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Thermal Stability and Crystallinity in Sputtered Scandia Stabilized Zirconia Thing Films

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Stability and Crystallographic Investigation of Scandia-Stabilized Zirconia for Solid Oxide Fuel Cell Applications

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Background

Solid oxide fuels cells (SOFCs) offer a highly efficient method of harnessing energy from hydrocarbon based fuels compared to traditional combustion technologies. Furthermore, SOFCs generate lower amounts of pollutants, such as nitrogen oxides (NO_x), than combustion technologies, can easily be adapted to carbon capture technologies, and are not limited by the Carnot cycle due to the fact that they are not heat engines[1]. This results in a reduction in the amount of CO_2 emissions per kW*h of energy produced.

Yttria-stabilized zirconia (YSZ) is a traditional material used as the solid electrolyte in SOFCs, which stabilizes the cubic phase of zirconia and provides interstitial sites to allow for oxygen ion diffusion throughout the lattice. However, YSZ has a large ionic resistance when the temperature of the electrolyte is below 800°C; requiring that the operating temperature to be above 850^{o}C. The high operating temperatures required to achieve appreciable oxygen ion conduction makes current SOFCs uneconomic.[2] Expensive interconnect materials that are resistant to thermal shock and can operate at these high temperatures are needed, as well as costly heat exchangers to control the operating temperature. Furthermore, these high temperatures cause interdiffusion of the electrolyte and electrode materials and can cause reaction between the different major parts of the SOFC, which lowers the overall SOFC lifetime.[3]

Lowering SOFC operation temperatures would make them more economically competitive with traditional combustion technologies.[4] In order to lower this prohibitive operation temperature, several new SOFC electrolyte materials have been investigated which have competitive oxygen ion conductivity at intermediate temperatures (500 ^{o}C–700^{o}C).[5-7] Scandia-stabilized zirconia (ScSZ) has gained recent attention as an alternative solid electrolyte material to YSZ, due to its mechanical similarity and increased oxygen ion conductivity at intermediate temperatures (ScSZ has an oxygen ion conductivity of BLAH at 700^{o}C, almost twice that of YSZ at the same temperature). The mechanism for oxygen transport is the same as YSZ but allows for use at intermediate temperatures. While the phase diagram for ScSZ is underdeveloped, the material has been shown to have a maximum oxygen ion conductivity at 10 to 13 mol.% Sc_2O_3 doping into ZrO_2.

While ScSZ performance is better than YSZ at intermediate temperatures, increasing the overall oxygen flux through a SOFC is desired. One method of increasing this flux is by making the electrolyte material very thin, creating very short diffusion pathways for the oxygen ions. One limiting factor to the thickness of the electrolyte material is the traditional ceramic synthesis method, which cannot easily create electrolytes that are less than 500 nm. An alternative synthesis technique that overcomes this limitation is magnetron sputtering. Magnetron sputtering is a physical vapor deposition technique that has classically been used in the semi-conductor industry to make thin films. Unfortunately, magnetron sputtering can make meta-stable high temperature phases when depositing materials, which is a major concern for ScSZ, which forms an undesired rhombohedral phase at temperatures in excess of 1100^{o}C. Additionally, thin-film materials can have different crystal phase stability when compared to the stable bulk crystal phase. Furthermore, deposited films from magnetron sputtering can be nanocrystalline, which is

undesired in a SOFC electrolyte as the films will have a relatively high defect concentration, creating a tortuous path for the oxygen to diffuse through.

Here, we investigated the crystal phase and crystallinity of sputtered 30 nm ScSZ films when synthesized under different sputtering conditions. For this study, a 3 level full 4-factorial design of experiments was used to investigate the effect of sputter gun power, oxygen concentration during sputtering, substrate temperature during sputtering, and post-deposited annealing time at 800^{o}C in air. The crystal phase, crystallinity, and the crystal texture of the as-deposited and post-annealed films were measured using x-ray diffraction.

Experimental

In order to determine the deposition rate for each sample, a series of nine 30 min calibration depositions from a RF sputtered 11 mol.% Sc_2O_3 ScSZ target were performed at the gun powers and oxygen partial pressures listed in **Table 1**. Substrates were rotated during deposition to ensure uniform thickness. The thicknesses of these calibration films were measured using both UV-Vis reflectometry and profilometry. The measured thicknesses were used to determine the deposition time required to achieve a uniform thickness of 30 nm for all of the sample deposition conditions.

