THIN FILM TETRAGONAL DOPED ZIRCONIA: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Yttria-doped zirconia thin films of about 0.5 microns were prepared by radio-frequency cathodic sputtering from a 3 mol% target at different powers, gas flow rates and pressures. X-ray diffraction techniques were used to examine the phase compositions. The results show a mixture of tetragonal and monoclinic phases in the as-deposited films. Increased crystallinity was observed in the films deposited at higher argon flow rates. Annealing reduces the monoclinic phase and enhances crystallinity of the tetragonal phase. Films annealed at 700°C for two hours showed significant changes in phase content resulting in at least 95% tetragonal phase consistent with reported phase diagrams. Electron microprobe used to examine the compositional homogeneity of the film showed uniform distribution of the zirconia content. No pinholes were detected.

1. INTRODUCTION

Cubic stabilized zirconia (CSZ) is currently the material of choice for many important applications requiring high oxygen ion conductivity such as gas sensors, solid-oxide fuel cells (SOFC's), and certain catalytic applications. However, recent studies (1-4) have shown that at temperatures below about 600°C, the yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) exhibit higher oxygen ion conductivity than its CSZ counterpart in spite of its lower oxygen vacancy density. TZP sintered bodies also possess higher thermal shock resistance and mechanical strength than the CSZ (5-7). Published phase diagrams (8,9) and recent studies (6,10) also show this material to be thermodynamically stable at temperatures between 550°C and 800°C when the correct yttria content (typically 1 to 3 mol%) is present. These properties make TZP an attractive electrolyte material for SOFC or other electrochemical operations in the intermediate or even lower temperature range.
However, despite these enhanced properties, optimum performance at such low temperatures is likely to require a thin film configuration. While relatively little work has been reported for TZP thin films, we believe that significant optimization of this material is possible.

In this work, thin films of TZP have been deposited by RF sputtering from a 3 mol% yttria-doped zirconia target. Material characterizations were conducted using X-ray diffraction technique (XRD), electron microprobe and scanning electron microscopy (SEM)/energy-dispersive X-ray (EDX) elemental analysis. Further characterizations using electrochemical impedance spectroscopy (EIS) and Raman spectroscopy to correlate the film characteristics as a function of processing parameters are underway.

2. EXPERIMENTAL CONSIDERATIONS

Yttria-doped zirconia films were deposited onto Corning 7059 glass substrates and silicon wafers using a Perkin Elmer 3140 RF diode cathodic sputtering system. The target material is a 3-mol% Y2O3-doped ZrO2 disk with a diameter of 8 in made by Cerac. Films have been deposited using argon gas flow rates from 10 to 100 sccm, forward power from 300 W to 500 W at chamber pressures from 2.66 Pa to 6.65 Pa. Both electrodes were maintained at near ambient temperature during deposition with water cooling. The deposited films are approximately 0.5 to 0.6 microns in thickness uniformly over a 4 in. diameter area. The film growth rate increases approximately linearly with power between 300 and 500 W but does not change significantly with argon gas flow or pressure over the range explored to date. Films are characterized as deposited and following a 2-hour anneal in air at 500°, 600° and 700°C. The samples are heated and cooled at a rate of 50°C/min to and from the annealing temperature. The films were generally transparent as deposited becoming slightly translucent after annealing. Table 1 summarizes the synthesis conditions and heat treatment history for each sample used in the work.

