Kurt Koch is a first year Masters student at the University of Missouri-Rolla (UMR) in Materials Science. He graduated from UMR in December 2003 with a Bachelor of Science in Physics. He has been involved in several research projects in the past, beginning with his work on radiation effects on semiconductors with Dr. Massimo Bertino and Dr. Akira Tokuhiro of UMR during an Opportunity for Undergraduate Research Experience (OURE) program. Later he was involved in TEM preparation and characterization of doped and annealed Silicon under Dr. Richard Vanfleet of the University of Central Florida through a NSF nanotechnology REU. In summer 2003 he participated in the SULI program at Pacific Northwest National Laboratory, working on cerium oxide films with Dr. Laxmikant Saraf. He plans to continue his MS studies and concentrate his research efforts on characterization techniques, with emphasis on TEM studies.

Dr. Laxmikant Saraf received his Ph.D. in Physics from University of Pune in 1999 in the areas of studies in functional oxides and novel materials. He completed his two years of post-doctorate fellowship program at University of Maryland, College Park in the area of heteroepitaxy in magnetic oxide films by pulsed laser deposition. He is currently working as a senior research scientist at Pacific Northwest National Laboratory, Richland WA. Dr. Saraf has authored and co-authored a number of peer reviewed research publications in various international journals in the area of growth of oxide thin films and related properties. His current research interests and responsibilities include, application of micro-fabrication and clean room technology to different materials systems, thin film processing of metal-oxide heterostructures using metal organic chemical vapor deposition (MOCVD), sputtering (DC/RF) and physical vapor deposition (PVD) for applications in the area of solid oxide fuel cells.

SYNTHESIS AND CHARACTERIZATION OF PURE AND DOPED CERIA FILMS BY SOL-GEL AND SPUTTERING

Kurt T. Koch, Laxmikant Saraf

ABSTRACT

Pure and doped Ceria are known for their ability to gain or lose Oxygen, which is of interest to the Solid Oxide Fuel Cell (SOFC) and catalyst community. Current efforts are focused in SOFCs to reduce the operating temperature of the cell while maintaining ionic conduction. Ceria is known for its high ionic conductivity in the intermediate temperature region. (600-800° C) We have prepared pure and doped Ceria films by Sol-gel and magnetron sputtering methods. Enhanced grain-boundary contribution in the conductivity can be studied in the Sol-gel process due to excellent control over the synthesis conditions, which enabled us to control the average grain size. Sputtered films were grown and investigated as a prelude to possible multi-layered CeO_2 structures in the near future. These films were characterized by X-ray diffraction (XRD), nuclear reaction analysis (NRA), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and Oxygen conduction measurements. We have observed greater volume diffusion in nanocrystalline Ceria compared to bulk polycrystalline films as a result of low density. Near surface diffusion properties with increasing temperature indicate a decrease in the volume diffusion as a result of grain growth. However, a linear increase in O_2 content at ~600nm depth was observed and can be correlated to the redistribution of O_2 in the samples. Surface roughness of <111> and <200> oriented Ceria films on Al_2O_3 and YSZ was observed to be 0.13nm and 0.397nm, respectively. In the case of Ceria grown on YSZ, structural properties from XRD results showed a highly oriented structure with cube on cube growth. XRD results from Ceria grown on Al_2O_3 showed an oriented structure whose degree of orientation appeared to be partially dependent on substrate temperature. Preliminary XPS results indicate reduction in Ceria from the Ce^{4+} to Ce^{3+} state near the surface.

INTRODUCTION

A major goal of fuel cell manufacturers has been to lower the operating temperature of fuel cells. Lower operating temperatures translate into less heat loss from the cell and less expensive construction materials, and the elimination of turbines from current “hybrid” fuel-cell/turbine designs, ideally increasing reliability without sacrificing efficiency. One of the problems in constructing fuel cells that operate in the intermediate temperature (IT) range has been finding a material that will conduct Oxygen in an IT environment. It has been shown that Cerium Oxide (CeO_2) will conduct Oxygen in the IT range [1]. Typically doping of 3+ elements enhances O_2 conduction in CeO_2 [2]. It has also been suggested that the orientation of CeO_2 partially determines the number of Oxygen vacancies and thus the O_2 conductivity of the material near the surface [3, 4].

The next step in its development is finding a means of producing CeO_2 films using inexpensive techniques and maintaining the desirable qualities of the material. Thus, Sol-gel techniques were employed and the quality of the films produced from the technique was investigated. Our analysis of the Sol-gel produced films specifically focused on O_2 conduction and diffusion within the films.

It is known [5] that thin multiple layer structures, because of their many interfaces and space-charge effects, have higher ionic conductivities parallel to the interfaces than the bulk materials. Since it is essential to grow smooth interfaces at a nanometer thickness level, we have studied surface roughness as well as surface state properties in Ceria films by D.C. magnetron sputtering. To limit oxide formation on the target surface Argon was introduced in the atmosphere and the sputter rate was kept fairly low. This set a stage to grow multilayer films with enhanced interface qualities, which has a tremendous potential to impact the ionic properties in multi-layers. Previous multi-layered structures were grown via Molecular Beam Epitaxy (MBE) and were limited in the number of layers grown because of the amount of time involved in producing them. Sputtered films should be able to be grown much faster than those grown via MBE without sacrificing quality.