A 3^4 factorial design of experiment was developed; the factors and values used for this design are shown in Table 1. 23 samples were deposited onto 7.62 cm by 2.54 cm single crystal silicon substrates. Prior to each deposition, silicon wafers were sonicated in ethanol, acetone and water for 15 minutes each. The substrate was then mounted in the chamber using kapton tape for the room temperature depositions and silver paste for the high temperature depositions. Each sample was deposited at a combination of the conditions shown in Table 1, with the exception of

35 W depositions in the presence of oxygen. These samples were not synthesized due to the prohibitively long deposition times. The thickness of these films was validated with reflectometry and the average thickness was found to be 30.24 ± 2.80 nm. Each sample was then cut into three 2.54 cm by 2.54 cm squares that were used for different annealing times. One of the squares from each deposition condition was left unannealed, while the remaining two squares were annealed at 800°C for 4 and 8 hours. This process generated a total of 69 films that were characterized. The crystallinity, crystal phase, and texturing of each film was measured via 2D X-ray diffraction using a SAXS Lab Ganesha 2000 with a Cu-Kα X-ray light source. These 2D diffraction patterns were converted to 1D diffraction patterns by integrating them with respect to χ.

Factor Level	Gun Power (W)	O_2 Concentration (Vol. %)	Deposition Temperature (^oC)	Annealling Times (hours)
High	65	10	650	8
Medium	50	5	500	4
Low	35	0	0	0

Table 1 The deposition parameters that were varied for the factorial design. A full 3^4 factorial design was employed. All anneals were performed at 800^{o}C.

Results and Discussion

Analysis

Crystal Phase Analysis

Previous studies have shown that the cubic phase of ScSZ is stable in the bulk below 1100°C, at which point it decomposes to a rhombohedral phase.[8] However, phase stability has not been studied in sputtered thin-films. For the sake of brevity only the sample deposited at room temperature and 65 W will be shown here, in **Figure 1**, and the rest are displayed in the supplemental material. Fig. 1 shows that the cubic phase of ScSZ was present in the as-deposited samples, and persisted through 4 and 8 hours of annealing at 800°C. It also shows that no secondary phases formed. This trend was seen in all deposited samples, indicating that the cubic ScSZ phase is highly insensitive to synthesis conditions and is stable at 800°C in air. Fig. 1 also shows that significant peak shifting (^{o} 2θ) between as-deposited and annealed samples, indicating that the crystals in the sample expanded upon annealing. The crystal expansion after post-annealing is likely due to an increase in the oxygen content of the ScSZ crystal lattice during the annealing process. It is known that oxygen deficiencies can form during sputtering, especially when sputtering is performed in low oxygen concentration environments. Therefore, during the annealing process in air, oxygen atoms can replace the defect sites in the crystal lattice, until stoichiometric ScSZ is formed.

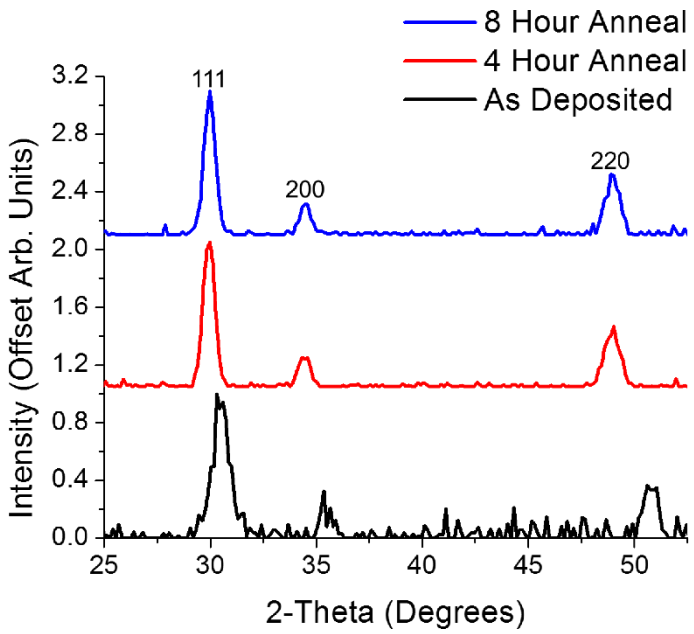

Figure 1 The XRD patterns of samples deposited at room temperature and 50 W with no oxygen in the chamber. The change in crystallinity can be seen between the as-deposited and those annealed for 4 and 8 hrs.

ScSZ Crystallinity Analysis

Once the presence of the cubic ScSZ phase was validated, the crystallinity of each sample was evaluated. During this analysis, each sample was determined to be either nano-crystalline, polycrystalline, or textured based on the peak width in the 1D and 2D diffraction patterns and the peak shape in the 2D diffraction pattern. The later analysis technique was used especially to identify the presence of texturing, as textured films show diffraction “points” instead of polycrystalline diffraction “lines”, as shown in Fig. 2.

