Atomic Layer Deposited Ceria and Zirconia-based Thin Films for Solid Oxide Fuel Cells Applications

BY

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THESIS

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A mi madre Ana Jaidiver Agudelo A mi abuela Julialba Henao de Rossero Y a mi esposa Viviana Botero Gutierrez Las mujeres más importantes de mi vida. Gracias por todo su amor

Las amo con toda el alma y el corazón

A mi abuelo Heriberto Rossero Porque con sus enseñanzas pude convertirme en el hombre que soy ahora.

A todos mis familiares y amigos Quienes pese a la distancia, Siempre me dieron una voz de aliento, los quiero mucho

Ŋ

a Laura Mercedes Castro

a pesar de todo

It is not true that people stop pursuing dreams because they grow old,

they grow old because they stop pursuing dreams.

Gabriel García Márquez (1927-2014)

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ABSTRACT

The efforts of this Ph.D. research were directed towards the design, fabrication and analysis of solid electrolyte materials that can potentially be used to develop practical and cost-effective set-ups of solid oxide fuel cell stacks operating below 800 °C (IT-SOFC).

Due to its high abundance and its ability of store, transport and release oxygen, Ceria, CeO_{2-x} ($0 \le x \le 0.5$), and Ceria-based materials hold promise as a cost-effective IT-SOFC electrolyte. In this thesis, CeO_{2-x} and yttria doped-CeO_{2-x} (YDC) were deposited via atomic layer deposition (ALD) using novel precursor chemistries based on cyclopentadienyl-type precursors and water vapor as the oxygen source. It was found that under optimized ALD conditions, the growth-rate of CeO_{2-x} and YDC films is 3 times higher than the one reported for similar materials using β -diketonates precursors and ozone. By combining surface and bulk characterization techniques, it was found that the deposited CeO_{2-x} have a non-stoichiometry gradient, (i.e., x in CeO_{2-x} increases from the bulk of the films towards the surface), with surface Ce⁺³ amounts ranging from 10 to 25 %. Evidence suggests that, in terms of coordination or number of nearest neighbors, the analyzed films have bulk-like characteristics and a significant density of point defects (e.g., oxygen vacancies or oxygen in interstitial places). These finding suggest that ALD can be an effective way to engineer stable CeO_{2-x} films with varying structures from near-bulk to nanometer scale with a large density of point defects not attributed to dopant atoms which may be advantageous for improving ionic and catalytic properties.

YDC films are deposited with precise composition and thickness control down to the atomic level, which became a very attractive way for scaling down the SOFC electrolyte to unexplored thicknesses that allow designing stacks towards cost-effective set-ups. It was found

that YDC films are stable under reducing atmosphere and that there are doping and thermal induced structural transformations that are relevant to the physical properties that affect the ionic conductivity.

Implementation of ultra-thin films of yttria stabilized zirconia, (YSZ), has been widely identified to be an effective means of increasing ionic conductivity of the electrolyte in IT-SOFCs. In this thesis, YSZ films are studied, at unexplored thickness levels, to better understand thermal and doping induced structural transformations and to relate the physical properties of YSZ at this thickness scale to electrochemical processes in IT-SOFC. YSZ films were deposited using novel precursor chemistry based on CP- precursors with water as the oxygen source. Characterization shows that at the explored thickness levels there are doping and thermal induced structural transformations that may be relevant to the electrochemical processes. The lattice parameter obtained for cubic YSZ ultra-thin film is lower than that estimated for cubic YSZ single crystals at the same composition, indicating that both, the processing and the precursor selection influence the microstructure of the YSZ. The activation energy for conduction at low temperatures was found similar to that calculated for bulk YSZ films at temperatures higher than 500 °C thus proving that ALD is an effective tool in scaling down SOFCs stacks.

YSZ/YDC composites were deposited using the same ALD reactor for establishing an atomically defined interfacial region and to minimize contamination. It was found that the composites have an oxygen vacancy gradient as determined by energy dispersive X-ray spectroscopy and electron energy loss spectroscopy. This gradient can progressively provide exchanger of oxygen ions among the surface, the lattice and most importantly improve the kinetics at the YSZ/YDC interface.

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1. Introduction

1.1. Motivation

A large majority of the current global energy requirements is currently supplied from nonrenewable sources such as oil, carbon and natural gas. Rapid expansion of world's population and higher standards of living has projected the energy consumption to increase from 16.2 TW in 2007 to over 30 TW by 2050 [1]. In order to reduce the CO_2 emissions to the environment that future global energy requirements will cause, it is necessary to find alternative ways of producing energy that meet not only efficiency but also environmental and long term requirements. Solid oxide fuel cells (SOFCs), are emerging as a promising next generation clean and renewable energy conversion device, in which chemical energy is converted into electrical work by utilizing fuel and oxidant gases at a required temperature and without the need of transferring heat to and from a working fluid [2]. SOFCs meet the demanding requirements for future energy conversion devices, including scalable feature size, high efficiency, good compatibility with a wide range of fuels, and low sensitivity to impurities in the fuel stream. Gases, such as hydrogen, natural gas, alcohols, or biofuels, can be used as fuels in a SOFC for converting energy with an expected efficiency up to 85%, which can be achieved by recovering high quality exhaust heat for cogeneration of power [3, 4].

Up to now, the operation of SOFCs generally requires a very high temperature, in the range of 800 - 1200 °C, to permit efficient transport of oxygen ions (O^{2-}) and good catalytic properties. This high operative temperature has limited practical applications of SOFC technology for economic reasons, especially because of the high cost of materials fabrication, long-term stability of the cell and process technologies [4, 5]. Recently, tremendous efforts have been devoted to reducing the operative temperature of the SOFCs to the so called intermediate temperature

region (600 – 800 °C *i.e.*, IT-SOFCs) which will allow the use of new construction materials, decrease the fabrication costs, increase the lifetime, reduce the startup and shut down time and also will allow broadening the applications of IT-SOFC into smaller, more mobile applications such as transportation [6, 7]. The main disadvantages of lowering the operating temperature are that the oxygen ion conductivity of the common solid electrolyte material, (*i.e.*, yttria stabilized zirconia, YSZ), decreases drastically when operated below 800 °C, poor catalytic activity at the cathode-electrolyte interface for the reduction of oxygen, and inefficient transport properties of mixed conducting oxide-based cathode materials [8-10].

Most of the technological challenges associated with reducing the operative temperature to the intermediate temperature range are related to materials science. For instance, implementation of ultra-thin films of YSZ, in nanometer scale, has been widely identified to be an effective means of increasing ionic conductivity of the electrolyte in IT-SOFCs. However, current mass production techniques can make electrolytes only as thin as a few tens of microns[11]. Also, the use of high-quality thin layers, either as electrodes or interlayers, such as catalysts, diffusion barriers, bond or protective layers have been proposed for applications of IT-SOFC with competitive performances [12, 13]. On the other hand, several efforts have been made in order to find materials with improved ionic transport properties. However, the severe operative conditions of IT-SOFCs limit the number of potential candidates [14].

Ceria, (CeO₂), and ceria-based materials have been proposed as materials for fabricating IT-SOFC electrolytes due to their higher ionic conductivity at lower temperatures with respect to YSZ. CeO₂-based materials are also advantageous as they can exhibit more efficient catalytic properties thereby permitting use of alternate fuels other than hydrogen, such as hydrocarbons and natural gas without the use of an upstream reformer on the fuel-side of the SOFC. Efficient catalytic reduction properties at the cathode side have been observed as well [10, 15].

Among the different CeO_2 -based materials, yttria doped cerium oxide, YDC, has gained a lot of attention mainly because of its relatively lower fabrication costs than other CeO_2 -based materials (i.e., Gadolinium and Samarium doped ceria) as well as other mixed ionic-electronic conductors like Lanthanum-Strontium-Gallium Manganite (LSGM) and higher ionic conductivity than the commonly used YSZ at low temperatures [10, 16].

Novel advanced material fabrication techniques are required for satisfying the performance criteria, and a few additional requirements, such as full coverage of three-dimensional features with dense and/or porous films, would be also important to enhance the efficiency of IT-SOFCs stacks [12]. With the development of thin film fabrication technologies, chemical vapor deposition processes such as atomic layer deposition (ALD) have been currently considered to be a powerful means of fabricating very thin structures for IT-SOFCs stacks [17]. ALD is a thin film deposition method based on sequential self-limiting surface reactions and can be used for obtaining dense, thinner electrolyte layers as well as electrode interfacial layers with accurate thickness and composition control [13, 15, 18, 19].

Application of ALD for the fabrication of thinner electrolytes or for building novel architectures at the interfaces that improve the overall performance of the cell, appears to be an effective solution to overcome the challenge for lowering the operating temperature without sacrificing energy conversion efficiency, and to empower the optimized IT-SOFCs for more mobile applications.

1.2. Overview of the Thesis

In this thesis, novel precursor chemistries for the atomic layer deposition of several oxides, including cerium oxide, yttrium oxide, and zirconium oxide as well as mixed oxides such as yttria doped ceria (YDC) and yttria stabilized zirconia (YSZ) with potential applications as faster ionic conductor materials for IT-SOFCs are presented and discussed.

Chapter 2 presents a summary of the fuel cell technology with emphasis on solid oxide fuel cells and intermediate temperature solid oxide fuel cells. In the same way, background information on ALD and its application for obtaining IT-SOFCs electrolyte materials is presented.

In chapter 3, a detailed description of the ALD equipment used in this work as wells as the characterization techniques used are listed.

Chapter 4 summarizes the ALD of oxygen deficient cerium oxide (*i.e.*, CeO_{2-x}) using novel precursor chemistry based on a cyclopentadienyl precursor along with water as the oxygen source. This chapter present special focus on the ALD process conditions, film structure before and after post-deposition annealing and stability of un-doped CeO_{2-x} under SOFC reducing conditions. It was found that the ALD-deposited CeO_{2-x} thin films have a large amount of superficial and bulk point defects that affect the microstructure of the film. Although the films were unstable under reducing conditions, it was found that these point defects can improve the photo-catalytic properties of ALD-CeO_{2-x} broadening the potential applications of this valuable material

ALD of Y_2O_3 and CeO_2 are combined for producing YDC films and the results are presented in chapter 5. Besides focusing on the ALD process conditions for depositing thin films of Y_2O_3 and CeO_{2-x} , with novel precursor chemistries, this chapter emphasizes on the characterization of ALD process conditions that allow obtaining YDC thin films with precise thickness and composition control as well as the doping level that gives improved or comparable values for the ionic transport. The obtained results are discusses in terms of doping control, composition and structural variations of as-deposited and post-deposition annealed films. This chapter also highlights structural variations with increasing the yttrium doping concentration. Stability of the YDC films under reducing atmosphere is also discussed in this chapter.

In chapter 6, ALD of zirconium oxide and YSZ are presented and the results show that it is possible to obtain cubic YSZ films after carefully tuning the composition of the yttrium in the film. It was also found that the ALD-YSZ films display the cubic phase but the calculated value of the lattice parameter is lower than that estimated for cubic YSZ single crystals at the same composition. The calculated activation energy of cubic-YSZ thin-films, studied in the temperature range of 100 to 400 °C, has comparable values than bulk YSZ film at higher temperatures indicating that these deposited films hold promise for reducing the operative temperature of SOFCs. This chapter also shows how it is possible to combine the results in chapter 5 for producing YSZ/YDC thin film structures using the same reactor in a continuous ALD process with novel precursor chemistry, precise thickness and doping control.