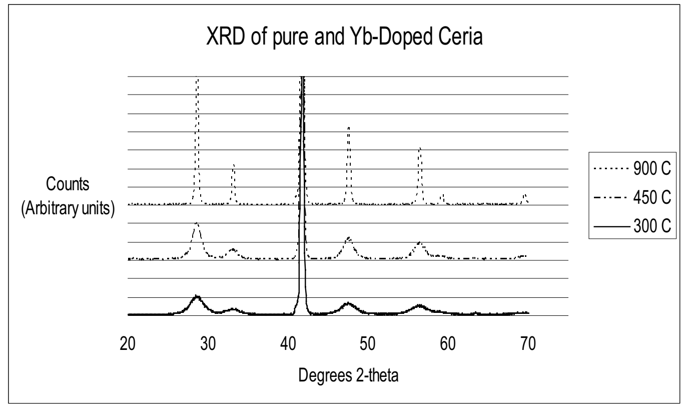

Figure 1. XRD of three CeO_2 films prepared via Sol-gel synthesis and annealed at different temperatures. At lower temperatures the CeO_2 peaks show significant broadening suggesting smaller grain sizes. The smaller grain size at lower temperature was typical for both doped and un-doped films.

MATERIALS AND METHODS

Sol-gel synthesis

Pure and Yb-doped CeO_2 Sol-gel solutions were prepared and spin coated using a Laurell Model WS-200-4T2/RPM/TIM/VAC spin-coater onto polished and un-polished Corundum (Al_2O_3) substrates. Yb was chosen as a dopant in part because of its close ionic radius to Ce. Also, there is relatively limited information on Yb-doped Ceria in the literature making it an open field for research. After each layer coating, the substrate and film were heated between 300 C and 650 C for 2 minutes and coated with several more layers in order to get the desired thickness. It was necessary to coat the substrates several times to ensure that no Al_2O_3 was exposed through the surface of the film. Once the substrates had been coated for the last time they were heated again for 1 hour at 300 C, 450 C, and 650 C respectively.

Sputter coating

Al_2O_3 and Yttrium Stabilized Zirconia (YSZ) substrates were sputter coated in a 33% O_2 and 66% Ar atmosphere at a total pressure of 5-8 millitorr. The distance between the sputter gun and the substrate was about 10 cm. The sputtering was carried out at 300 V and 0.05 A. Substrates were heated between 300 C and 700 C and the coating was done for 1 hour and 30 minutes. After deposition, typical cooling rate down to 150 C was maintained at 2.5 C/min in Ar/O_2 atmosphere.

RESULTS

Figure 1 shows part of the XRD data obtained for the Sol-gel prepared samples.

Using Sherrer's Law:

$t = 0.9\lambda/B\cos\theta_B$

where t is thickness of the grain, λ is the wavelength of the X-Rays used, B is the full-width at half maximum, and θ_B is the angle of incidence, average grain sizes were estimated to be 3.8

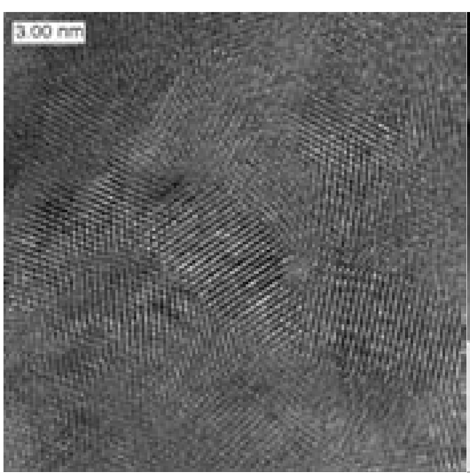

Figure 2. TEM image of Sol-gel prepared CeO_2 film. Using the scale marker it can be seen that individual grains are roughly 3nm in size.

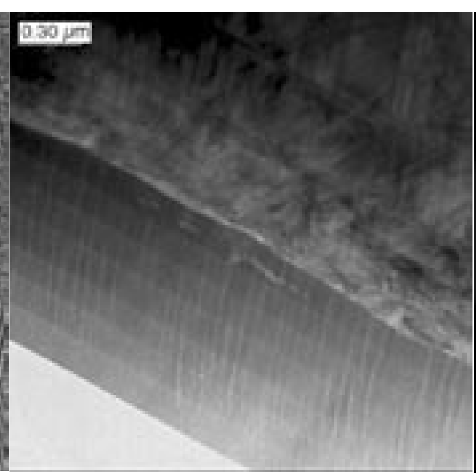

Figure 3. Low resolution TEM image. In the lower left individual layers can be seen.