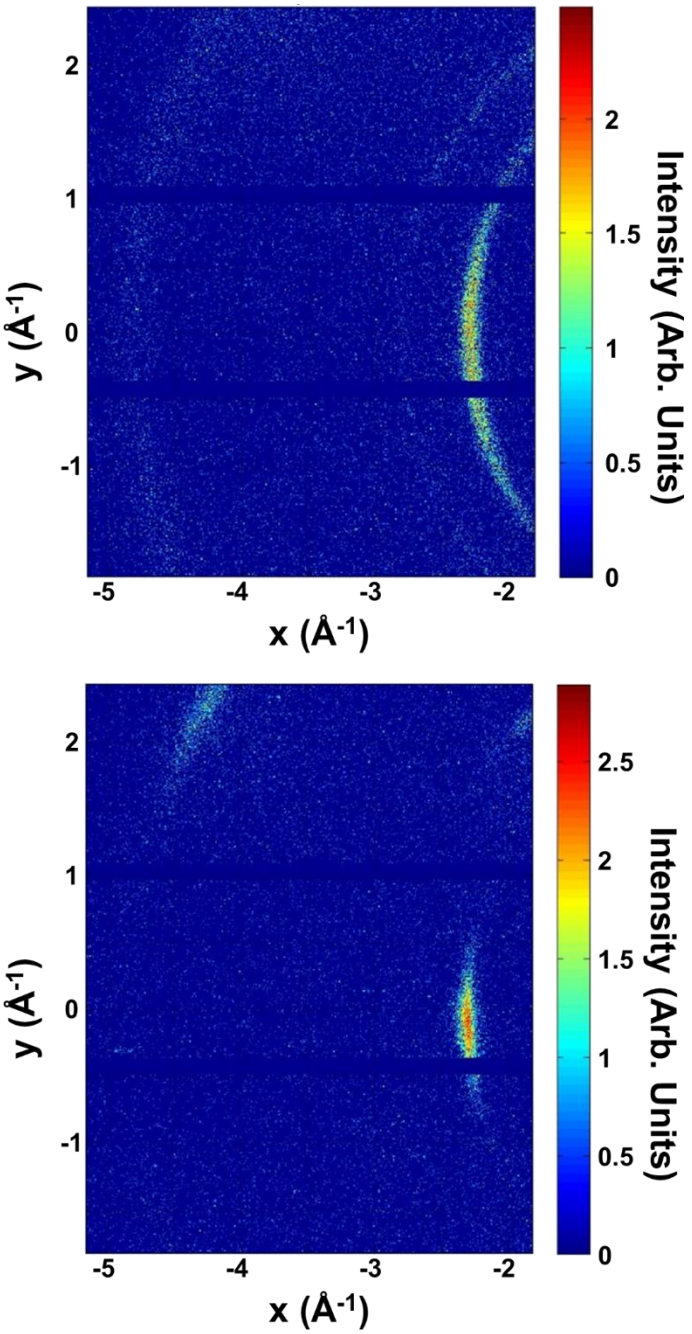

Figure 2: 2D area diffraction patterns from an as-deposited top) polycrystalline ScSZ sample deposited at 500°C and no O_2 and a bottom) textured ScSZ deposited at 500°C and 5 vol.% O_2.

Figure 3 shows the crystalline trends of the samples on a multilayer graph. Samples sputtered at room temperature and with no post-anneal showed a nanocrystalline structure with a broad peak at 27 and 48 2θ, which correspond to the (111) and (220) planes respectively,

regardless of the deposition power or oxygen concentration. When these samples were subject to a post anneal, the samples became polycrystalline, indicated by peak sharpening as seen in Figure 1. This change in crystallinity is likely due to both grain growth and the inclusion of oxygen into the lattice. The lack of oxygen atoms in the as-deposited crystal lattice causes a disordered structure. During the high-temperature anneal, the vacant sites are filled with oxygen inclusions in addition to grain coarsening.