2. Literature Review

2.1. Fuel Cells

Fuel cells are electrochemical devices that transform chemical energy into electrical work without the need of transferring heat to and from a working fluid. Fuel cells can use a variety of fuels such as natural gas, alcohols or pure hydrogen and since they do not rely on a combustion process, the use of fuel cells does not threaten environmental air quality and reduces the emission of greenhouse gases that contribute to global warming. Therefore, by using these electrochemical conversion devices it is possible to satisfy global needs for efficient and environmentally safe energy production. [2].

The basic structure of a fuel cell consists of an electrolyte layer in contact with two porous electrodes (anode and cathode). The most common classification of fuel cells is by the type of electrolyte used [20]. Using this classification it is possible to find:

- Polymer electrolyte fuel cell (PEFC) also known as proton exchange membrane (PEM) fuel cell
- Phosphoric acid fuel cell (PAFC)
- Molten carbonate fuel cell (MCFC)
- Solid Oxide fuel cell (SOFC)

A more detailed classification of fuel cells is presented in Table 1. This table enlarges the previous arrangement by summarizing different types of fuel cells using a classification based on the chemical characteristics of the electrolyte used as the ionic conductor, the operative temperature and the fuel/oxidant combination used but in high temperature fuel cells does not take into account increase of efficiency by capture and use of waste heat.

Table 1, Description of fuel cell technology using as a classification based on the chemical characteristics of

Type of fuel cell	Electrolyte used	Operating Temperature (°C)	Fuel used	Oxidant
Alkaline (AFC)	Potassium hydroxide	50 - 200	Pure hydrogenHydrazine	O ₂ /Air
Direct Methanol (DMFC)	Polymer	60 - 200	• Liquid methanol	O ₂ /Air
Phosphoric Acid (PAFC)	Phosphoric acid	160 - 210	Hydrogen from hydrocarbonsAlcohols	O ₂ /Air
Sulfuric Acid (SAFC)	Sulfuric acid	80 - 90	alcoholimpure hydrogen	O ₂ /Air
Proton Exchange Membrane (PEMFC)	Polymer, proton exchange membrane	50 - 80	 less pure hydrogen from hydrocarbons or methanol 	O ₂ /Air
Molten Carbonate (MCFC)	Molten salts like carbonates, nitrates or sulphates	630 - 650	 hydrogen carbon monoxide natural gas diesel 	CO ₂ /O ₂ /Air
Solid Oxide (SOFC)	Ceramic and perovskites	800 - 1200	natural gaspropane	O ₂ /Air
Protonic ceramic (PCFC)	Thin membranes of Barium-Cerium oxide	600 - 700	• hydrocarbons	O ₂ /Air

the electrolyte used as the ionic conductor, the operative temperature and the oxidant used [4, 20, 21]

Although fuel cells have components similar to a battery, they differ in several aspects. While batteries are energy storage devices with a determined maximum energy available, fuel cells are energy conversion devices that, in theory, can produce electrical energy uninterruptedly on condition that fuel and oxidant are continually supplied to the electrodes [22].

Fuel cells have many beneficial aspects including small size, low levels of noise and the ability to meet specific load requirements. This makes them ideal candidates for a diverse amount of applications where they can be matched and placed close to the source of power demand. The disadvantages vary with each type of fuel cell, for instance the main disadvantage of molten carbonate fuel cells MCFC is its very corrosive and mobile electrolyte, which requires the use of nickel and high-grade stainless steel as the cell components [22].

2.2. Solid Oxide Fuel Cells (SOFCs)

Of the different cell types presented in table 1, solid oxide fuel cells, SOFCs, are particularly interesting due to their high energy conversion, environmental safety, high fuel flexibility and also because they give the possibility of recovering high quality exhaust heat for cogenerating power [4]. The SOFC is the fuel cell with the longest continuous development period, starting in the late 1930's because the electrolyte is solid, the cell can be cast into various shapes, such as tubular, planar, or monolithic [22, 23].

Figure 1 shows a schematics of a typical planar solid oxide fuel cell in which the main functional elements are show. Similar to other kind of fuel cells, the SOFC generally consists of two electrodes sandwiched around an electrolyte that in this case is a ceramic electrolyte instead of a liquid or a polymer. SOFC have the user practicality and general robustness of solid-state construction from metal and metal oxide ceramics but, up to present technology, require high operative temperatures (up to 1200 °C) to permit efficient oxygen ion (*i.e.*, O^{-2}) transport.

In the production of energy using SOFCs, fuel is applied to the anode side while an oxidant is applied to the cathode side and, in theory, the fuel SOFC should be able to provide electrical work as long as fuel and oxidizer are provided [2]. Compared to other fuel cells, this operation has to be performed at higher temperatures, and thus several advantages and disadvantages are offered. For instance, reduced poisoning effect from CO is observed, non-precious metals electrodes may be used, the kinetics of the cells is relatively fast and use of internal reforming allows the use of fuels others than hydrogen. Also, the solid construction of the cell reduces corrosion problems and the solid electrolyte does not move or flood in the electrodes making the design simpler. Nonetheless, the high operative temperatures limits the applications of SOFCs to stationary power plant units [2].



Figure 1, Scheme of a planar solid oxide fuel cell (SOFC) operated with hydrogen and air

2.2.1. SOFCs Components

As seen in figure 1, there are 3 main components on a SOFC: the cathode, the anode and the electrolyte. The cathode (*i.e.*, air side) is the electrode where the O^{-2} ions are produced by reduction of oxygen. The choice of the cathode is a compromise between a number of factors including chemical stability and relatively low interactions with the electrolyte, good ionic and electronic conductivity for minimizing the effective resistance, should catalyze the dissociation of oxygen and its thermal expansion coefficient (TEC) has to match the one of adjacent components. Also it has to be porous in order to allow the diffusion of oxygen to its active sites [8, 20, 24, 25].

The cathode operates in an oxidizing environment at high temperature and the main reaction can be described as follows:

$$\frac{1}{2}O_2(g) + 2e^- \longrightarrow O^{-2}(s) \qquad eq \ (1)$$

This indicates that oxygen in the gas phase is reduced to oxide ions consuming two electrons in the process.

Perovskite materials with the form ABO₃ with substitution of calcium and strontium at the A-site are generally used as the cathode material. At high temperatures, the conduction process of these materials occurs mainly via surface path which involves oxygen adsorption, dissociation, surface diffusion to the triple phase boundary (*i.e.*, the place where the electrolyte, the electrode and the gas meet), and incorporation into the electrolyte [25-28]. New cathode materials have been proposed such as those belonging to the perovskite family (layered perovskites and double perovskites) and spinels (A_2BO_4), however the activation energy for oxygen reduction of these cathodes is still very high [29-31]. The anode (*i.e.*, fuel side) acts as an electro-catalyst for the oxidation of the fuel by the oxygen ions that are transported through the electrolyte. As the cathode, the anode has to be chemically stable under the operation conditions, has to match the TEC of the electrolyte as well as that of adjacent components and it has to be an electronic conductor. Additionally, has to be porous in order to facilitate the diffusion of fuel to the interface ant the exhaust gases away from it. It should accept hydrogen, natural gas, carbon monoxide, and various light hydrocarbons as fuels. Therefore, anode should avoid coke deposition when CO or hydrocarbon fuels are used [8, 32-34].

The anode operates in a reducing environment at high temperature and the main reaction can be described as follows:

$$0^{-2}(s) + H_2(g) \longrightarrow H_2O(g) + 2e^- \qquad eq(2)$$

This indicates that hydrogen in the gas phase is combined with the oxygen ions to form water and to produce two electrons in the process.

Up to now, 3 types of anodes have been explored, pure metals (iron, nickel and platinum), cermets (Metal-Ion conductor *e.g.*, Ni-YSZ) and mixed ionic electronic conductors (MIEC *e.g.*, $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3.6}$). While pure metal anodes were found to have unacceptable and unreliable performance due to larger TEC of the metal compared to the electrolyte [4], Ni-YSZ cermets have serve as the benchmark anode since its introduction in 1970 [35]. The use of these cermets helps to match the TEC of the electrolyte and stabilizes the microstructure. On the other hand, Ni-YSZ anodes provide a conduction path for electrons, and also are an effective catalyst for the oxidation of hydrogen [8, 32]. However, these anodes cannot be used directly with hydrocarbon fuels because the catalytic cracking leads to carbon deposition. These problems have been tried to be solved by introducing mixed ionic electronic conductor materials, however

the fabrication of these materials introduce a high level of complexity and their electrochemical activity appears to be modest when compared to the ones obtained using Ni-YSZ cermets [36]. Another approach to overcome these limitations is to use modified cermets or interlayers of materials with improved catalytic activity towards the oxidation of hydrocarbon fuels such as yttria doped ceria (YDC)/YSZ, Ni/Ce-ZrO₂, Cu/TiO₂/ZrO₂ or Cu/CeO₂/YSZ [37].

The electrolyte is generally a solid oxide ion conductor and its functionality is to transport oxygen ions, O^{-2} , continuously from the cathode to the anode under a gradient of oxygen chemical potentials. Solid electrolytes have to separate the redox reactions occurring at the cathode and anode while satisfying a large number of requirements, such as fast ionic transport, negligible electronic conduction, and thermodynamic stability in the temperature and oxygen partial pressure range, compatible TEC and negligible interaction with electrodes under operation conditions. Furthermore, the electrolyte has to be dense in order to effectively separate the fuel from the air, easy to make and low cost [16, 31, 38]. Partially cation-substituted ZrO_2 (*i.e.*, fluorite structure) and LaGaO₃ (*i.e.*, perovskite structure) electrolytes have been the most extensively studied materials for SOFC [16, 21]. Recently, electrolytes with apatite and partially substituted apatite structures have been synthesized [26, 39]. These materials have drawn interest because of good ionic conductivity *via* a novel O^{-2} ion transport mechanism that is facilitated by interstitial oxide-ions. Extensive reviews on the fabrication methods and the properties of these materials along with other interesting electrolyte materials can be found in [16, 21, 22, 38, 40].

There are other components on a SOFC such as seals and interconnectors that help to conduct the electrons through an external circuit and also to link individual cells together in series or parallel, however they are out the scope of this thesis. Supplementary information on materials of choice for seals and interconnectors used in SOFCs can be found elsewhere [22, 38].
2.3. Intermediate Temperature SOFC (IT-SOFC)

Up to present technology, the operation of SOFCs generally requires a very high temperature, in the range of 800 - 1200 °C, to permit efficient transport of oxygen ions (O^{2-}) and good catalytic properties. However, high operating temperature of the SOFC has its drawbacks. There are thermal expansion coefficient mismatches among materials which induces mechanical stress. High operating temperature also places severe constraints on materials selection which results in difficult fabrication processes plus problems such as electrode sintering and interfacial diffusion between electrolyte and electrodes has also been observed [22, 41].

Despite their high efficiency, one of the main disadvantages is that practical applications of high temperature SOFC are is still limited to stationary power plants. Hence, there is considerable interest in reducing the operation temperature of the SOFC to the so called intermediate temperature region (600 - 800 °C) which decreases fabrication costs and startup times thereby broadening the potential use of SOFCs into smaller, more mobile applications such as transportation [6]. Reducing the operating temperature to this intermediate temperature region also brings other economical and operational benefits, among them [9, 22, 42, 43]:

- Less sintering and creep of the stack materials. This helps maintain high surface area of reaction.
- Reduction of thermal stress. Improvement of material properties and overall areaspecific-resistance.
- Material flexibility. The type and range of materials is greater at lower temperatures. In particular some metals may be incorporated into SOFC stack designs.
- Reduction of fabrication and operative cost.
- Reduction of heat Losses.

- Lower start-up and shut-down time.
- Broadening of the application field. From small electrical plants, auxiliary power units for domestic use and for transportation.

