Tunability of Atomic Layer Deposition of Yttria-Stabilized Zirconium Oxide for use in Solid Oxide Fuel Cells

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Abstract:

Thin films of yttria-stabilized zirconium oxide (YSZ) were successfully deposited using atomic layer deposition (ALD) for use in solid oxide fuel cells (SOFCs). YSZ was deposited on p-Si(100) by ALD using Tris(isopropyl-cyclopentadienyl)yttrium [(iPrCp)3Y] and tris(dimethylamino)cyclopentadienylzirconim [ZyALD] as metal precursors and ozone as oxidant. The normalized ALD cycle ratio of yttria cycles / total cycles used in making these films was varied to investigate the tunability of this process. Spectral ellipsometry was used to measure the thickness of the films. X-ray photoelectron spectroscopy (XPS) analyses were used to evaluate the composition and binding environments of as-deposited YSZ films. The normalized cycle ratio and the yttrium atomic percentage (Y atoms / metal atoms) have a linear relationship with a strong correlation, implying excellent tunability for this process. The binding environment analyses determine the oxidation state of the metals and show that decreasing the cycle ratio decreases the extent of yttrium hydroxidation.

Introduction:

Solid Oxide Fuel Cells (SOFCs) show great potential for future energy generation[1]. SOFCs are more efficient and have better stability than other types of fuel cells, but generally operate at very high temperatures (750-1000 °C)[2]. The electrolyte of SOFCs must conduct ions between the electrodes but not conduct electricity. The high operating temperatures of SOFCs is due to the high temperatures required by the solid electrolytes to conduct ions[2]. One way to reduce the operating temperature of SOFCs while maintaining functionality is to make the electrolyte thinner[1]. A very thin electrolyte reduces the resistance of the electrolyte, allowing the SOFC to be operated at lower temperatures.

Many thin film deposition techniques exist, but of particular interest is atomic layer deposition (ALD). ALD is a modified type of chemical vapor deposition (CVD) in which gas phase reactants are introduced one at a time. Excess reactants are purged after each exposure, leaving a monolayer of reactant on the substrate. This monolayer then reacts with the other gas-phase reactant to create solid product on the substrate. Growth of film per cycle is generally constant[3], which allows deposition of highly conformal, thickness-controlled films[4]. ALD is of particular interest for use in SOFCs due to its ability to control thickness to the sub-monolayer level. ALD can also be used to deposit composite materials or ternary oxides by alternating cycles of each component or oxide[4].

Yttria-stabilized zirconia (YSZ) films have been regarded as one of the leading components for enabling future fabrication of intermediate temperature SOFCs (ITSOFCs).

Also, YSZ has been widely investigated as a traditional electrolyte for SOFCs because of its high ionic conductivity and low electronic conductivity[5]. YSZ has been deposited using many physical vapor deposition techniques such as electron beam evaporation[6], laser ablation[6], and plasma spraying[7].

YSZ thin films have also been deposited using ALD. Zirconium with cyclopenadiene and methyl groups have been used as a zirconium precursor in the ALD of YSZ[8, 9]. These precursors yielded high growth rates but carbon and hydrogen impurities[8, 9]. $ZrCl_4$ has also been used as a zirconium ALD precursor, but has been shown to leave chlorine impurities[5, 8]. $Y(thd)_3$ has been used as a yttrium precursor for ALD of YSZ[5, 8, 9], however it has been found to leave carbon impurities[5]. The use of tris(dimethylamino)cyclopentadienylzirconim in ALD of Zirconium oxide has been investigated to some extent[10], but its use in YSZ deposition has not been fully explored. The use of this and tris(isopropyl-cyclopentadienyl)yttrium as zirconium and yttrium precursors, respectively, for ALD of YSZ has not to date been extensively investigated.

As a composite, film composition of YSZ can be largely controlled by varying the number of yttria cycles to zirconia cycles, or the cycle ratio. However, the composition of the film is not exactly the cycle ratio because less than one monolayer of material is deposited per cycle due to steric hindrance. In this study, the relationship between the ratio of yttria cycles : zirconia cycles and the final composition of the film is determined. Impurities from the above precursors are also investigated.

Experimental:

Tris(isopropyl-cyclopentadienyl)yttrium and tris(dimethylamino)cyclopentadienylzirconim were the yttrium and zirconium precursors, respectively. UV radiation of oxygen gas (99.999% purity) immediately upstream of the reactor was used to generate the ozone (1000 ppm ozone), which was used as the oxidizing agent. Argon (99.999% purity) was used as a carrier for the metal precursors and as a purge gas.

A custom-built hot wall reactor was used. (See Fig. 1) The base pressure of the reactor was 2.67 Pa (20 mTorr) and the base temperature of the reactor was 25-450 °C. The reaction chamber was kept at 66.7 Pa (500 mTorr) and 270 °C. The yttrium precursor was kept at 110 °C, the zirconium precursor was kept at 50 °C, and each line from the precursor to the reaction chamber was kept 20 °C higher than the respective precursor bubbler. During a yttria cycle, yttrium precursor was pulsed for 8 s and purged for 10 s. Ozone was pulsed for 1 s and also purged for 10 s. Zirconium precursor was pulsed for 5 s per cycle, with purge and ozone pulse times the same as with the yttria cycle.

Samples were grown on p-type Si(100) wafers (15 mm x 20 mm). Wafers were cleaned using a 1:1:5 solution of $NH_4OH:H_2O_2:H_2O$ for 15 min, then rinsed with deionized water to remove any organic residues. Wafers were dried under N_2 then dipped in 1% HF for 10 s, rinsed with deionized water, and dried again under N_2. This process was performed to reduce the native oxide layer on the silicon surface. Samples were made with yttria cycles : zirconia cycles of 1:7, 1:2, and 1:1.