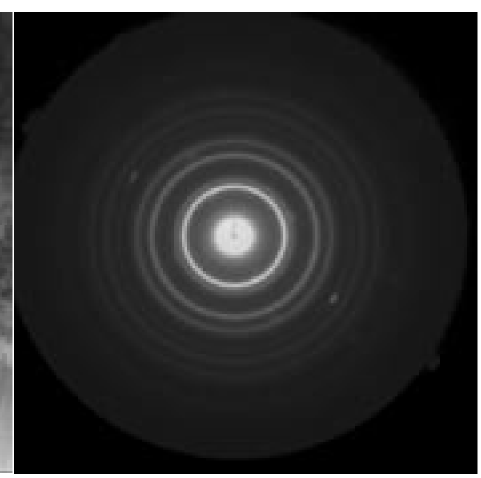

Figure 4. Electron diffraction pattern of the film in Figure 2 and 3. The rings indicate the presence of CeO_2 and Al_2O_3 substrate.

nm, 6.0 nm, and 35.4nm for Ceria prepared and deposited on Al_2O_3 using the Sol-gel synthesis at 300 C, 450 C, and 900 C, respectively.

Grain sizes calculated above from Sherrer's law in the case of a sample prepared at 300 C was confirmed by recording a high-resolution TEM micrograph. Figure 2 shows randomly oriented grains about 3-6nm in size.

A low resolution TEM image of the same sample as in Figure 2 is shown in Figure 3. Film thickness was determined to be about 1000nm. The light and dark bands on the lower-left side of the image clearly show seven distinct layers of Sol-gel deposited CeO_2.

Figure 4 shows an electron diffraction pattern from the film in figures 2 and 3. Bright rings represent diffraction lines spaces with a distance "d". The fluorite cubic structure of Ceria was observed from these patterns

Figure 5 displays some of the information obtained via NRA $^{18}O_2$ diffusion profiles. It shows O_2 concentration versus anneal temperature and time for a Sol-gel sample prepared

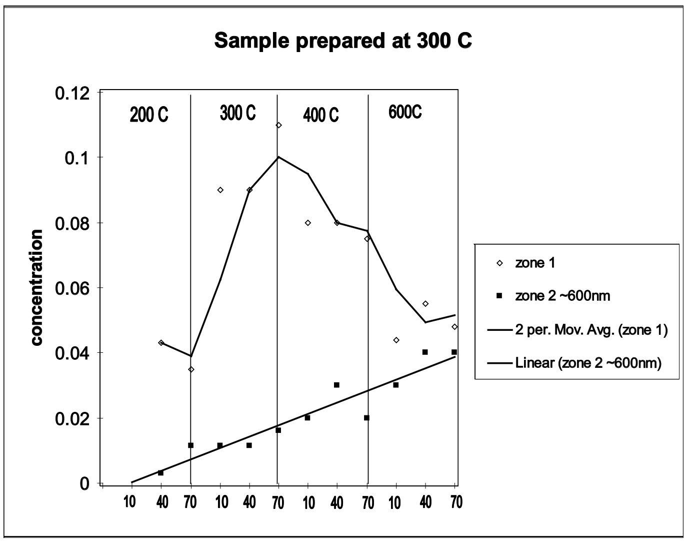

Figure 5. Oxygen measurements for a sample prepared at 300 C. The amount of Oxygen near the sample's surface peaks at the longest time at 70 minutes at 300 C. The Oxygen deeper with in the sample continues to increase.

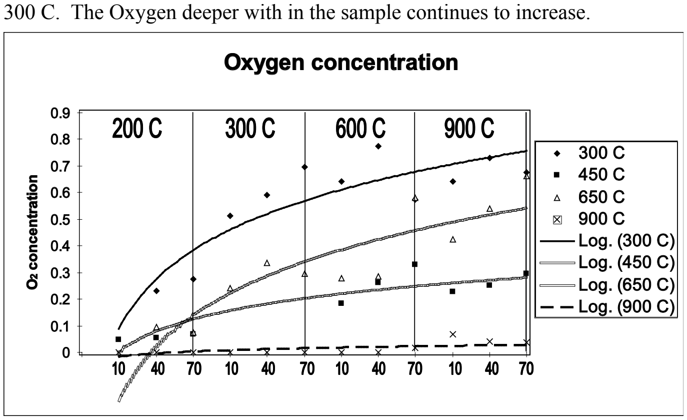

Figure 6. Total Oxygen concentration in a sample. It can be seen that for any sample its total Oxygen content tends to saturate. Logarithmic fits were the closest fit available, even though they do not converge to a set value they do help show that as time and temperature increase Oxygen does not, or at least does not increase much. It can also be seen that generally speaking, the smaller the grain size the higher the amount of Oxygen a sample can hold.

at 300 C. Data was plotted for two sections of the sample's diffusion profile. Zone 1 represents the surface area where for a given measurement the sample's diffusion profile peaked. There is an abrupt decrease in the peak values as the anneal temperature increases above 300 C. Zone 2 represents an area deeper in the film, approximately 600nm from the surface, where O_2 content seems to increase with increasing measurement temperature. The line for zone 1 is a moving average and the line for zone 2 is a linear fit. The fitting lines associated with the data for zone 1 and zones 2 are in place to help guide the eye.