The main disadvantages of lowering the operating temperature are that the oxygen ion conductivity of the traditional solid electrolyte material, (*i.e.*, yttria stabilized zirconia, YSZ), decreases drastically when operated below 800 °C, poor catalytic activity at the cathode-electrolyte interface for the reduction of oxygen, and inefficient transport properties of mixed conducting oxide-based cathode materials [8-10].

For overcoming these problems, there are two approaches that can be applied so that the IT-SOFCs have comparable performance to the ones operates at higher temperatures. The first one is reducing the thickness of the traditional electrolyte material (*i.e.*, YSZ), from several microns to a few nanometers in order to maintain a similar ohmic loss in the electrolyte and also reduce the area specific resistance of the cell [22]. The second one is to research on new materials for the components of the IT-SOFC so faster ionic conductors or improved electrodes with faster catalysis for the oxygen ion incorporation on can be used in order to improve the total power output of the IT-SOFC stack [14, 19]. This thesis is focused on the fabrication of 2 promising ultra-thin electrolyte materials (YSZ and YDC) as well as the option of fabricating hybrid YSZ/YDC interlayers using a continuous ALD process and the literature review related to these topics is presented below.

2.3.1. Ultra-Thin YSZ as Electrolyte Material for IT-SOFC

150 μ m-thick films of YSZ with 8 % mol yttria (Y₂O₃) have been widely used as solid-state electrolytes for high temperature SOFC because of their chemical stability, mechanical

properties and high oxide ion conductivity. However, its ionic conductivity decreases drastically from a value of 1.3 S.cm⁻¹ when operated at 1000 °C, to a value of 0.03 S-cm⁻¹ when the operating temperature is reduced to 800 °C [10, 12, 44, 45]. Implementation of ultra-thin films in nanometer scale, (50 - 200 nm), has been widely identified to be an effective means of increasing ionic conductivity of the electrolyte in IT-SOFC [19, 46, 47].

Several physical and chemical deposition methods have been used in order to deposit thinner films of YSZ including standard ceramic technology and co-precipitation [44, 48], electrophoretic deposition [45], plasma spraying [49], RF-sputtering [50, 51], pulsed laser deposition [52, 53] and liquid injection metal organic chemical vapor deposition MOCVD[54]. More recently, further improvement of ultra-thin YSZ materials was obtained by using corrugated YSZ films which increases the total electrochemically active surface area [19]. This indicates that novel fabrication technique are required in order to satisfy the previous established criteria for solid electrolytes, but also indicates that a few additional requirements, such as fully coverage of three-dimensional features with dense and/or porous films, would be also important to enhance the efficiency of IT-SOFCs.

2.3.2. Ceria-based Electrolyte Materials for IT-SOFC

Cerium oxide, CeO_2 , and cerium oxide based materials, such as gadolinia doped cerium oxide (CGD), samaria doped cerium oxide (SDC) or yttria doped cerium oxide (YDC), have been proposed as promissory materials for fabricating intermediate temperature solid oxide fuel cell (IT-SOFC) electrolytes due to their higher ionic conductivity at lower temperatures (below 750 C) with respect to YSZ [43, 55, 56]. CeO₂-based materials are also advantageous as they can exhibit more efficient catalytic properties thereby permitting use of alternate fuels other than

hydrogen, such as hydrocarbons and natural gas without the use of an upstream reformer on the fuel-side of the SOFC. Efficient catalytic reduction properties at the cathode side have been observed as well [10, 15].

Among the different CeO₂-based materials, YDC has gained a lot of attention mainly because of its relatively lower fabrication costs than other CeO₂-based materials (Gd, Sm) as well as other mixed ionic-electronic conductors like Lanthanum-Strontium-Gallium Manganite (LSGM) and higher ionic conductivity than the commonly used YSZ at low temperature but show mixed ionic electronic conductivity above 750 C which make CeO₂-based materials optimal for uses in IT-SOFC technology [10, 16]. The main problem of using CeO₂-based materials arises from partial reduction of Ce⁺⁴ to Ce⁺³ under reducing conditions. This can cause expansion of the lattice which may lead to mechanical failure [16]. Due to its technological importance, CeO₂ and doped-CeO₂ materials have been deposited by several methods including: standard ceramic technology [57], ammonium carbonate co-precipitation methods [58], glycine-nitrate process [59], wet chemical synthesis [60] and tape casting [61]. In view of IT-SOFC applications, thin films of CeO₂ and doped-CeO₂ films have been produced using physical vapor deposition methods including screen printing [41], dc-sputtering [62] and e-beam evaporation [63].

In order to further improve ionic conductivity in IT-SOFC, there is considerable interest in not only minimizing the thickness of the YSZ, but in potentially use an interlayer between cathode and the YSZ electrolyte so the cathode kinetics improves. YDC has been recognized as a material with higher oxygen ion incorporation coefficient which may facilitate the charge transfer kinetics at lower temperatures in the IT-SOFC stack [15, 18, 19, 64, 65].

2.4. Atomic Layer Deposition for Fabrication of IT-SOFC Electrolytes

It has been identified that for empowering the development of IT-SOFC, several technological challenges related to material science need to be overcome [13]. Thin electrolyte films with dense and pinhole free structure need to be fabricated and the composition of these films need to be precisely controlled in order to deliver comparable power outputs at lower operating temperatures. In the same way, development of novel 3D-structures that increase the total electrochemical area requires the deposition of materials in conformal manner and the fabrication of interlayered films necessitate interfacial tailoring in order to avoid induced resistances at the interface.

Atomic layer deposition (ALD), is a powerful deposition technique which is capable to yield pinhole free and highly uniform dense ultra-thin films on top of flat or 3D-structures [66, 67]. ALD utilizes sequential precursor gas pulses to deposit thin film one monolayer or sub-monolayer at a time base by using alternate self-limiting surface reactions at low pressure (0.1 – 1 Torr). During the ALD process, vapor of different reactants are pulsed into the reaction chamber in a sequentially fashion. Each of the reactant pulses are followed by an inert gas purging or evacuation to clean the reaction chamber of reactant residue in gas phase and/or physically adsorbed on reaction surface. This unique way of pulsing vapor reagents effectively prevent reactants from reaction in gas phase and induce unique self-limiting surface deposition mechanism. Compared to other thin film deposition techniques, ALD offers several benefits, including precise thickness and stoichiometry control, low impurity, excellent uniformity and conformality on 3-D structures [67-70]



Figure 2, representation of the sequential steps of an ALD process

Figure 2 shows a schematics of an ALD process for the production of an oxide using a metal precursor (blue molecule) and water (yellow molecule) as oxygen donor. Four steps are identified and they are performed in a sequential fashion. The first step is to inject the metal precursor in the reaction chamber so the substrate surface gets saturated with a monolayer of precursor. The second step is a purging step in which byproducts and excess of precursor are removed. The chemical reaction is introduced in the third step. In this case, water as the oxygen donor forms the oxide and gives additional active sites. Since ALD can be used for fabricating several material including sulfides [71], other co-reagents may be used in this step. The fourth step is, again, a purging step that helps to remove byproducts and unreacted water vapor. The

combination of these 4 steps is known as an ALD-cycle and the number of cycles can be repeated until the desire film thickness is achieved.

2.4.1. Atomic Layer Deposition of YSZ

Yttria stabilized zirconia (YSZ) films have been widely studied due to their excellent properties as a ceramic material including low thermal conductivity, good corrosion resistance, relatively low elastic modulus, good optical properties and in view of SOFC because of its high ionic conductivity, low electronic conductivity, and the stability at high temperatures and under operating conditions [44, 50]. The maximum ionic conductivity of YSZ is observed when the concentration of the dopant is close to the minimum necessary to completely stabilize the cubic fluorite-type phase. However, it has been reported that this minimum concentration, and its corresponding conductivity, is dependent on the processing and microstructural features [16, 44].

Up to now YSZ with an yttria concentration of 8 % mol has been used as the state-of-the-art electrolyte material in SOFCs. The doping of zirconia with this level of yttria has been identified as the one that can induce the higher ionic conductivity due to the creation of a considerable amount of oxygen vacancies while simultaneously inducing the cubic fluorite-type crystalline structure in the film. However, further addition of yttria decrease the ionic conductivity due to increasing association of the oxygen vacancies and dopant-cations into complex defects of low mobility [16, 72]

150 μm-thick YSZ films have been typically fabricated using physical deposition techniques however this rather thick films cannot be used for IT-SOFCs due to inefficient oxygen ion transport below 800 °C [10, 12, 44, 45]. For overcoming this, reducing YSZ membrane thickness to several nm (50 - 200nm) can significantly reduce ohmic losses, give acceptable area specific resistance values of the electrolyte and in general, improve the performance of SOFCs operated in the intermediate temperature range [19, 47, 62].

With the development of thin film fabrication technologies, chemical vapor deposition techniques have been currently considered to be a powerful means of fabricating very thin structures for IT-SOFCs applications due to the ability of depositing films with superior properties (*i.e.*, pinhole free and highly dense ultra-thin films) and also because these methods satisfy additional fabrication criteria, such as fully coverage of three-dimensional features for all needed dimensions.

Metal organic chemical vapor deposition MOCVD was used in 1999. B-diketonates precursors along with ozone were used for depositing YSZ films over alumina and silicon substrates at high temperatures (450-850 °C). For this process and this precursor chemistry, growth-rates as high as $0.7 \,\mu$ m-min⁻¹ were obtained and the resulting films exhibited fine-grained microstructures [73].

ALD as a method for depositing YSZ films was firstly introduced in early 2000's using soda lime glass, silicon as well as Ni-YSZ cermets as substrates and a variety of metal precursors with a variety of ligands including chloride, β -diketonates, and cyclopentadienyl [74, 75]. In 2007, YSZ films were synthesized by ALD using tetrakis-(dimethylamido)-zirconium, Tris(methylcyclopentadienyl)yttrium and water as the oxygen source. A free-standing structure made of 60 nm-thick ALD YSZ sandwiched between sputtered platinum were reported to have a maximum power density of 270 mW/cm² at 350 °C [46]. In 2008, a low temperature SOFC with corrugated electrolyte membrane was developed and tested. 70 nm-thick YSZ membranes were deposited using the same precursor chemistry onto pre-patterned silicon substrates and a maximum power density of 677 mW/cm² at 400 °C was found and attributed to the increased electrochemical active surface area. More recently, in 2013, a 10 nm-thick YSZ layer with a higher yttria doping level was deposited using ALD on a 500 μ m-thick single crystal YSZ. The results indicate that nano-laminates of slightly higher yttria doping level at the electrode/electrolyte interface significantly enhance the oxygen exchange kinetics.

Decreasing the thickness of YSZ films to several tens of nanometers, as wells as nanoengineered interfaces is therefore confirmed as effective routes for enhancing O^{-2} transport. However, it is of importance to further understand the properties of the film grown *via* ALD using different precursor chemistries and how the film processing affects not only the microstructure but also the physical properties related to electrochemistry processes in IT-SOFCs. This fundamental understanding can be applied for optimizing the construction and working conditions of IT-SOFCs.

2.4.2. Atomic layer Deposition of Ceria and Ceria-based Materials

Ceria, CeO_2 , is a well know material widely used in heterogeneous catalysts, particularly in three-way catalysts for the treatment of exhaust gas from automobiles and in the removal of SO_x from fluid catalytic cracking flue gases as well as for catalytic steam reforming of ethanol [76, 77]. Other interesting properties of CeO_2 , such as high dielectric constant, high refractive index and the ability of store, transport and release oxygen, have made CeO_2 suitable for applications in the semiconductor and energy field; for instance, it has been explored as dielectric material for complementary metal oxide semiconductor (CMOS) and memory applications [78], as well as for buffer layers for high temperature superconductors [79].

