage was applied, which indicated the initial ion movement based on the applied electrical field and the formation of an electric double layer near the electrode. After that the current almost became stable and the film began to precipitate. Well crystallized films with smooth surfaces and few cracks were formed when the applied voltage was 2.5 V and a precursor solution with a 0.5 vol% of NH$_3$(aq) was used. When voltage exceeding 3.0 V was applied, the deposition rate increased due to the electrolysis of water. When the amount of added NH$_3$(aq) was larger in the range of 0 to 0.5 vol%, the thicker films were also deposited in the same deposition time. However when the as-deposition film thickness exceeded about 2 μm or the deposition rate was too fast, it was not favorable because many cracks tended to develop during the heat treatment. When the amount of added NH$_3$(aq) exceeds 0.75 vol% or higher voltage was applied, a gel like product precipitated easily and became hard to deposit. This indicated that the crystallization process of YSZ thin film from an aqueous zirconium oxynitrate solution progressed by adding a small amount of NH$_3$(aq).

In this method, since a radical exchange and precipitation reaction occurred with the assistance of the electric field, they were influenced by the applied voltage. The stability of the ZrO(NO$_3$)$_2$, ZrO(OH)$_2$, and the deposition of the film was also affected by the subtle acidity change near the substrate. Figure 1(b) shows a schematic of ion movement during deposition. At the surface of the minus electrode, an electric double layer is probably formed, and then mutual repulsion between the ions and the hydroxide ion concentration also rose locally near the glass substrate. Therefore the film was deposited on the glass substrate surface of the minus electrode side. In this study the film-deposited place is unique compared to the conventional EPD method, and the gap distance between the substrate and the minus electrode is considered one important parameter that will be mentioned later.

As-deposited films were smooth and transparent but amorphous, and no obvious X-ray diffraction peaks were detected. For that reason samples were heat-treated at 573, 673, and 773 K for 3 h afterwards to obtain crystallized YSZ. After heat treatment, transparent, pure, and relatively hard thin films were obtained. The YSZ peaks were observed at samples annealed at 673 and 773 K. Since definite crystallization can’t be detected at samples annealed at 573 K, the samples were heat-treated at 773 K after this. The composition of the films was almost the same as with that of the aqueous solution. Figure 2 shows the surface and cross-section micrographs of the YSZ thin film. In this case film thicknesses were about 1.0 μm, and some cracks existed at the surface (Fig. 2(a)). When the thickness of the as-deposition film exceeded about 2 μm, cracks tended to occur during heat treatment due to shrinkage. Films with thick-
nesses less than about 1 μm shrunk mainly along the direction perpendicular to the substrate surface and the film areas without cracks became large. Using the degree of peak shift of the XRD profile, we calculated that about 500 MPa residual tensile stresses existed along the substrate surface.

### 3.2 Influence of gap distance

As films were deposited on the glass substrate facing the minus electrode, the film thickness changed based on the gap between the substrate and the electrode. Gap adjustment was performed by mending tapes whose thicknesses were measured beforehand. Figure 3 indicates the relationship between the gap distance and the grown film thickness. At the narrow gap region, wider space produced thicker film. But for a gap distance wider than 500 μm, the film was hard to deposit. This phenomenon can be explained as follows. As indicated in Fig. 1(b), by the electrolysis of H₂O and the formation of an electric double layer, the concentration of hydroxide ion increased near the surface of the minus electrode, and Zr(OH)₄ precipitated and formed film on the glass substrate. When the gap distance was moderate, then enough Zr⁺⁺ cation and OH⁻ anion existed near the glass substrate and formed a thicker film. But when the gap distance was too large, the electric double layer was not affected, OH⁻ anion diffused into the solution before reaching the glass substrate, and the film became hard to precipitate. Therefore the growth rate of the film could be controlled by adjusting the gap distance between the substrate and the electrode. In this study when the gap distance was less than 100 μm, films were formed with few cracks.

### 3.3 Influence of pulsed electrical field

When a pulsed electrical field was applied, the film thickness, the surface defects, and the roughness changed according to the frequency. When the frequency was 0.5 Hz, the surface condition of the deposited film was almost the same as the film deposited using a constant electrical field, but the thickness was about half with the same deposition time because the duty of the pulse was 50 : 50. Figure 4
shows the effect of the pulse frequency on film thickness. At 2 Hz, the film fabricated effectively, and thick film was obtained. But in this case, the film surface was rough with many defects (Fig. 5), and smoother, well crystallized films with fewer defect surfaces were deposited at a pulse frequency of 5–10 Hz. By applying a higher pulse frequency of 10–100 Hz, films resulted with fewer defect surfaces but only thinner films can be deposited. On the other hand X-ray profiles indicate that well crystallized film was deposited at 5 Hz (Fig. 6). These observations suggest that an electrical field of 2–10 Hz affects the electrical double layer formation/deformation or ion movement. We conclude that 5 Hz is the proper cycle for film formation with this method.

4. Conclusion

In our present study, YSZ thin films were grown on glass substrates in an aqueous complex solution with the assistance of a constant or a pulsed electrical field. ZrO(NO$_3$)$_2$·2H$_2$O and Y(NO$_3$)$_3$·6H$_2$O were used as Zr and Y sources. An ammonia solution in appropriate quantities was added to adjust the acidity and to promote the radical exchange reaction between ZrO(NO$_3$)$_2$ and NH$_4$OH to produce an intermediate form of ZrO(OH)$_2$. YSZ precursor thin film was deposited on the minus electrode side of the glass substrate that was placed above the carbon minus electrode with a gap distance of 48 to 100 μm by applying voltage of 2.5 V for 300 s. As-deposited films were smooth and transparent but amorphous. After heat treatment at 773 K for 3 h, crystallized YSZ films were obtained. When the pulsed electrical field was applied between the electrodes the film thickness, the surface defects, and the roughness changed. At 2 Hz, the film was deposited effectively and thick film was obtained, but films with smoother and fewer defect surfaces were obtained by applying a higher pulse frequency of 10–100 Hz. In this study we concluded that a pulse frequency of 5 Hz was the proper cycle for film formation with smooth, fewer defect surfaces, and appropriate thickness.

REFERENCES