Figure 6 shows relative O_2 concentration as a function of temperature and time. The trend lines are plotted to show that sample preparation temperature affects the amount of O_2 diffused in the sample. It was also noticed that O_2 concentration tends to saturate in the films after certain temperatures.

Figure 7 is a plot of the O_2 concentrations at 70 and 40 minutes for 300, 450 and 900 C. From the slope of the trend lines one can find the volume diffusion coefficient for the respected sample.

Figure 8 compares O_2 ionic conduction for an un-doped Sol-gel film prepared at 450 C to a 5% Yb doped Sol-gel

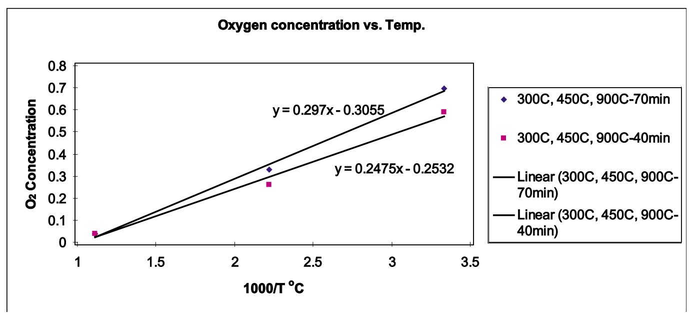

Figure 7. From this figure volume diffusion coefficients can be determined from the slope of the lines above.

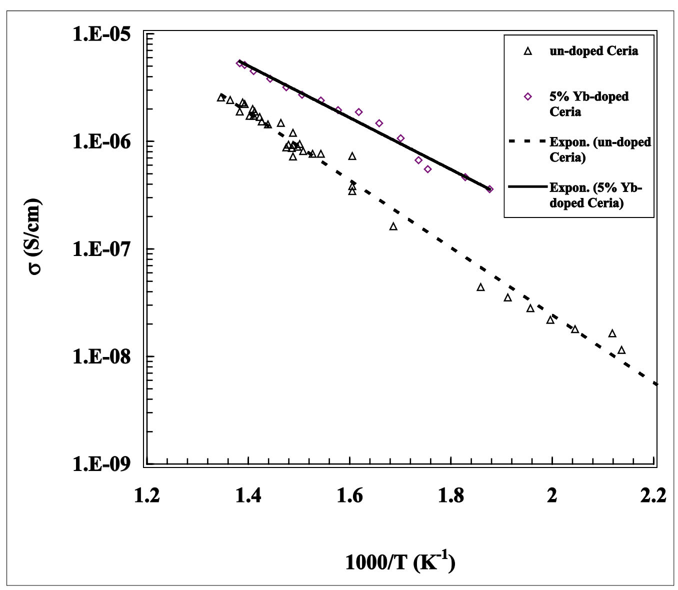

Figure 8. 5% Yb doped Ceria film is compared with an un-doped Ceria film. The 5% doped film shows a higher conductivity than the un-doped film.

film prepared at the same temperature. The doped film was observed to have an activation energy of 0.5 eV whereas the undoped film had an activation energy of 0.7 eV.

Using XRD structural properties of CeO_2 films deposited by magnetron sputtering at 650 C are given in Figure 9. This film, CeO_2 on Al_2O_3 substrate, is observed to be highly oriented in the <111> direction with trace amounts of <200> reflection. However, highly oriented cube-on-cube growth is observed when Ceria is grown on YSZ substrate.

Figure 10 is the XRD plot from CeO_2 sputtered onto YSZ.

Pole plots of the CeO_2 sputtered onto Al_2O_3 and YSZ are represented in Figure 11 and Figure 12 respectively. From these plots it can be seen that the CeO_2 on Al_2O_3 is highly oriented, but not nearly as much as the CeO_2 on YSZ which shows no other orientations, but the <200> orientation, this is suggestive of cube-on-cube growth.

X-ray reflectivity measurements were carried out to determine thickness and uniformity in these films. The sputtered CeO_2 film on Al_2O_3 was estimated to be 24.5nm thick with a surface roughness of about 0.6nm and substrate roughness was estimated to be about 0.4nm. A similar scan was performed on the sputtered CeO_2 film on YSZ. The film on YSZ was estimated to be about 21.7nm thick with a surface roughness of about 0.8nm. The YSZ substrate surface roughness was estimated to

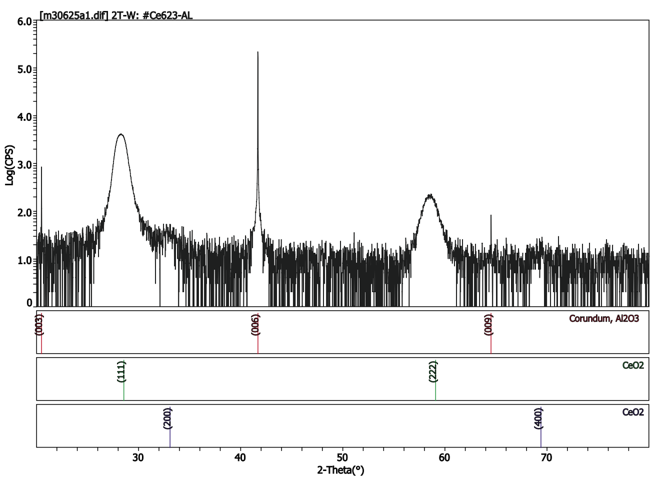

Figure 9. XRD of CeO_2 on Al_2O_3. The red lines are diffraction from the Al_2O_3, the green and blue are from different orientations of the CeO_2. It can be seen that there is very little CeO_2 in the <200> orientation.