In view of IT-SOFC application, CeO_2 and doped- CeO_2 electrolytes have shown higher oxygen ion conductivity at lower temperatures when compared to YSZ. Among the different

CeO₂-based materials, YDC has gained a lot of attention mainly because of its relatively lower fabrication costs than other CeO₂-based materials (Gd, Sm) as well as other mixed ionicelectronic conductors like Lanthanum-Strontium-Gallium Manganite (LSGM) and its derivatives. The composition of doped ceria plays an important role in the ionic conductivity. As with all ceramic electrolytes, the grain boundaries are partially blocking to ionic transport across them. This generates an extra contribution to the total resistance which has been reported to be dependent on impurities that segregate to the boundaries and therefore highly depend on the microstructure and processing history of the material [16, 55].

The main disadvantages of using CeO₂-based materials such as YDC, arises from a transition of pure ionic conductivity to mixed ionic electronic conductivity at high temperatures and also from partial reduction of Ce^{+4} to Ce^{+3} under reducing conditions and high temperatures. This can cause short circuit on the cell along with expansion of the lattice which may lead to mechanical failure [10, 16]. The high ionic conductivity of Ceria-based materials (compared to YSZ) at lower temperatures, combined with the problems arising from reduction as well as mixed ionic electronic conductivity at high temperatures make ceria-based electrolytes viable only for intermediate to low temperature operation.

 CeO_2 and YDC films have been produced using physical vapor deposition methods including dc-sputtering [62] and e-beam evaporation [63]. However, as discussed previously, a chemical vapor deposition method, such as atomic layer deposition (ALD), is preferred due to the fact that ALD allows a precise control of layer thickness by depositing the material one atomic layer at a time giving outstanding film properties such as conformality, dense and pinhole free films [13, 68, 70].

The most studied precursor chemistry for the deposition of CeO_2 is the one based β diketonate precursor under highly oxidizing conditions (*i.e.*, using ozone as the oxygen source). For example, in 2002, CeO₂ thin films were deposited using ALD with Ce(thd)₄ and ozone for applications as buffer layers. In this study, a characterization of the ALD variables is presented giving as a result an ALD window for the process ranging from 175 to 250 °C and a growth rate of 0.32 Å/cycle. Also, microstructure analysis determined that no preferential orientation on the deposited CeO₂ films is found which limits the application of CeO₂ [79]. In 2011, the same precursor chemistry was used for depositing CeO₂ thin films on Ni/YSZ substrates. These films were crystalline but no preferential orientation was found. This work was complemented with a theoretical approach (DFT calculations) for calculating the interaction of CeO₂ thin films with the common reagents that will be used in an IT-SOFC anode [80]. Epitaxial CeO₂ films on cubic YSZ, SrTiO₃ and LaAlO₃ were also produced by using the precursor chemistry based on β diketonates and ozone in 2012. In this study, a rather low growth-rate (~0.2 Å/cycle) was obtained which was identified as the key factor for being able to grow smooth epitaxial films with good film stoichiometry [81].

Other type of precursors have been used for the ALD of CeO₂, for instance in 2011 King *et al.*, used a monomeric homoleptic Ce⁺⁴ alkoxide precursor with water vapor as the oxygen source for studying the dielectric properties of ALD-CeO₂. They report that the deposited films are crystalline and also claim that the crystallite size depends on the deposition temperature [82]. Cyclopentadienyl precursors (CP-type precursors) have also been used for the deposition of CeO₂ thin films. One advantage of using these cyclopentadienyl-ligand precursors is that they are more reactive towards water than precursors with β -diketonate ligands and thus aggressive oxidants like ozone are not necessary [83]. Using these CP-type precursors, Kim *et al*, used

plasma enhanced atomic layer deposition (PE-ALD) for the fabrication of CeO₂ thin films for gate dielectric applications. Using Si as substrates, they use tris(isopropylcyclopentadienyl)-Cerium, Ce(i-prcp)₃, and oxygen plasma in order to characterize first the deposition conditions and then to investigate further applications of the deposited films on microelectronics [84, 85]. Kouda *et al.* also used CP-type precursors for a comparative study of CVD and ALD deposited CeO₂ for applications as gate dielectrics. In this study, CeO₂ films deposited *via* CVD at 350 °C showed good thickness uniformity were polycrystalline and exhibit the cubic structure. However they were not able to fully characterize the ALD parameters for having self-limiting growth and good thickness uniformity [86].

In the fabrication of YDC *via* ALD, the precursor chemistry of choice is also based on β diketonate precursors and ozone. In 2009, Balle *et al.* used Y(thd)₃, Ce(thd)₄ and ozone for the fabrication of YDC on different substrates obtaining a growth rate for YDC of 0.4 to 0.5 Å/cycle. Their deposited thin films were polycrystalline even without annealing but the measured electrical properties were lower when compared to bulk YDC [87]. Fan *et al.* used a mixed precursor chemistry based on an yttrium-CP-Type precursor and a cerium- β -diketonate precursor for fabricating YDC films as interlayers for enhancing the properties of traditional YSZ films. The individual growth rates reported for this process is 0.75 and 0.53 Å/cycle for CeO₂ and Y₂O₃ respectively. Their films presented excellent tunability of the yttrium doping with the ALD cycle ratio and electrical measurements show that using YDC as an interlayer between the cell performance is enhanced and depends on the interlayer film thickness [18, 64, 65]

Based on the literature review it is clear that thin film deposition techniques such as ALD have a tremendous advantage for facing the technological challenges for reducing the operating temperature of SOFC. This thesis will attempt to give fundamental understanding that can be

applied for optimizing the construction of solid electrolytes of un-doped and doped cerium oxide *via* ALD using CP-type precursors which are capable of producing CeO₂ and YDC films with higher deposition rates, good tunability and stable under reducing conditions. This approach is expected to become an attractive means to explore the scalability limits of using ultra-thin CeO₂ and YDC films as electrolytes in IT-SOFC. Since the microstructure of the CeO₂ and YDC films play a significant role in catalytic and ionic transport properties, this thesis also attempts to characterize defects in the microstructure (*i.e.*, nonstoichiometry and other point defects) as well as the effect of the doping level.

This thesis also explores the application of ALD for the fabrication of YSZ in nanometer scale. In the same way as YDC films, novel precursor chemistry will be used for the fabrication of these films and an optimization of the ALD variables will be used for obtaining films with good composition tunability. Since it was found that the microstructure of YSZ films depends on the processing history, a systematic approach will be used in order to understand the effects of doping concentration and ALD conditions on the YSZ microstructure and ionic conductivity at this thickness level. Optimized ALD conditions for YSZ and YDC will be used for fabrication of hybrid YSZ/YDC composites in a continuous processes which will reduce processing time as well as possible contamination at the interface. Electrochemical performance of the deposited films will be discussed.

3. Experimentation and Characterization Techniques

3.1. Atomic Layer Deposition

All the ALD experiments were carried out using a custom design and built tubular hot wall ALD which is shown in figure 3 [88, 89].



Figure 3, Schematic diagram of the ALD reactor used. Updated system presented previously in [90]

The reactor manifold has two separate lines, one for moisture and one for precursor, which lead to the reaction chamber. Using this ALD reactor, depositions can be carried out at temperatures ranging from 25 to 450 °C. A K-type thermocouple is attached on the reactor chamber wall, which is just on top of the substrate holder for temperature monitoring. The

substrates are mounted in a quartz holder and located at the center of the reaction chamber with the substrate surface perpendicular to the gas flow. The base pressure of the ALD chamber is less than 20 mTorr and the operating pressure is 180mTorr. All the valves required for cyclic operation are controlled by a Lab-View® computer program.

Thin films of CeO₂, Y_2O_3 , ZrO₂, YDC, YSZ and YSZ/YDC composites were deposited with novel CP-type precursor chemistries using in all cases water vapor as the oxygen source. During deposition, the precursors were kept in stainless steel vessels at the operating temperature displayed in table 2. Deionized water, maintained at 0 °C using an ice bath, was used to introduce pulses of water vapor into the reactor. All lines downstream the precursor vessels were maintained at least 10 °C higher in order to prevent condensation of precursor in the manifold.

Material	Dragurage	Precursor operating
	Fiecuisor	temperature (°C)
CeO ₂	tris(isopropyl-cyclopentadienyl)Cerium	120
	[Ce(i-prcp) ₃]	
Y_2O_3	tris(isopropyl-cyclopentadienyl)Yttrium	110
	[Y(i-prcp) ₃]	
ZrO ₂	tris(dimethylamino)cyclopentadienyl-Zirconium	55
	[ZyALD]	
YDC	[Ce(i-prcp) ₃]/ [Y(i-prcp) ₃]	120/110
YSZ	[ZyALD]/[Y(i-prcp) ₃]	55/110

Table 2, Metal precursors and operating conditions used for the ALD of the different materials investigated in the development of this thesis

Before deposition, silicon (100) substrates were cut into squares of about 1.5 cm X 1.5 cm and cleaned using standard Radio Corporation of America (RCA) SC-1 cleaning method in order

to remove organic contamination, followed by a 10 s dip in a 2% HF solution which reduces the native silicon oxide layer below 7 Å as measured by spectral ellipsometry (JA Woollam Co., Inc. model M-44 - info available at <u>http://www.jawoollam.com/</u>). Each of the cleaning steps was followed by a thorough deionized water rinse and final dry with N₂. Immediately after the cleaning process, the samples were loaded into the reactor chamber and pumped down to deposition pressure (180 mTorr).

All the metal precursors were injected into the reactor as pulses by backfilling precursor reservoir with N_2 and evacuating this N_2 with precursor vapor under vacuum into the reactor, each pulse lasting 1 s. The precursor dosage per ALD cycle was controlled by increasing the number of precursor pulses. After a number of precursor pulses were completed for saturating the Si-substrate surface, the reactor and both lines of the manifold leading to the reactor were purged with N_2 for ~15 s to remove any excess precursor from the manifold and reactor. After this purging step, the three-way moisture valve was activated momentarily, for 60 ms, in order to divert a small portion of flowing wet N_2 gas into the reactor. After the moisture pulse, both lines of the manifold and the reactor were purged with N_2 for 20 s to remove excess moisture from the reactor. Description of each ALD cycle for individual oxides can be found in table 3 and detailed information about reactor set up and operation can be found elsewhere [90, 91].

Material	Number of	Precursor purge	Water pulse	Moisture purge
	Precursor pulses	duration (s)	duration (ms)	duration (s)
CeO ₂	6	12	60	20
Y ₂ O ₃	10	15	60	20
ZrO_2	6	12	60	20

Table 3, experimental conditions used in each ALD cycle for individual oxides studied.

3.2. Thin Film Characterization

3.2.1. X-ray Photoelectrons Spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to the investigate the elemental bonding state and also used to determine the stoichiometry of individual oxides and thus compositional tunability of the YDC and YSZ films fabricated via ALD. The XPS spectra were collected using a Kratos AXIS-165. The surface analysis system was equipped with a monochromatic Al K α (1486.6 eV) X-ray source and a concentric hemispherical analyzer coupled with a charge neutralizer operated at 15 kV and 10 mA. High resolution spectra were collected at a take-off angle 90° with pass energy of 20 eV, step size of 0.1 eV, and dwell time of 200 ms. The quantitative elemental analysis was performed by fitting the spectral peak areas with Shirley background correction and applying the appropriate sensitivity factors. The binding energy was referred to the adventitious carbon in the C1s spectra at a value of 284.8 eV.