The as-deposited and annealed Y-ZrO2 films have been characterized by standard X-ray diffraction technique with a Scintag PAD V diffraction system using CuKα1 radiation. A broad diffraction angle scan from 2° to 80° was performed first for phase identification. A narrow angle scan between 22-33° was subsequently used to quantitatively analyze the relative amounts of monoclinic and tetragonal phases. However, since quantitative phase analysis of thin film phase composition using the XRD peak integral intensity may vary with variations of crystallinity and grain size, we are now attempting to characterize the phase content of the samples by the Raman spectroscopy. The elemental composition of some samples were determined
by both electron microprobe analysis (using a Cameca SX-50 system) and energy-dispersive X-ray elemental analysis (using an ISI-SX-40A SEM and a Princeton Gamma Technology EDX). With the microprobe operating with an electron beam of 15 kV, the secondary electron back scattering beams were obtained to image the topography of the film. Simultaneously, X-ray photodetectors were tuned to monitor the Lα lines of the Zr and Y emission to measure the compositional distribution of the elements across the film surface. However, since we do not yet have standard samples for calibration, quantitative results will be reported at a later date. An SEM topographical analysis was also performed using a 20 kV electron beam and a 30 kV beam for EDX analysis. The higher energy beam in the EDX was used to separate the Kα lines of Zr and Y, since their Lα lines showed significant overlap.

3. RESULTS AND DISCUSSION

Figure 1 shows typical diffraction scans for (a) an annealed film (sample 12d) over a wide angle scan, (b) an as-deposited film (sample 16a) in a narrow angle scan, and (c) a sample (sample 16d) annealed for two hours at 700°C, respectively. Similar scans have been obtained for all the films made in this work. The two distinct peaks at about 2θ = 30.3° and 28.2° are assigned to the tetragonal (111) and monoclinic (111), respectively, according to the JCPDS files (11) and the consideration of the yttria content. The integral intensities of the peaks were determined by deconvolution into two Gaussian distributions. The ratio of monoclinic to tetragonal plus monoclinic is then calculated from these integral intensity values. The background corrections were made using a linear subtraction between points at approximately 2θ = 26° and 31.5°. While sensitive to the baseline selection, the uncertainty in the ratio of the phases is much less than the changes observed with the heat treatment.

Figure 2 summarizes the relative percentage of the monoclinic phase as a function of RF power, argon flow rate, and annealing temperature. At all deposition conditions, the as-deposited films displayed the highest content of the monoclinic phase, between 23-33%. Within the uncertainty of the XRD result, there was no correlation of the monoclinic content with the argon flow rate or RF power above 400 W forward. As the annealing temperature increased, the proportion of tetragonal phase increases in all samples to greater than 95% tetragonal for samples annealed at 700°C independent of the deposition conditions. The significant changes in phase content and crystallinity in the sample annealed at 700°C are consistent with changes expected based on the published phase diagrams (8,9).
Samples deposited at 300 W exhibited very weak and broad peaks at the positions similar to the tetragonal (111) and monoclinic (111). An additional peak at $2\theta = 34^\circ$ was present in most of the 300 W samples. We assigned this peak to possibly the monoclinic (002). Although increasing noticeably with the annealing temperature, the relative fraction of tetragonal phase in these films remained significantly lower than those deposited at higher powers and annealed similarly.

The intensity of the tetragonal (111) and monoclinic (111) peaks were higher and the width narrower in the films deposited at higher argon flow rates, indicating a higher crystallinity of the film. A similar trend was observed with increasing annealing temperatures for films deposited at the same condition, as shown in Figures 1 (b) and (c), which clearly show the effect of annealing on crystallinity. Although this change with increasing annealing temperature was expected, the effect with argon flow rate is not easily explained. It may be related to the oxygen partial pressure due to background gases. Additional understanding is expected to result from the ongoing analysis of the Raman spectra and the use of argon/oxygen mixtures as the sputtering gas.

Figure 3 shows the result of the EDX analysis of a sample that has been annealed at 600°C for 2 hours. Elements displayed in the spectrum are Si, Y, Zr, Ba and Pb. The peaks of Si, Ba and Pb are believed to be from the glass substrate. Both the Kα and Lα lines of Zr and Y are shown. The Y Lα peak is indistinguishable from the large Zr Lα peak. The Kα lines are separated and clearly indicate the presence of Y. A composition of 2 mol% of yttria was estimated, assuming all the elements were present uniformly within the detection volume with a stoichiometric oxygen content. However, inclusion of the substrate background in this analysis may have resulted in a slight underestimation of the fluorescence from the top zirconia layer. The actual composition may be very close to the original target value, as reported by others (12,13) using RF sputtering and targets of different compositions.