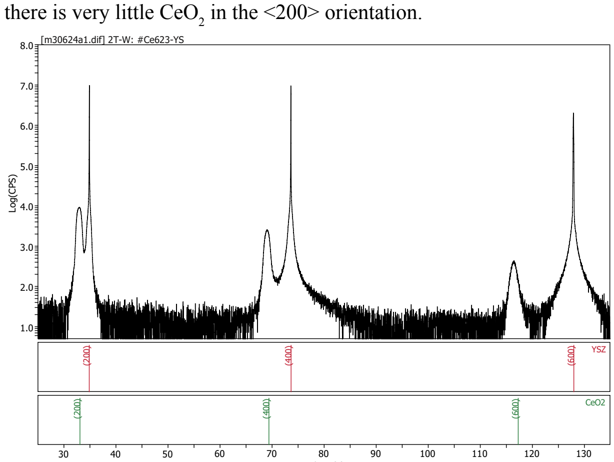

Figure 10. XRD of CeO_2 on YSZ. Red indicates the YSZ and Green indicates the <200> orientation of CeO_2. There are no other orientations present.

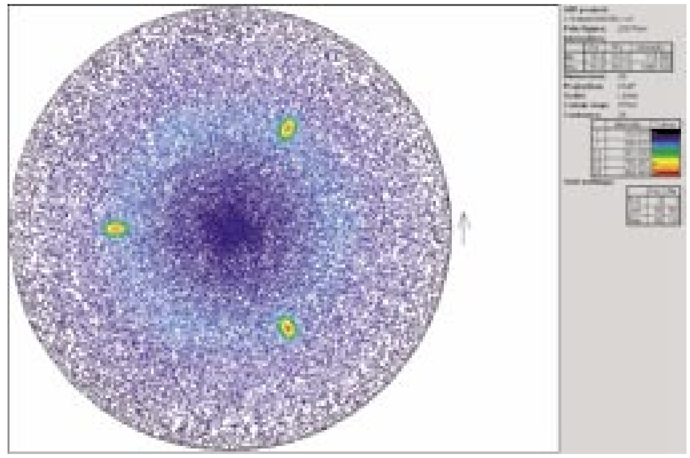

Figure 11. Pole plot of CeO_2 on Al_2O_3. It can be seen that the CeO_2 is highly oriented in the <111> direction.

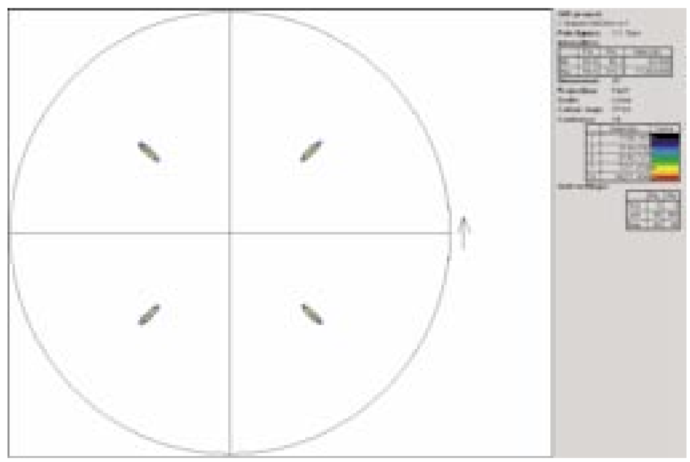

Figure 12. This pole plot shows CeO_2 grown on YSZ has no other orientations but the <200>.

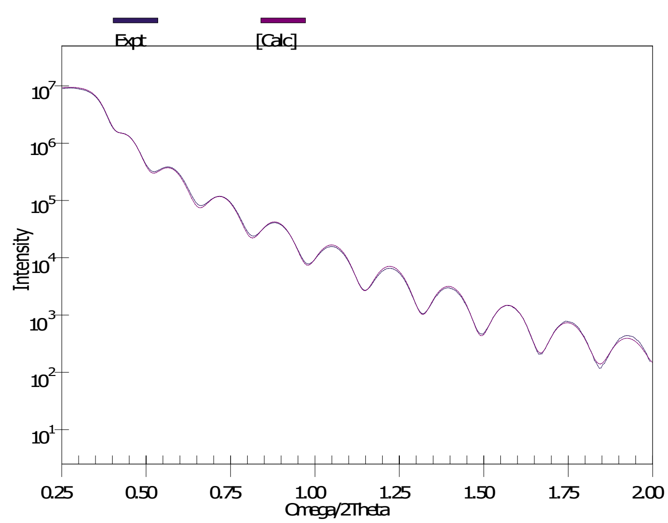

Figure 13. X-ray reflectivity scan for CeO_2 on Al_2O_3. From scans like this, surface roughness and film thickness can be estimated.