3.2.2. Transmission Electron Microscopy/Electron Energy Loss Spectroscopy

Detailed information of the crystalline structure of the deposited YSZ films as well as film stoichiometry and interfacial interaction for YSZ/YDC composites was obtained using transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS). TEM micrographs were obtained using a JEOL JEM-3010 microscope equipped with Gatan digital cameras and Thermo-Noran XEDS. Energy loss spectroscopy (EELS) was performed in a JEM-ARM200CF STEM/TEM with a cold field emission source, equipped with a Gatan Enfina EELS detector with a 0.35 eV energy resolution to confirm the stoichiometry obtained with XPS and to identify change in oxidation states across the YDC/YSZ/Si interfaces. The EELS spectra were

collected using beam energy of 200 keV, a convergence semi-angle of 35 mrad and a collection semi-angle of 155 mrad.

3.2.3. X-ray Diffraction (XRD)

X-ray diffraction is a rapid non-contact technique that was used for determining the structure as-deposited and annealed YDC films (33 nm-thick). An x-ray diffractometer (X'pert, PANalytical BN Co.) was used to achieve glancing incidence x-ray diffraction (GIXRD) patterns of YDC thin films. The filament is operated at 45 kV and 40 mA during measurement. The x-ray beam is filtered with Ni film. Therefore, monochromatic Cu k α x-ray emission line (λ =0.1542 nm) with a bandwidth of 0.05 nm is generated and used for characterization. The overall diffraction angle (2 θ) resolution is 0.15°. GIXRD diffractograms are collected at an incident angle of 1° to enhance diffraction sensitivity within the film and to minimize interference from the single crystal Si (100) substrate. The crystalline features are identified using the International Center for Diffraction Data database of diffraction pattern Powder Diffraction Files

3.2.4. X-ray absorption spectroscopy (XAS)

40 nm-thick CeO₂ and YDC samples were studied under reducing conditions (4% H_2 in Helium, at 700 °C at 1 atm) by using X-Ray absorption spectroscopy (XAS) for obtaining film stability, coordination number (N) and bond distance (d). L₃ cerium edge (5723 eV) was collected in fluorescence mode using an ion chamber with Stern Heald geometry at the 10-ID line of the MRCAT at Argonne National Laboratory. Higher harmonic x-rays were rejected using a rhodium coated mirror and the ionization chamber was filled with a mixture of 80 % He and 20 % N₂ for incident monitor, and Ar for fluorescence chamber. X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) analyses were performed using WinXAS [92]. The CeO₂ and YDC samples were placed in an air-tight quartz fluorescence cell and then purged for 10 min at room temperature using 200 sccm of Helium. The samples were then annealed at 700 °C for 10 min under the same flow of He and cooled down to room temperature (under continuous He flow) for collecting XAS spectra. The same procedure was repeated using H₂ (200 sccm of 4% H₂ in He at 700 °C). Before collecting the XAS spectra of H₂ treated samples, the samples were cooled down while purging the fluorescence cell with a continuous 200 sccm flow of He. CeO₂ nanoparticles (<25 nm) from Sigma-Aldrich and cerium(III) acetylacetonate hydrate also from Sigma-Aldrich were used as standards for the XANES analysis.

3.2.5. Electrochemical Impedance Spectroscopy

The electrochemical properties of as-deposited and annealed films were analyzed by electrochemical impedance spectroscopy. These measurements were carried out under ambient air, using an Bio-Logic SP-240 potentiostat with 10 mV ac dignal amplitude (Δ V) and without dc polarization in the 7 MHz to 10 µHz frequency range (10 points per decade) in a temperature range varying from room Temperature to 400 °C. 2 circles of 3mm diameter using igh temperature silver paste (Heraeus C8729-conductor paste) were used as support for pasting platinum wires that worked as working electrode.and counter electrode The obtained impedance diagrams were analyzed using equivalent circuit simulation software EC-Labs commercially available from the potentionstat vendor

3.3. UV-VIS spectroscopy

Photocatalytic activity of as-deposited and annealed ALD-CeO₂ was studied by following the degradation of a 10 mg/L solution of methyl-orange using UV-VIS spectrometry. 1.5 cm x 1.5 cm sample of 14 nm-thick CeO₂ on p-type silicon was introduced facing up into 50 mL beaker and 15mL of the 10 mg/L of methyl-orange solution was poured into the beaker. The beaker was irradiated with UV light (55 Watt lamp with λ =254 nm) at a distance of 5cm. 2 mL samples were collected before irradiation (which work as control sample), after 30 minutes and 1 hr of irradiation. The same procedure was repeated for annealed samples. The photocatalytic activity of CeO₂ was monitored by observing changes in the absorbance of methyl-orange at ~464 nm using a UV-VIS spectrophotometer (Shimadzu UV 1601).

4. Use of a Cyclopentadienyl-Precursor for Atomic Layer Deposition of CeO_{2-x} Films with High Concentration of Point Defects. Stability and Photo-catalytic Properties

4.1. Introduction

Cerium Oxide, CeO₂, is a material widely used in heterogeneous catalysts, particularly in three-way catalysts for the treatment of exhaust gas from automobiles, removal of SO_x from fluid catalytic cracking as well as for catalytic steam reforming of ethanol [76]. Other desirable properties of CeO₂ such as high dielectric constant (~26), large band gap (6 eV), high refractive index (2.3) and its ability of store, transport and release oxygen, have made CeO₂ attractive for applications in the semiconductor and energy fields [93, 94]. For instance, CeO₂ has been explored as an optically passive counter-electrode layer [95], a dielectric material for complementary metal oxide semiconductor and memory applications [78, 85] as well as a buffer layer for high temperature superconductors [79]. More recently, CeO₂ and CeO₂-based materials have been explored as electrolytes in solid oxide fuel cells (SOFC), allowing a reduction in the operating temperature from ~1000 °C to the intermediate temperature range (500 – 800 °C) [16]. The higher ionic conductivity of these materials, within this temperature range, is attributed to the formation of point defects such as oxygen vacancies created by the redox activity of the Ce^{+3}/Ce^{+4} pair [96-98]. Furthermore, studies on the microstructure of CeO_2 films have shown that the crystal size plays a significant role in the ionic conduction, indicating that when nanocrystallinity is introduced, the oxygen ion conduction can be increased by several orders of magnitude [97, 99].

Atomic Layer Deposition (ALD) can be used to obtain higher quality CeO_2 thin films with outstanding attributes such as nano-crystallinity, low residual carbon content, high conformality and pinhole free layers. β -diketonate precursors and ozone are the most studied precursor chemistry for the deposition of CeO₂ films *via* ALD yielding a growth rate of ~0.4 Å/cycle [65, 79, 80, 87].

It is well known that the main drawback of ALD is its long processing time [66]; therefore, it is important to develop ALD processes that reduce the processing time and increase the effectiveness of the process without compromising the quality of the film. Deposition of rareearth oxides using cyclopentadienyl–ligands (CP-type) precursors along with water have shown higher deposition rates than those with the conventional β -diketonate/ozone reaction system due to the higher reactivity of the CP-type precursors with water [83].

In this chapter, the CP-type precursor tris(isopropyl–cyclopentadienyl)Cerium, Ce(i-prcp)₃, and water vapor as the oxygen donor were used for the deposition of CeO_{2-x} films using ALD on p-type silicon (100) substrates in a custom-designed and built hot wall ALD reactor. First, the ALD process variables were characterized by measuring the growth rate as a function of precursor dosage, water vapor dosage, reactor temperature and number of ALD cycles. After obtaining reaction conditions for self-limiting growth, deposition of CeO_{2-x} thin films was performed and the crystalline structure of as-deposited and annealed films was analyzed using transmission electron microscopy (TEM). XPS was performed to determine the film stoichiometry and was also used to characterize the presence of point defects in as-deposited and annealed films. Since ALD processes using CP-type precursors are capable of producing CeO₂-x thin films with higher deposition rates and high concentration of point defects, it could be desirable to explore them not only in the fabrication of other interesting CeO₂-based materials such as yttria doped ceria (YDC) for applications in solid oxide fuel cells but also to explore potential uses of in the catalysis area

4.2. Experimental Methods

CeO_{2-x} deficient deposited Oxygen thin films were using tris(isopropylcyclopentadienyl)Cerium, Ce(i-prcp)₃, (Air Liquide, USA), and water vapor as the oxygen donor in a custom-designed and built hot wall ALD reactor. The $Ce(i-prcp)_3$ precursor was maintained at 120 °C while all lines downstream of the precursor vessel were maintained at least 10 °C higher in order to prevent precursor condensation in the manifold. The water source was maintained at 0 °C using an ice bath. Before deposition, silicon (100) substrates were cut into squares of about 1.5 X 1.5 cm and cleaned using standard Radio Corporation of America (RCA) SC-1 cleaning method in order to remove organic contamination, followed by a 10 s dip in a 2% HF solution which reduces the native silicon oxide layer to less than 7 Å as measured by spectral ellipsometry (JA Woollam Co., Inc. model M-44). Each of the steps was followed by a thorough deionized water rinse and final dry with N₂. Immediately after the cleaning process, the samples were loaded into the reactor chamber and pumped down to an operating pressure of 180 mTorr. Ce-precursor was injected into the reactor as pulses by backfilling the precursor reservoir with N₂ and evacuating this N₂ with precursor vapor under vacuum into the reactor, the duration of each pulse is 1 s and the precursor dosage was controlled by increasing the number of precursor pulses. Detailed information about the reactor set up and operation can be found elsewhere [90, 91].

Post-deposition annealing, when indicated, was performed in a three zone furnace (Lindberg/Blue) for 5 min, in an inert environment of flowing 5 sccm of N_2 at 1 atm. Asdeposited and annealed samples were prepared for transmission electron microscopy (TEM) analysis using a JEOL JEM-3010 with Gatan digital cameras and Thermo-Noran XEDS in order to obtain detailed information of the crystalline structure. X-ray photoelectron spectroscopy (XPS) was used to investigate the stoichiometry and the elemental bonding state of the asdeposited and annealed CeO_{2-x} samples using a Kratos AXIS-165. The surface analysis system was equipped with a monochromatic Al K α (1486.6 eV) X-ray source and a concentric hemispherical analyzer coupled with a charge neutralizer operated at 15 kV and 10 mA. High resolution spectra were collected at a take-off angle 90° with pass energy of 20 eV, step size of 0.1 eV, and dwell time of 200 ms. The quantitative elemental analysis was performed by fitting the spectral peak areas with Shirley background correction and applying the appropriate sensitivity factors. The binding energy was referred to the adventitious carbon in the C1s spectra at a value of 284.8 eV. Energy loss spectroscopy (EELS) was performed in a JEM-ARM200CF STEM/TEM with a cold field emission source, equipped with a Gatan Enfina EELS detector with 0.35 eV energy resolution to confirm the stoichiometry obtained with XPS. The EELS spectra were collected using beam energy of 200 keV, a convergence semi-angle of 35 mrad and a collection semi-angle of 155 mrad.

40 nm-thick CeO₂ and samples were deposited on P-type silicon and studied using X-Ray absorption spectroscopy (XAS) for obtaining film stability, coordination number (N) and bond distance Ce-O (r). As-deposited films as well as films annealed in an inert environment (He at 700 °C) and under reducing conditions (4% H₂ in He at 700 °C at 1 atm) were analyzed. L₃ cerium edge (5723 eV) was collected in fluorescence mode using an ion chamber with Stern Heald geometry at the 10-ID line of the MRCAT at Argonne National Laboratory. Higher harmonic x-rays were rejected using a rhodium coated mirror and the ionization chamber was filled with a mixture of 80 % He and 20 % N₂ for incident monitor, and Ar for fluorescence chamber X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) analyses were performed using WinXAS [92]. The CeO₂-x

samples were placed in an air-tight quartz fluorescence cell and then purged for 10 min at room temperature using 200 sccm of Helium. The samples were then annealed at 700 °C for 10 min under the same flow of He and cooled down to room temperature (under continuous He flow) for collecting XAS spectra. The same procedure was repeated using H₂ (200 sccm of 4% H₂ in He at 700 °C). Before collecting the XAS spectra of H₂ and He treated samples, the samples were cooled down while purging the fluorescence cell with a continuous 200 sccm flow of He. CeO₂ nanoparticles (<25 nm (BET) from Sigma-Aldrich and cerium(III) acetylacetonate hydrate also from Sigma-Aldrich were used as standards for the XANES analysis.