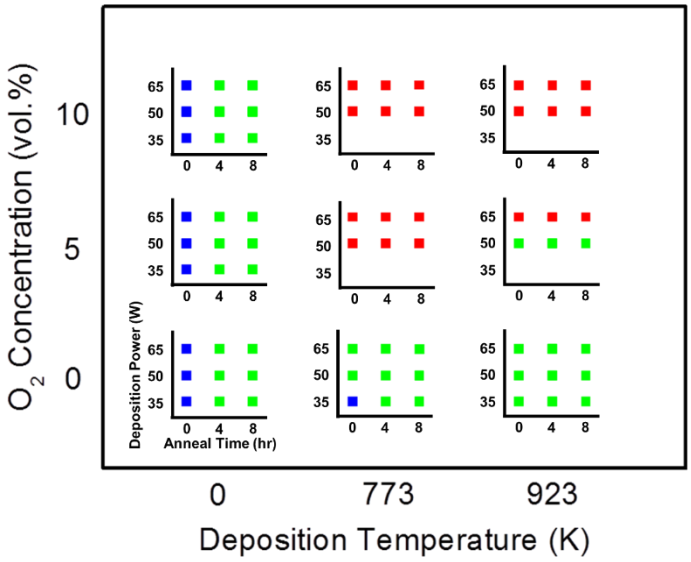

Figure 3: A representation of the crystallinity of each sample. In the representation ■ – Nanocrystalline, ■ – Polycrystalline, and ■ – Textured.

Figure 3 also shows that when the substrate is heated to 500 °C and 650 °C during deposition, the nanocrystalline structure is no longer present and instead the ScSZ exhibits a polycrystalline structure. Additionally, when the concentration of oxygen is increased alongside the increased substrate temperature, a highly textured film is formed as seen in Figure 3. When the substrate temperature increases, there is more energy at the surface to allow for the sample to deposit in a preferred lattice orientation. When substrate heating is combined with the reactive sputtering gas, the films have enough oxygen in the lattice to form an organized structure.

Deposition energy can also contribute to film texturing, as seen in Figure 3 at 650 °C and 5 vol.% O_2, but the main driving factor is substrate surface energy.

ScSZ Texture Analysis

Texturing of electrolyte materials can have an effect on their ultimate performance in a fuel cell. The reason for this is that a textured film has a lower defect density than a nano-crystalline or polycrystalline film, creating more direct paths of diffusion for the oxygen ions. Evaluation of the film texturing was performed by fitting the diffraction peaks of each sample with a pseudo-Voigt profile and calculating the ratio of (111) to (220) peak intensities. While determining the absolute degree of texturing in a thin film is a non-trivial task, the ratio of peak intensities of two separate families of planes can be used as a qualitative metric of film texture. The results of this analysis are shown in Fig. 5. It should be noted that the peak ratios from the samples deposited at 500^{o}C and 5 vol.% O_2 and the 500^{o}C and 650^{o}C, 5 vol.% O_2 samples that were annealed for 8 hours have been removed from Fig. 5. These samples all showed signs of silver paste contamination, and so accurate texture analysis on these films was not possible.