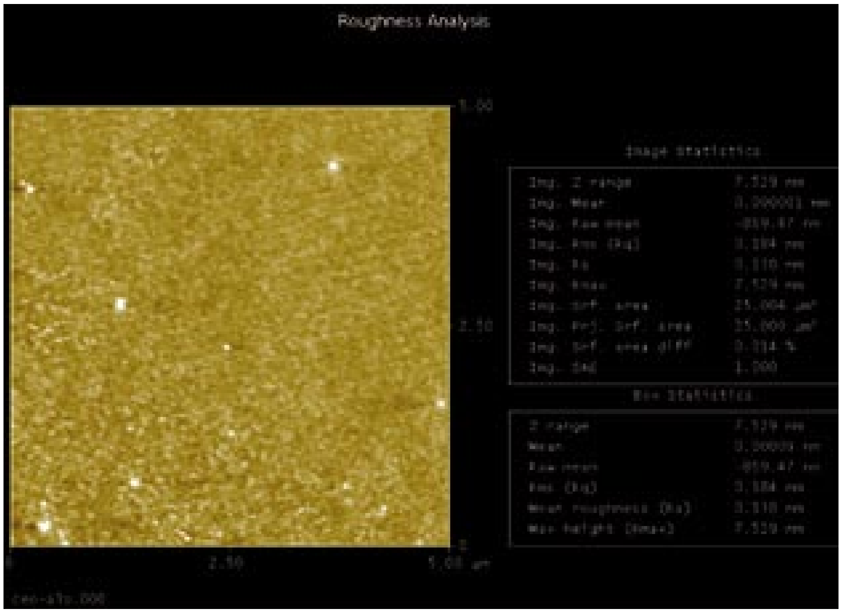

Figure 14. AFM image of CeO_2 deposited on Al_2O_3. From this image mean roughness of the sample was found.

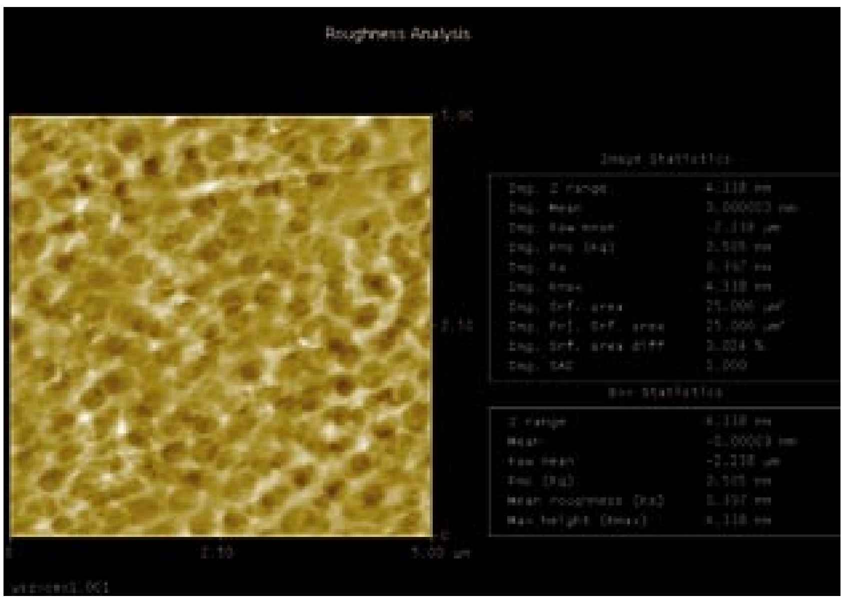

Figure 15. AFM image of CeO_2 deposited on YSZ. From this image mean roughness of the sample was found.

be about 0.6nm. The results from a typical reflectivity scan can be found in Figure 13.

AFM images of sputtered CeO_2 film on Al_2O_3 are represented in Figure 14. The difference in the surface roughness parameters in this case from the X-ray reflectivity measurements can be a result of the difference in the total scanned area in both of the techniques.

Figures 15 AFM images of sputtered CeO_2 film on YSZ. Surface roughness measurements were within a factor of 2 in agreement with the X-ray reflectivity measurements at a value of 0.397nm.

The surface properties of Ceria films were investigated using XPS measurements. Figures 16 and 17 are XPS measurements made at 3 different angles for sputtered CeO_2 film on Al_2O_3 and YSZ, respectively. It was noticed that the surface region has Ce^{3+} which increases with decrease in the incident angle.

Figure 18 represents XPS measurements made at 3 different angles for sputtered CeO_2 film on Al_2O_3. This measurement was made of the Oxygen 1s peak. The shoulder peak seems to be increasing as the angle of incidence decreases. Similar results were observed in the case of Ceria grown on YSZ.