Thickness of samples was analyzed using a spectral ellipsometer (J.A. Woollam Co., Inc., model M44). Compositional analysis was performed using high-resolution X-ray photoelectron spectroscopy (XPS) (Kratos Analytical Ltd., Kratos AXIS-165). This XPS uses a monochromatic Al Kα (1486.6 eV) X-ray source which operates at 10 mA and 15 kV.

Results and Discussion:

All samples were found to be 14 nm thick using spectral ellipsometry. The thickness was highly uniform across all samples.

XPS data can be found in Figure 2. Before calibration, yttrium 3d peaks can be found at a binding energy of 156-157 eV, zirconium 3d peaks can be found at 179-180 eV, and oxygen peaks can be found at 528 eV. These values are consistent with other XPS data of YSZ[11]. As the cycle ratio decreased (number of yttria cycles decreased with respect to zirconia cycles), the intensity of the yttrium 3d peaks decreased and the intensity of the zirconium 3d peaks increased.

Using the XPSPEAK software, the atomic fractions of yttrium and zirconium (Y atoms / total metal atoms and Zr atoms / total metal atoms respectively) were determined from the XPS data. The yttria atomic fraction was compared to the normalized cycle ratio (yttria cycles / total cycles) to determine the tunability of this process. For a cycle ratio of 1:1, it was found that 53.2% of the metal atoms in the film were yttrium. At a cycle

ratio of 1:2, 35.6% of the metal atoms in the film were yttrium, and at a cycle ratio of 1:7, this number was 13.1%. This data is highly consistent with other research on the ALD of YSZ[12,13]. Figure 3 shows the correlation between atomic yttrium fraction and normalized cycle ratio. The line of best fit has slope of 1.071 ± 0.008 and an intercept of -0.002 ± 0.003 and a correlation value of 0.9999. This shows that changing the cycle ratio changes the amount of zirconium and yttrium in a linear manner.

The XPS data was calibrated using the carbon peak location using the XPSPEAK software. The location of our calibrated peaks are also consistent with literature[11]. The zirconium 3d and yttrium 3d peaks were fitted using component peaks using this software. Figure 4 shows the yttrium 3d peaks and their component Y_2O_3 and YOH peaks. The intensity of the yttrium peaks, and therefore the amount of yttrium, decreases with decreasing cycle ratio. The intensity of the YOH peak also decreases with decreasing cycle ratio. The peak for the sample with cycle ratio of 1:7 was fitted by only a Y_2O_3 peak and therefore this sample contained no YOH. Figure 5 shows zirconium 3d peaks and their component ZrO_2 peaks. The amount of zirconium increased with decreasing cycle ratio. All of the zirconium peaks were fitted using only ZrO_2 peaks, meaning that all of the zirconium in the film is in the form of zirconium oxide.

Conclusions:

When the cycle ratio is decreased, there are more total number of zirconia cycles than at higher cycle ratios, making the sample have more zirconia. The total number of yttria cycles decreases with decreasing cycle ratio, so it is expected that the amount of yttrium also decreases with cycle ratio. Similarly, the amount of zirconium is expected to increase with decreasing cycle ratio.

The strong correlation between metal composition and cycle ration implies good compositional tunability for this ALD process. The cycle ratio can be changed to accurately change the composition of the film. This good tunability is most likely due to the consistency of the ALD reactor used as well as the efficacy of the precursors.

It was also found that decreasing the cycle ratio decreased the amount of YOH. The last cycle in these films was always zirconia, therefore the higher the cycle ratio, the more zirconia cycles were on top of the last yttria cycle. As yttrium forms YOH when exposed to air, YOH was most likely prevented from forming at lower cycle ratios by these additional zirconia layers between the yttrium and the air.

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Figure Captions:

Figure 1. Schematic of the custom-built hot walled ALD reactor used. Argon was used as a carrier and purge gas. Ozone was generated from UV radiation of oxygen gas. Valves were controlled using a LabVIEW program.

Figure 2. XPS data for samples with cycle ratios (yttria cycles : zirconia cycles) of 1:1, 1:2, and 1:7. Data is not calibrated. Oxygen, zirconium 3d, and yttrium 3d peaks are shown with a dashed line. With decreasing cycle ratio, amount of yttrium decreases and amount of zirconium increases.

Figure 3. Normalized cycle ratio (yttria cycles / total cycles) is compared to atomic percentage of yttrium. Linear line of best fit is shown with a slope of 1.071 ± 0.008 and an intercept of -0.002 ± 0.003 and a correlation value of 0.9999.

Figure 4. XPS yttrium peaks. Peaks have been calibrated and software used to calculate the YOH and Y_2O_3 peaks that combine to make the data peaks. YOH peaks are dotted, Y_2O_3 peaks are dashed, and their sum is shown in black. The data is shown in grey. In the peaks for cycle ratio of 1:7, the data lines, sum of peaks line, and Y_2O_3 peak line are all very similar and may be difficult to differentiate. As cycle ratio decreases, the total amount of yttrium decreases and the amount of YOH decreases.

Figure 5. XPS zirconium peaks. Peaks have been calibrated and software used to calculate the ZrO_2 peaks that would fit the data. ZrO_2 peaks are dashed and the data is shown in grey. All ZrO_2 peaks are consistent with the data. The data lines, ZrO_2 peak lines, and sum of peaks lines may be difficult to differentiate as they are so similar. As cycle ratio decreases, amount of zirconium increases.