Photocatalytic activity of as-deposited and annealed ALD-CeO_{2-x} was studied by following the degradation of a 10 mg/L solution of methyl-orange using UV-VIS spectrometry. 1.5 cm x 1.5 cm sample of 14 nm-thick CeO_{2-x} deposited on p-type silicon was introduced with the film facing up into 50 mL beaker and 15mL of the 10 mg/L of methyl-orange solution was poured into the beaker. The beaker was irradiated with UV light (55 Watt lamp with λ =254 nm) at a distance of 5cm. 2 mL samples were collected before irradiation (which work as control sample), after 30 minutes and 1 hr of irradiation. The same procedure was repeated for annealed samples. The photocatalytic activity of CeO_{2-x} was monitored by observing changes in the absorbance of methyl-orange at ~464 nm using a UV-VIS spectrophotometer (Shimadzu UV 1601).

4.3. Results and Discussion

Characterization of ALD variables using Ce(i-prcp)₃ and water is shown in Figure 4. The growth rate was measured as function of precursor dosage, water vapor dosage, reactor temperature and number of ALD cycles. As seen in Figure 4(a), 6 pulses of precursor are enough for saturating the surface on which a constant growth rate of ~1.4 Å/cycle is obtained. Figure

4(b), shows that water pulse of 60 ms is required to fully react with the saturated surface while Figure 4(c) shows a relatively wide ALD temperature window ranging from 210 to 280 °C. Below this region, a higher growth rate is observed indicating precursor condensation on the sample; moreover, a non-self-limiting growth indicated by the large error bar is seen. Beyond 280 °C, an increase in the growth rate is observed and it can be attributed to precursor decomposition on the surface. In order to verify the self-limiting growth of the process, the film thickness dependence with the number of ALD cycles was analyzed and a linear growth with increasing the number of ALD cycles was obtained (Figure 4(d)).

All data points presented in figure 4(d) were obtained using 6 pulses of precursor (with duration of 1 s each), water pulse duration of 60 ms and a reactor temperature of 250 °C. A linear regression analysis shows that the growth-rate is 1.41 Å/cycle, a value that is at least 3 times higher than the growth rate values reported for the ALD of CeO₂ using β -diketonates precursor and ozone [65, 80, 87] or that obtained using Ce(i-prcp)₃ *via* plasma enhanced ALD (PE-ALD) [84, 85]. From the finding presented in figure 4, it is possible to say that using this precursor combination in a conventional ALD process is a very interesting and viable option for scaling the production of CeO_{2-x} films for diverse applications as a significant improvement in the growth-rate and appreciable thickness control is achieved. This may allow reduction of the processing time therefore making the process more efficient. As explained by Niinistö *et al.*[83], these higher values of the deposition rate might be attributed to the high reactivity of the cyclopentadienyl – ligands towards water.



Figure 4, Growth rate of CeO_{2-x} as a function of precursor pulses (a), water pulse duration (b), reaction temperature (c) and number of ALD cycles (d). The depositions were carried out at a precursor temperature of 120 °C and reactor pressure of 180 mTorr. Data points in Figure 1(d) were obtained using 6 pulses of precursor (1 s each), water pulse duration of 60 ms and a reactor temperature of 250 °C. In all cases, the vertical error bars indicate film uniformity across the sample.



Figure 5, TEM images of as-deposited films show lack of interfacial SiO₂ (a), as-deposited films are shown to be mostly amorphous with small cubic crystals (b), annealed films show formation of interfacial SiO₂ (~ 2 nm-thick)
(c), and annealed films show polycrystallinity with no preferred orientation (d). Radially weighted averaged FFT of selected areas in as-deposited (e) and annealed (f) films show that the films exhibit the cubic phase. All TEM samples were ~ 50 nm-thick and ALD conditions were the same as in figure 4(d).

Examination of the microstructure in CeO_{2-x} films was performed *via* TEM, and is presented in Figure 5. As seen in Figure 5(a), the as-deposited films do not show any interfacial SiO₂ layer. It is also possible to see that as-deposited films are mostly amorphous with some small crystals (Figure 5(b)). These crystals have an average d-spacing of ~0.3175 nm which is in good agreement with the reported values for cubic CeO₂ (111) [100]. As seen in Figures 5(c) and 5(d), full crystallization is achieved after annealing the films in N₂ for 5 minutes at 600 °C and 1 atm. Also, a small amorphous interfacial SiO₂ layer ~2 nm-thick is formed which may limit applications of these ALD-CeO₂ films in applications field such as high- κ dielectric material, since further miniaturization of transistors requires a well-defined interface of the oxide with silicon.

Fast Fourier transform (FFT) allows resolving the Bragg pattern on the selected regions of as-deposited and annealed films, indicating that both films display the cubic structure with no preferential orientation. Figures 5(e) and 5(f), show radially weighted averages which allow the determination of the lattice constant to 5.56 ± 0.04 Å and be 5.51 ± 0.12 Å for as-deposited and annealed films, respectively. These values indicate an apparent expansion in the lattice constant that may be attributed to the presence of point defects created by the non-stoichiometry in the film [101].

Ce-3d XPS core spectra for as-deposited and annealed samples were collected for the determination of the film stoichiometry and the results are presented in Figures 6(a) and 6(b). It is well known that the fitting of the Ce-3d XPS spectra is challenging due to a number of satellite peaks (shake ups) resulting from strongly hybridization of the O-2p valence band with the intense and localized Ce-4f orbitals [102, 103]. The spectra consist of several duplets (v-u) which are labeled according to the nomenclature established by Burroughs *et al.* [104] and are related to the spin–orbit splitting Ce-3d^{5/2} – Ce-3d^{3/2}.



Figure 6, Ce-3d XPS core spectra of as-deposited (a) and annealed (b) CeO_{2-x} samples. These samples were 15 nmthick and were prepared via ALD. Deposition conditions were the same as in Figure 4(d). Annealing was carried out in N_2 for 5 min at 600 °C and 1 atm.

In these spectra, duplets v–u and v"–u" are related to the mixed Ce^{+4} final state $4f^{1}(5d 6s)^{0}3d^{9}$, whereas the duplet v""–u"" is related to the mixed Ce^{+4} final state $4f^{0}(5d 6s)^{0}3d^{9}$. Reduced Ce^{+3} phases can be recognized from the mixed final states $4f^{2}(5d 6s)^{0}3d^{9}$ and $4f^{1}(5d 6s)^{0}3d^{9}$ that are indicated by the duplets v₀–u₀ and v'–u', respectively [105]. By fitting this spectra, it is possible to obtain the film non stoichiometry, CeO_{2-x} , were x is the indicative amount of Ce^{+3} in each sample. The fitting, based on the procedure presented by Paparazzo [106], indicates that the surface of both analyzed films are non-stoichiometric with a Ce^{+3} content of ~25 % and ~21 % for as-deposited and annealed samples, respectively. This corroborates the assumption that the apparent lattice expansion may be caused by the presence of defects in the film. Detailed information on peaks location for the analyzed films as wells as the calculated stoichiometry are included in Table 4. Validation of peak position was obtained by collection and analyzing XPS spectra of a commercial CeO₂ standard (data presented in Apedix A)

Table 4, experimentally determined binding energies and film stoichiometry (via XPS and EELS) of asdeposited and annealed CeO2-x films grown via ALD

Ce-3d Binding	energy (eV) and stole	chiometry analysis		
obtained experimentally via XPS and EELS			Binding Energy	Binding Energy
Peak I D	as-denosited	Annealed	(eV),Ref.[107]	(eV), Ref.[108]
I Cak I.D	as-ucposited	Annealed		
v ₀	880.50	880.52	880.60	880.10
V	882.20	882.40	882.60	882.30
v'	883.87	884.60	885.45	884.80
v''	888.36	888.83	888.85	888.80
v'''	898.16	898.31	898.40	898.20
u ₀	898.64	898.77	898.90	898.80
u	900.72	900.92	901.05	901.00
u'	902.10	902.99	904.05	903.50
u''	907.11	907.37	907.45	907.40
u'''	916.60	916.70	916.70	916.70
stoichiometry by XPS	$Ce^{+3} = 25 \pm 2\%$ (CeO _{1.875})	$Ce^{+3} = 20 \pm 2\%$ (CeO _{1.90})		
stoichiometry by EELS	$CeO_{1.70}$ $Ce^{+3} = 60\%$	$CeO_{1.90}$ $Ce^{+3} = 20\%$		
		43		



Figure 7, EELS spectra of an as-deposited $45nm CeO_{2-x}$ sample prepared via ALD. Deposition conditions were the same as in Figure 4(d). Annealing was carried out in N_2 for 5 min at 600 °C and 1 atm.



Figure 8, EELS spectra of an annealed 45nm CeO_{2-x} sample prepared via ALD. Deposition conditions were the same as in Figure 4(d). Annealing was carried out in N_2 for 5 min at 600 °C and 1 atm

Possible ambiguity in the analysis of the Ce-3d XPS core spectra in determining the film stoichiometry was resolved using electron energy loss spectroscopy (EELS) analysis and the spectra for as-deposited and annealed samples is presented in figures 7 and 8 respectively.

Quantification of the analyzed areas, performed relative to the oxygen K line (O-K) and the cerium M line (Ce-M) shows an average composition of $62.5\pm2.2\%$ for oxygen and $37.4\pm2.2\%$ for cerium (*i.e.*, CeO_{1.7}) for as-deposited samples, while for annealed samples the average composition was $65.10\pm7.9\%$ and 34.90 ± 7.9 for oxygen and cerium, respectively % (*i.e.*, CeO_{1.9}).



Figure 9, O-1s XPS core spectra of as-deposited (a) and annealed (b) CeO2-x samples. All other conditions were the same as in Figure 6.

Figures 9(a) and 9(b) display the O-1s XPS core spectra for as-deposited and annealed ALD deposited CeO_{2-x} samples, respectively. Figure 9(a), displays 3 main peaks in which the dominant one, located at 529.7 eV, can be attributed to the presence of oxygen in the lattice structure of the oxygen deficient CeO_{2-x} films [109]. The shoulder feature located at 532.67 eV in Figure 9(a) is likely due to –OH species from absorbed moisture on the surface, either from the ALD reaction or from exposure to ambient atmosphere, [105] and that is corroborated by its desorption after annealing in an inert environment, as seen in Figure 9(b). The nature of the lateral peak at ~531.7 eV, observed in both as-deposited and annealed samples, has been under dispute; while some researchers suggest that this peak likely arises from the presence of absorbed carbon species in the form of carbonates (CO₃⁻²) [105], others indicate that it may be due to the presence of molecular oxygen species (peroxide, superoxide) absorbed on the surface or lack of structural homogeneity at CeO₂ grain boundaries [110, 111].

Figure 10 show the carried C-1s XPS core spectra analysis performed on a 15 nm-thick CeO_{2-x} . Although there is small feature around 288.5 eV, it is difficult to resolve a peak that can be associated to the presence of absorbed carbonate species in the surface of CeO_{2-x} thin films due to the large noise around this binding energy area. Also, it has been discarded that the lateral peak in figure 9 may be only due to the presence of molecular oxygen species (peroxide, superoxide) absorbed on the surface since it has been suggested that the presence of this species on the film surface may reduce the hydrophobicity of the deposited films [112]. Figure 11 allows seeing that both, as-deposited and annealed films are hydrophobic, with water contact angling higher that 80 °. Furthermore, as seen in Figure 5, as-deposited and annealed films have quite different microstructure making it difficult to relate the presence of this peak to grain boundary impurities or structural non-homogeneity.