Figure 19 is an XPS measurement of the Cerium 4s and Carbon 1s peaks for CeO_2 film on Al_2O_3. As the angle of incidence is decreased the Carbon peak increases in intensity when compared to the corresponding Cerium peak.

DISCUSSION

It was noticed that grain-size in Ceria strongly depends upon the synthesis temperature. The cubic fluorite structure was observed in grains as small as 3nm, which indicates high stability of Ceria at low synthesis temperature. Sol-gel prepared films with smallest grain size and corresponding lowest density had the highest volumetric O_2 diffusion. These films showed a decrease in O_2 content near the surface when the temperature of O_2 diffusion measurements was increased beyond the original preparation temperature. It is suspected that the change in surface O_2 content is related to grain growth. In samples where the O_2 measurement temperatures were not increased past preparation temperature, no decrease in surface O_2 content was seen. Even though the O_2 content near the surface began to decrease, the measurable O_2 content deeper within the samples continued to increase. (Figure 5) The mechanism behind the increase in observable O_2 deeper within the sample ~600nm could be the result of an $^{18}O/^{16}O$ exchange reaction resulting from improved kinetics at high temperature. The total O_2 content in a sample seemed to increase until it reached some saturation point. (Figure 6) The reason all samples did not saturate at the same level is because of smaller grain size and corresponding larger number of surface sites for O_2 to fix on.

From O_2 conduction measurements it was found that a 5% Yb doped Sol-gel film showed higher ionic conductivity than an un-doped film prepared in a similar fashion. (Figure 8) The reason for this is that Yb has a 3+ valence, so when it is used as a dopant some of the Oxygen in CeO_2 that would normally be bonded to the Ce^{4+} is freed and available to participate in conduction.

The samples prepared via magnetron sputtering in a 33% O_2 and 66% Ar atmosphere and observed via X-ray reflectivity measurements, AFM and XRD showed that thin, smooth and highly oriented CeO_2 films could be grown on YSZ and Al_2O_3.

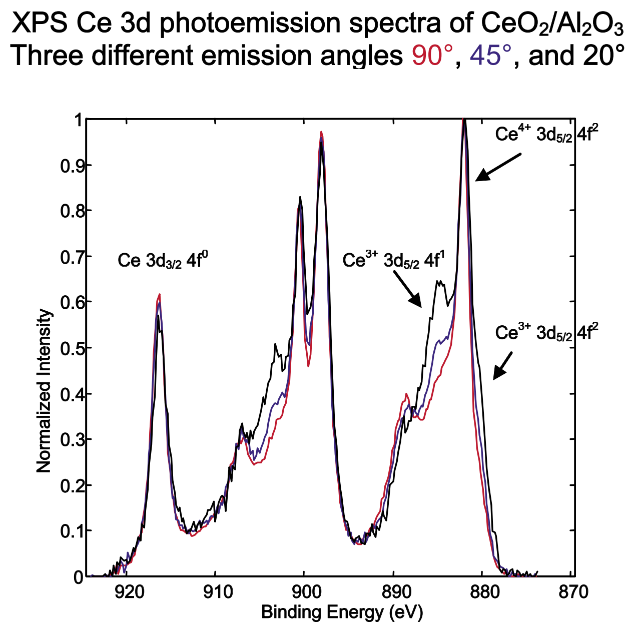

Figure 16. XPS of CeO_2 on Al_2O_3. It appears that the Ce^{3+} state is common at the surface from the 20° scans.

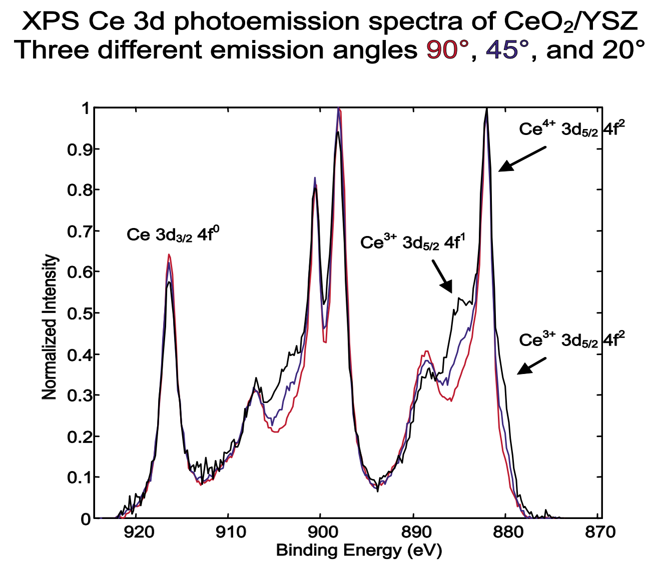

Figure 17. XPS of CeO_2 on YSZ. Again it appears that the Ce^{3+} state is common near the surface from the 20° scans.