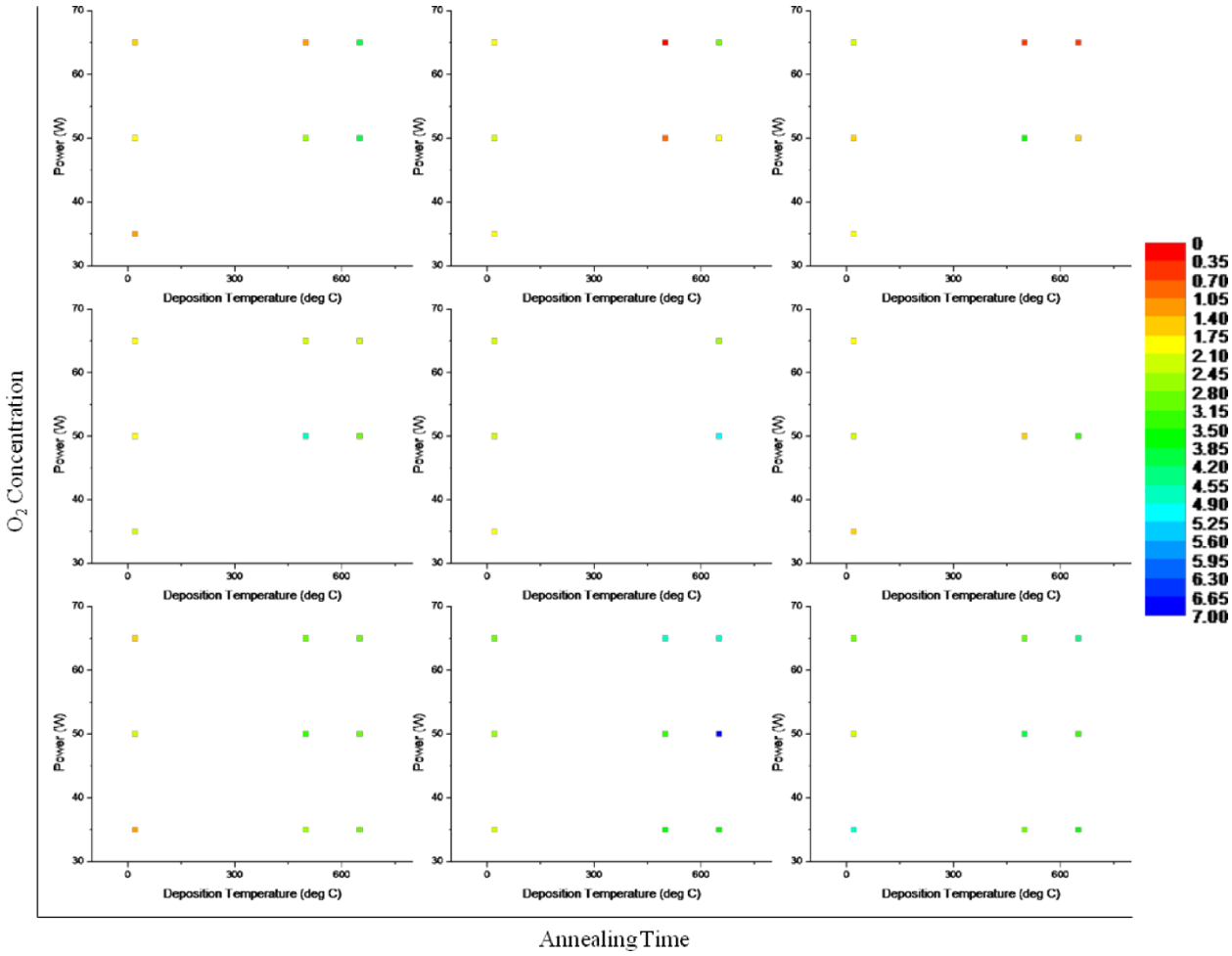

Figure 5: The ratio of the 111 to 220 diffraction peak intensities for the measured thin films.

Fig. 5 shows that all of the as-deposited films that were synthesized without O_2 and with 5 vol. % O_2 became more (111) textured as they were annealed for 4 hours. This texturing dissipates for the samples that were annealed for 8 hours. Fig. 5 also shows that for the samples deposited with 10 vol.% O_2 and at 50 W or 65 W, the films become more textured in the (220) direction when annealed for 4 hours. This trend continues as the samples are annealed for a total of 8 hours. While a physical explanation for these trends has not currently been discovered, the lasting (220) texturing in these samples is a strong indication that the film texture is stable and that these films have a low defect density.

An overall analysis of the crystal phases, crystallinity, and texturing of the films shows that it is advisable to deposit ScSZ thin films at a higher power (65 W with the current sputtering chamber), at a high temperature, up to 650^{o}C, and under at least a 10 O_2 vol.% because these samples showed stable textured (220) cubic ScSZ formation. It is also advisable to perform a post anneal on the samples to allow the crystals to grow and to rid the samples of any latent oxygen deficiencies that may have formed during the initial sample deposition.

Conclusions

Scandia-stabilized zirconia is a promising intermediate temperature electrolyte material to replace YSZ in SOFCs. While ScSZ has better performance than YSZ in the intermediate temperature regime, it is desirable to have thin electrolyte materials to further increase the oxygen flux through the SOFC. Magnetron sputtering can be used to facilitate such thin electrolyte material growth, but has the potential of depositing the undesired rhombohedral phase of ScSZ due to the highly energetic particles used during the sputtering process. Here, samples from a RF sputtered 11 mol.% Sc_2O_3 ScSZ target were deposited on Si using a 3^4 factorial design of sputtering conditions and annealing times to investigate the effect of these factors on deposited ScSZ crystal phase, crystallinity and texture using x-ray diffraction.

The x-ray diffraction showed that all deposited samples had the desired cubic phase of ScSZ, and that the cubic phase did not decompose as the samples were annealed for 4 and 8 hours at 800^{o}C in air. A peak shift in the diffraction peaks was observed in samples after the post anneal, attributed to the inclusion of oxygen in the as-deposited films. Analysis of the crystallinity showed that the samples became more ordered at higher deposition oxygen concentrations and substrate temperatures. An analysis of the texture of the films showed

transient texturing of the (111) crystal plane in samples that were deposited with 0 vol.% O_2 or 5 vol.% O_2 as the sample was annealed. It also showed a stable texturing of the (220) crystal plane for samples that were deposited with 65 W and 10 vol.% O_2. The presence of a stable cubic ScSZ phase, high crystallinity, and persistent (220) texturing in the samples that were deposited at 65 W and 10 vol.% O_2 indicates that films deposited at these conditions will have a low defect density. This also indicates that these films have a high potential to perform well in future fuel cell tests.

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