Figure 10, C-1s XPS core spectra of as-deposited CeO2-x sample s. $^{=}CO_3$ species should appear around 288.5 eV [105]. C-1s spectra collected before Ar^+ sputtering. All other conditions were the same as in Figure 6.



Figure 11, water contact angle collected on as-deposited (a) and annealed CeO_{2-x} samples (b). $5\mu L$ of DI-water were used for collecting the images. CeO_{2-x} samples were 15 nm-thick. Deposition conditions were the same as in figure 6
Evidence suggests then, that the whole intensity of this lateral peak cannot be only related to absorbed surface species (e.g., -OH or carbonates) but can also be related to the presence of point defects (Point-defect-O) such as oxygen vacancies created by the film surface non-stoichiometry or oxygen occupying an interstitial site in sub-surface layers of the CeO_{2-x} film that may be contributing not only to the intensity of the lateral peak but also to the expansion of the lattice compared to the theoretical value, which was determined to be 5.411 Å by applying X-ray diffraction (XRD) on a CeO₂ standard (Appendix A). One way to validate the assumption that the nature of the lateral peak in figure 9 may be attributed to the presence of point defects in the film (e.g., non-stoichiometry, interstitial oxygen or oxygen vacancies), and not merely related to surface contamination is through Ar⁺ sputtering treatment of the samples which removes the top monolayer of the analyzed film. Figure 12 shows the XPS O-1s core spectra of as-deposited and annealed samples collected after treatment with Ar⁺ bombardment at different times (5 and 10 minutes). It can be seen that for as-deposited samples, (figures 12(a) and 12(b)), there is an apparent shift of the main feature (latticeO) towards higher binding energy, when compared to figure 9(a). This shift is related to the reduction of Ce^{+4} towards Ce^{+3} due to the removal of oxygen [103, 107, 113]. This apparent shift is least obvious in the annealed samples (Figures 12(c) and 12(d) compared to Figure 9(b)) and is believed to be related to higher O-Ce⁺⁴ interactions, introduced by the crystallization of the film. As seen in Figure 13, these O-Ce⁺⁴ interactions can be specifically assigned to those with Ce^{+4} in the final state $4f^{0}(5d \ 6s)^{0}3d^{9}$ peak u''' (related to pure CeO₂) and mixed Ce⁺⁴ final state $4f^{1}(5d \ 6s)^{0}3d^{9}$, doublet v-u. XPS analysis using different collection angles are presented in appendix A section 9.2

It is hypothesized then, that the natural occurrence an interaction of Ce^{+3}/Ce^{+4} oxidation states at the films surface, leads to incorporation of oxygen available from the ALD hydrolysis

reaction into interstitial places in the form of oxide ions or Frenkel anions (*i.e.*, O^{-2}) and stored as the films grows. These oxide ions are expected to be highly polarized and to induce a different coordination level in the defective film and as a consequence a shift in the binding energy should be expected since the covalent degree of the Ce-O bond would be higher [76, 111]. As researchers are focused on the intentional introduction of defects into the CeO_{2-x} lattice in order to favor the high oxygen mobility and improve catalytic properties, these results are of great interest for potential application of ALD-CeO_{2-x} as active phases in catalysis [114].



Figure 12, O-1s XPS collected for as-deposited (a, b) and annealed (c, d) samples after treatment with different Ar+ sputtering times. The samples were 15 nm-thick. Deposition and annealing conditions were the same as in Figures 6

and 9



Figure 13, Ce-3d XPS core spectra collected after 10 min of Ar+ sputtering for as-deposited (a) and annealed (b) CeO_{2-x} samples deposited via ALD. Samples were 15 nm-thick. Deposition and annealing conditions were the same as in Figures 6 and 9

It was observed that by annealing the CeO_{2-x} in an inert environment, these interstitial oxygen defects (*i.e.*, oxide ions in subsurface of) have high mobility. This can be verified by the formation of a thin SiO₂ interfacial layer (Figure 5c), and an increase in the intensity of the metal-oxygen peak in the O-1s XPS spectra, (Binding energy ~529.7 in figure 6 (b)), which is related to oxygen occupying lattice places. An elemental analysis, (table 5), shows that when the O:Ce ratio is calculated using only the integral area of the peak located at ~529.7 eV (latticeO)

calculated film stoichiometry resembles the one calculated previously using Ce-3d XPS core level spectra and corroborated using EELS. However, when the integral area of the lattice along with the area of the point defect oxygen peaks (column 3 in table 5 - $_{(lattice + PD)}O$) is used, the calculated film stoichiometry is CeO_{2.60} and CeO_{2.83} for as-deposited and annealed samples, respectively. This stoichiometry is possible in other fluorite-type structures such as UO_{2+x} but does not exist for CeO₂ [98]. The last three columns of table 5 show that by removing the top monolayers using Ar⁺ sputtering, the relative area ratio ($_{(Point defect)}O/_{lattice}O$) remains fairly constant, indicating that the point-defects are not merely superficial but can also be bulk related. These ratios (last three columns of table 5) appear to be in good agreement with the ratios obtained when analyzing the O-1s XPS core spectra of the CeO₂ standard (Appendix A)

Table 5, Elemental analysis of CeO_{2-x} samples and relative area point-defects/lattice ratios collected at different Ar+ sputtering times. The oxygen contribution for performing the quantitative elemental analysis is done as follows: total O corresponds to the total oxygen area in the spectra, ($_{lattice + PD}O$ indicates that the calculation is performed using the integral area of the lattice and point defects peaks only

Analyzed sample	totalO:Ce	(lattice+PD)O:Ce	latticeO:Ce	Relative O- peak areas of as-inserted samples	Relative O- peak areas of 5min Ar ⁺ sputtering samples	Relative O- peak areas of 10 min Ar ⁺ sputtering samples
				Point	Point	Point
				defects/Lattice	defects/Lattice	defects/Lattice
as-deposited	3.26	2.60	1.80	0.60	0.50	0.48
annealed	2.83	2.83	1.83	0.59	0.39	0.42

Factors that may limit the applications of CeO_2 films as electrolyte for SOFCs are the Ce^{+4} stability under reducing conditions and the mixed ionic electronic conductivity at high temperatures and low oxygen partial pressures, which may increase the local electronic conduction of the film [65, 115]. X-ray absorption near edge spectroscopy (XANES) and X-ray fine structure spectroscopy (EXAFS) were used for determining the stability of CeO_2 films at high temperature under reducing conditions and to determine the local structure of as-deposited and annealed films.

Figure 14 show the normalized EXAFS spectra of Ce⁺³ and Ce⁺⁴ standards. As seen in figure 14(a), Tetravalent Ce-materials, Ce⁺⁴, have a pre-edge feature and two peaks in the XANES white line, *i.e.*, interaction between 4f orbitals of the Ce-metal and 2p orbitals of the ligands. Trivalent Ce-materials, Ce⁺³, have a single white line with the leading edge shifted to lower photon energy (figure 14(b)). Therefore, the amount of Ce⁺³/Ce⁺⁴ can be quantified for asdeposited and annealed ALD - CeO_{2-x} samples by fitting the collected spectra using the standards [116]. A XANES fitting performed on as deposited samples indicates that there is 5% of Ce⁺³ in the bulk. Figure 15(a) shows a comparison of the XANES spectra for as-deposited and annealed CeO_{2-x} films. It is possible to see that samples that were annealed an inert environment, *i.e;* 200 sccm of He, at 700 °C for 10 min (dotted spectra in Figure 15(a)), display a shift of the edge to a higher the photon energy. A XANES fitting on the annealed spectra indicate that the structure of these ALD fabricated CeO_{2-x} film is identical to CeO₂ nano-powder standard.



Figure 14, Normalized EXAFS spectra of a $Ce^{+4}(a)$ and $Ce^{+3}(b)$ standard CeO_2 nanoparticles (<25 nm (BET)) and cerium (III) acetylacetonate hydrate were used as Ce^{+4} and Ce^{+3} , respectively. Both standard were bought from Sigma-Aldrich

This indicates the presence of interstitial oxygen in the deposited films, *i.e.* point defects that can be thermally activated so they occupy a lattice or a vacancy site. On the other hand, when the samples are annealed in a reducing environment, *i.e;* 200 sccm of H₂, at 700 °C for 10 min (dotted spectra in Figure 15(b)), there is a clear shift of the edge to a lower photon energy indicating a clear reduction on the amount of Ce⁺⁴ phases. This shows that the ALD-CeO_{2-x} films presented here are not suitable as IT-SOFC electrolyte due to instability under reducing

conditions that may cause electronic conduction and also expansion of the lattice which may lead to mechanical failure. A XANES fitting performed on these spectra indicates that there is 30 to 35 % of Ce⁺³ in the film after H₂ treatment.



Figure 15, XANES comparison of as-deposited CeO_{2-x} films vs films annealed in an inert environment (200 sccm of He at 700 °C and 1 atm) (a) and a reducing environment (200 sccm of 4 % H₂ in He at 700 °C and 1 atm) (b). Films were 40 nm-thick and were deposited with the same conditions as in figure 6

Extended X-ray absorption fine structure spectroscopy (EXAFS) was applied for determining changes in the lattice atomic structure of as-deposited and annealed in an inert environment CeO_{2-x} samples. Figure 16 shows the experimental χ functions collected for the CeO₂ standard (black solid line), as-deposited CeO_{2-x} (blue solid line) and annealed CeO_{2-x}. It is possible to see that, compared to CeO₂ standard (black solid line in figure 16), the collected χ -functions for as-deposited and annealed films of CeO_{2-x} present high levels of noise in k-values higher than 6 Å⁻¹, which limits the analyses.



Figure 16, experimental χ -functions obtained from the EXAFS spectra collected for CeO₂ standard (black), asdeposited CeO_{2-x} film (blue) and annealed CeO_{2-x} film (red). Deposition and annealing conditions are the sames as those in figure 6



Figure 17, Radial distribution function of as-deposited (a) and annealed (b) CeO_{2-x} thin films. Solid and doted lines denote experimental and fitted data, respectively. Samples were 40 nm-thick, deposition conditions are the same as in figure 6.

Figure 17 shows the Fourier transform of k^2 -weighted EXAFS spectra of as-deposited (17a) and annealed (17b) CeO_{2-x} thin films. The data range that was used for transformation into Fourier space was 2.20 to 6.5 Å⁻¹. The structural parameter were obtained from fitting in r-space in the

interval 0.86 to 3.5 Å, which correspond to the first coordination shell, and the results of the simulation are displayed in table 6.

Sample	% Ce ⁺³ via	Ce-O distance	Coordination (N)	σ^2	Lattice
	XANES	(Å)	Coordination (IN)		parameter (Å)
standard	-	$2.343 \pm 2E-4$	8.013 ± 0.014	0.001± 4.31E-5	5.411*
as-deposited	5	$2.325\pm2\text{E-4}$	7.604 ± 0.002	$0.002\pm5.62\text{E-}5$	$5.56\pm0.04^{\$}$
annealed in	0	2 336 + 1E-4	8 247 +0 013	0.001 + 4.35E-5	$551 \pm 012^{\$}$
Helium	0	2.550 - 11	0.217 _0.015		0.01 - 0.12

Table 6, Fitting results for the 1st coordination shell of Ce in as-deposited and annealed CeO_{2-x} thin films

*lattice constant obtained from the literature [117], [§]from TEM experiments (figure 5)

It is possible to see in table 6 that in general, the coordination number of the analyzed CeO_{2-x} films resemble the theoretical coordination of bulk CeO_2 standards [118]. However, the fitted results show that the bond-length Ce-O of both, as-deposited and annealed films is shorter that the theoretical value. It has been shown that the calculated lattice parameter for as-deposited and annealed films (last column in table 6) is larger than the theoretical value thus the average cation–anion distance must also be larger. The EXAFS results show otherwise, which implies that the previous assumption that the observed difference may be attributed to the presence of point defects in the film (*e.g.*, oxygen vacancies or interstitial oxide ions) is validated.