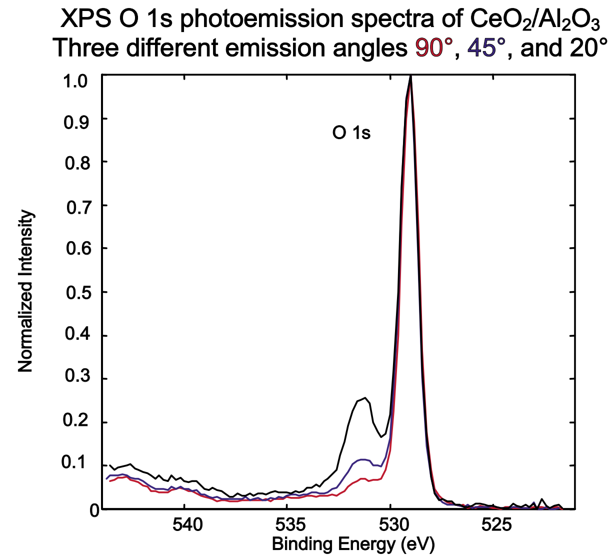

Figure 18. XPS results for the O 1s peak, the second peak (from right to left) seems to be the result of something near the surface of the film, but what it is remains in question. A similar scan on CeO_2 on YSZ was performed with similar results.

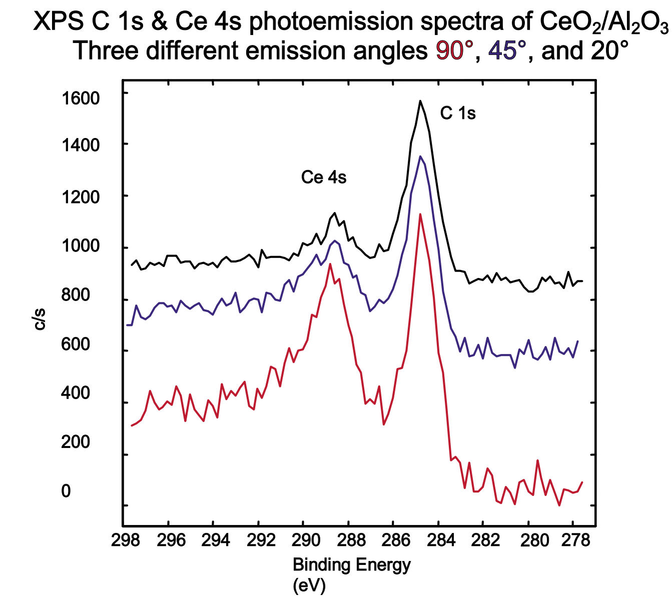

Figure 19. Several scans of CeO_2 on Al_2O_3 at different angles of incidence. It appears that there is little Ce^{4+} near the surface and some Carbon contamination. The y-axis is accurate only for the 90° results. The rest of the results were shifted up.

(figures 9-15) The <200> phase of CeO_2 on Al_2O_3 could not be entirely eliminated because of lattice mismatch. The pole plot of CeO_2 on YSZ in figure 10 shows that there are no other orientations, but the <200> orientation, suggesting cube-on-cube growth. The quality of these films, in terms of a crucial quality, smoothness, is very well suited for future multi-layer and doped multi-layer film growth. Hopefully, this technique for growing CeO_2 films will speed up sample preparation times without sacrificing film quality.

XPS results of the sputtered films showed that at shallow angles of incidence Carbon, Ce^{3+}, and an unnamed peak next to the Oxygen 1s peak increase. (Figures 16-19) Shallow angles of incidence suggest that all these increases were predominantly near the surface of the films. Carbon contamination seems natural since the sample was removed from vacuum before it was analyzed via XPS. The Ce^{3+} and unnamed peak, however, suggest that the surface of the films are partially reduced and may contain Oxygen vacancies respectively. The Oxygen 1s peak may be due to Oxygen vacancies or OH^-.

CONCLUSIONS

Higher ^{18}O diffusion was seen in the sample prepared at 300 C than in samples prepared at 650 C and 900 C suggesting that the effects seen were a result of increased surface area with smaller grain size. Improved Oxygen conduction is observed when Ceria is doped with 5% Yb. It was also seen that Ceria films grown via sputtering were both smooth and promising for future experiments, especially when compared to the time involved in MBE prepared samples.

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REFERENCES

[1] Harry L. Tuller, "Ionic conduction in nanocrystalline materials," Solid State Ionics, vol. 131, Feb. 2000, pp. 143-157.

[2] E. Ruiz-Trejo, J.D. Sirman, Yu.M. Baikov, J.A. Kilner, "Oxygen ion diffusivity, surface exchange and ionic conductivity in single crystal Gadolinia doped Ceria," Solid State Ionics, vol. 113-115, Dec.1998, pp. 565-569.

[3] Jose C. Conesa, "Computer modeling of surface and defects on cerium dioxide," Surface Science, vol. 339, May 1995, pp. 337-352.

[4] G.S. Herman, "Characterization of surface defects on epitaxial CeO_2 (001) films," Surface Science, vol. 437, Jun. 1999, pp. 207-214.

[5] N. Sata, K. Eberman, K. Eberl, J. Maier, "Mesoscopic fast ion conduction in nanometer-scale planar heterostructures," Nature, vol. 408, Dec. 2000, pp. 946-949.