Figure 4 (a) shows a topographical/morphological image of the same film from the back-scattering electrons of the microprobe. A microstructure of fine grain-like features about 1 micron size and less dispersed randomly across the film was observed. A similar morphological image was observed in the SEM study. Figure 4 (b) shows the corresponding elemental analysis on the Zr Lα line across the same sample area. A uniform distribution of the Zr was found with no apparent correlation to the observed microstructure.

Films are currently being deposited on Pt/glass substrates for characterization of the electrochemical properties using the impedance
spectroscopy. The ionic conductivity of these films will be correlated with microstructure and phase content to identify optimum chemical and structural characteristics for applications as thin film electrolytes and to identify optimum deposition conditions. As-deposited and annealed samples will be maintained for extended periods of time at intermediate temperatures under both dry and humid conditions to characterize stability as a function of film properties.

4. CONCLUSIONS

TZP thin films were prepared by RF sputtering from a 3 mol% yttria-doped zirconia target. X-ray diffraction techniques were used to characterize the phase composition of the films deposited at different powers, argon flow rates and pressures. The as-deposited films showed a mixture of tetragonal and monoclinic phases with increased crystallinity at higher argon flow rates. Annealing increased the tetragonal content and crystallinity. Films annealed at 700°C for 2 hours showed over 95% of tetragonal phase, as expected from the phase diagrams. Elemental analyses indicated films were homogeneous in composition.

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### TABLE 1

History of the RF-Sputtered Thin Film Samples

| Sample No. | Ar Flow Rate, sccm | Power, W | Sputtering Time, hours | Thickness, μm | Annealing* Temperature, °C |
|------------|-------------------|---------|------------------------|---------------|---------------------------|
| 12a        | 100               | 500     | 2                      | as-deposited  |
| 12b        |                   |         |                        | 500           |
| 12c        |                   |         |                        | 600           |
| 12d        |                   |         |                        | 700           |
| 12f        |                   |         |                        | 600           |
| 13a        | 100               | 400     | 2.5                    | as-deposited  |
| 13b        |                   |         |                        | 500           |
| 13c        |                   |         |                        | 600           |
| 13d        |                   |         |                        | 700           |
| 13f        |                   |         |                        | 600           |
| 14a        | 100               | 300     | 3                      | as-deposited  |
| 14b        |                   |         |                        | 500           |
| 14c        |                   |         |                        | 600           |
| 14d        |                   |         |                        | 700           |
| 14f        |                   |         |                        | 600           |
| 15a        | 10                | 500     | 2                      | 0.47          |
| 15b        |                   |         |                        | 500           |
| 15c        |                   |         |                        | 600           |
| 15d        |                   |         |                        | 700           |
| 16a        | 50                | 500     | 2                      | as-deposited  |
| 16b        |                   |         |                        | 500           |
| 16c        |                   |         |                        | 600           |
| 16d        |                   |         |                        | 700           |

* Each annealed sample has been subjected to a 2 hour annealing.
Figure 1  
(a) XRD spectrum of sample 12d  
(b) Profile fitted XRD spectrum of sample 16a, showing the integral intensity of both monoclinic and tetragonal phases  
(c) Profile fitted XRD spectrum of sample 16d, showing the large decrease of monoclinic phase after annealing at 700°C for 2 hours
Figure 2  Phase analysis of the yttria-doped zirconia films from the XRD integral intensity data, showing the effect of annealing

Figure 3  EDX elemental microanalysis of a film sample
Figure 4  (a) Topographical image taken by back scattering electrons in the microprobe for the film sample in Figure 3
(b) Corresponding Zr element analysis across the same sample area. A uniform distribution was found, which does not correlate with the microstructure in (a).