Figure 18, water contact angle collected on as-deposited (a) and annealed CeO2-x samples (b) after UV light exposure for 1 hr (55 Watt lamp with λ =254 nm). 5µL of DI-water were used for collecting the images. CeO_{2-x} samples were 15 nm-thick. Deposition conditions were the same as in figure 6

Although the applications of un-doped CeO_{2-x} films is limited due to reduction of Ce^{+4} toward Ce^{+3+} under SOFC environment (Figure 15b), it is important to analyze any enhancement on the catalytic activity of ALD- CeO_{2-x} materials with a large concentration of point defects. I have shown that the CeO_{2-x} films have a large concentration of point defects in both, the bulk and the surface. The observed non-stoichiometry of the surface (figure 5 and table 5) makes possible that oxygen vacancy defects can be rapidly formed and eliminated, and these surface oxygen vacancies are proposed to participate in many chemical reactions applied to removal of air pollutants[76], however recent studies suggest that CeO_2 is equally effective in photocatalytic degradation of organic contaminant present in waste water [119, 120].

Choudhury *et al.* have proposed a reaction model for the photo-degradation of methyl-orange on UV-treated CeO₂ nanoparticles [112, 121]. In this reaction mechanism, several super-oxide, hydroxyl and hydroperoxy-radicals are form in the surface. Figure 18, shows water contact angle measurements on as-deposited and annealed CeO_{2-x} samples that were irradiated for 1 hr using a 55 Watt UV lamp with λ =254 nm. It is possible to see that compared to figure 11, the surfaces become hydrophilic indicating the formation of these radicals.

Photocatalytic activity was studied by following the degradation of a 10 mg/L methyl-orange solution using UV-VIS spectrometry with as-deposited and annealed ALD-CeO₂ films as catalyst. Figure 19(a) shows the absorption curves of methyl-orange at different times in which as-deposited CeO_{2-x} film was used for degrading the organic dye under irradiation of UV light. In the same way, figure 19(b) shows de absorption curve for the same procedure but using annealed ALD fabricated CeO_{2-x} film.



Figure 19, absorption curves of methyl-orange solution in which the degradation of the organic dye was catalyzed under UV-light irradiation using as-deposited (a) and annealed (b) CeO_{2-x} . CeO_{2-x} samples were 14 nm-thick, the UV source was a 55 Watt lamp with $\lambda=254$ nm.

Although it was shown that the ALD-CeO_{2-x} films have a large concentration of point defects in both, the surface and the bulk, there is a slower decrease in the absorption intensity of methylorange with increasing the irradiation time for the catalytic degradation of the dye using asdeposited CeO_{2-x} thin films compared to the same procedure using anneal films. This suggests that as-deposited CeO_{2-x} films have lower activity towards photodegradation of organic materials using this kind of UV light. This lower activity can be explained by analyzing the equation for oxygen vacancies formation which is described by the Kröger-Vink equation [98].

$$O_o + 2Ce_M \longleftrightarrow V_{\ddot{o}} + 2Ce'_{Ce} + \frac{1}{2}O_2 \qquad eq(3)$$

In this equation O_0 and Ce_M represent oxygen and cerium metal atoms in their respective sites in the crystal lattice and $V_{\ddot{0}}$ represents a double positively charged oxygen vacancy. Since the as-deposited CeO_{2-x} was determined to be mostly amorphous (figure 5(a) and (b)), the formation of oxygen vacancies is limited due to low grain boundary interaction [121]. Also, as determined by XPS, as-deposited CeO_{2-x} films have larger content of Ce^{+3} in the surface of the film. This may induce an expansion of the lattice in this region and development of strain arising from loss of oxygen from surface region [122]. It has been suggested that the free electrons available upon oxygen vacancies formation along with the superficial oxygen, play a significant role in the mechanism for photodegradation of the organic material with CeO_{2-x} as catalyst since their charged nature may control band-bending and thus electron-hole pair separation necessary for photocatalytic activity [112, 119], thus loosing oxygen in the surface region may affect negatively the degradation rate.

A different behavior is observed under UV-light irradiation using annealed CeO_{2-x} films (figures 19(b)). A faster response on the reduction in the absorption intensity with increasing irradiation time is observed. This suggest faster kinetics for the photodegradation of methylorange and its attributed to a higher concentration of oxygen vacancies in the surface and the bulk of the film created by introducing crystallinity in the film (figure 5(d)).

These results suggest a new potential application field for ALD deposited CeO_{2-x} films. However further development need to be performed in order to introduce ALD technology into pollutant treatment present in water streams. For instance, film thickness effect and other UV- sources need to be explored and characterized with the purpose of optimizing the conditions for water waste treatment.

4.4. Summary

In this chapter, oxygen deficient cerium oxide, CeO_{2-x}, thin films were deposited via ALD on p-type silicon (100) using tris(iso-propylclopentadienyl)cerium and water vapor. The growth-rate was measured as a function of precursor dosage, water vapor dosage, reactor temperature and number of ALD cycles. The growth-rate was found to be 3 times higher than the one reported for similar materials using β -diketonates precursors and ozone. Transmission electron microscopy results show that as-deposited films are mostly amorphous with small crystalline domains and no interfacial SiO₂ formation. Films annealed at 600 °C form a 2 nm-thick SiO₂ interface, are polycrystalline and exhibit the cubic phase. An evident expansion in the CeO_{2-x} lattice constant was observed and attributed to the existence of point defects in the film. X-Ray photoelectron spectroscopy (XPS) indicates that the films are non-stoichiometric, *i.e.*, CeO_{2-x}, with superficial Ce⁺³ amounts between 10 and 30 % ($0.05 \le x \le 0.013$). XPS also help in the validation of the presence of point-defects such as oxygen vacancies or oxygen in interstitial places and that these point-defects are film related rather than superficial. It is hypothesized that during film deposition, the shift between Ce^{+3} to Ce^{+4} oxidation states at the films surface, leads to incorporation of oxygen available from the hydrolysis reaction into an interstitial places and stored as the films grows. Annealing in an inert environment shows that a SiO₂ interface is created while the concentration of Ce^{+3} is decreased corroborating the presence of point-defects and their high mobility within the film lattice. Stability of the films under reduction conditions was tested using X-ray absorption spectroscopy. By fitting the X-ray absorption near edge

spectra (XANES), it was possible to determine that as-deposited films have a small amount of Ce^{+3} in the bulk of the film, (~5 %), which may contribute to the lattice parameter expansion. Films that were annealed in an inert environment (200 sccm Helium at 700 °C for 10 min) were identical, within noise, to the CeO₂ standards (*i.e.*, only Ce⁺⁴ phases were present) indicating that there are thermally induced structural transformation that can change physical properties of CeO_{2-x} thin films relevant to catalytic or electrochemical processes. Extended X-ray Absorption Fine Structure EXAFS show that the deposited films have local atomic structure (coordination and bond distance) close to the theoretical values of bulk CeO₂ materials. Fitting the EXAFS spectra showed that in average the interatomic Ce-O bond distance is shorter that the theoretical reported value. This might be explained in terms of strain created by oxygen vacancies which has been reported to have a larger average distance (*i.e.*, Ce-Oxygen vacancy) than the reported for Ce-O in a lattice position. Annealing at 700 °C, 1 atm in a reducing environment created by flowing 200 sccm of 4% H₂ in He, lead to partial reduction of the ALD fabricated CeO_{2-x} films which limits the applications of undoped CeO_{2-x} as IT-SOFC electrolyte.

It was shown that the thermally induced structural transformation on the CeO_{2-x} thin films have an impact on the physical properties relevant to photocatalytic processes. Prove of this are the results of the photocatalytic activity of as-deposited and annealed ALD-CeO₂. It was found that thin CeO_{2-x} films (14 nm-thick) are suitable for photodegradation under UV light irradiation (λ =254 nm) and the photocatalytic activity was attributed to both, surface and bulk point defects. It is important to remark that this is the first time that ALD-CeO_{2-x} thin films deposited with the procedure presented in this chapter are studied in the photodegradation of organic contaminants.

It is then concluded that the results presented in this chapter are of great interest toward better understanding the formation and mobility of point defects in ALD fabricated CeO_{2-x} thin films which may be beneficial for the improvement of ceria-based electrolyte materials but also may generate an impact in other technological fields such as catalysis and photo-catalysis. ALD is an effective way of fabricating stable and continuous CeO_{2-x} films with varying thicknesses, from unexplored ultra-thin nanometer levels to bulk-like levels, and it is possible to introduce a large density of defects into the CeO_{2-x} lattice which are mobile and may favor oxygen mobility and/or improve catalytic properties.

5. Atomic Layer Deposition of Yttria Doped Ceria Using Cyclopentadienyl-ligand Precursors and Water Vapor. Composition Tunability, Post-deposition Annealing Behavior and Stability Analysis

5.1. Introduction

Solid oxide fuel cells (SOFCs) are emerging as a promising alternative for generating power in an environmental friendly way. However, practical applications of this technology are still limited because of the high operating temperatures (>1000 °C) [4, 5]. Research efforts are driven towards reducing this operating temperature to the intermediate temperature range (500 – 800 °C), which decreases fabrication costs and startup times thereby broadening the potential use of SOFCs into smaller, more mobile applications such as transportation[6].

The main disadvantages of lowering the operating temperature are that the oxygen ion conductivity of the solid electrolyte material, (*i.e.*, yttria stabilized zirconia, YSZ), decreases drastically when operated below 800 °C, poor catalytic activity at the cathode-electrolyte interface for the reduction of oxygen, and inefficient transport properties of mixed conducting oxide-based cathode materials[8-10]. Ceria and ceria-based materials have been proposed as materials for fabricating intermediate temperature solid oxide fuel cell (IT-SOFC) electrolytes due to their higher ionic conductivity at lower temperatures with respect to YSZ. CeO₂-based materials are also advantageous as they can exhibit more efficient catalytic properties thereby permitting use of alternate fuels other than hydrogen, such as hydrocarbons and natural gas without the use of an upstream reformer on the fuel-side of the SOFC. Efficient catalytic reduction properties at the cathode side has been observed as well [10, 15].

Among the different CeO₂-based materials, yttria doped cerium oxide, YDC, has gained a lot of attention mainly because of its relatively lower fabrication costs than other CeO₂-based materials (Gd, Sm) as well as other mixed ionic-electronic conductors like Lanthanum-Strontium-Gallium Manganite (LSGM) and higher ionic conductivity than the commonly used YSZ at low temperatures[10, 16].

It has been demonstrated that the ionic conductivity of YDC films strongly depends on the amount of yttria (Y_2O_3), having the higher ionic conductivity values with doping levels of 10 - 20 % atomic Yttrium [18, 123]. In order to further improve ionic conductivity of electrolytes in SOFC, there is considerable interest in minimizing the thickness of the electrolyte layer in the SOFC stack, and for this atomic layer deposition (ALD) has become an attractive way of depositing thinner electrolyte layers as well as electrode interfacial layers[15, 18, 19].

ALD is a thin film deposition method based on sequential self-limiting surface reactions and can be used for obtaining dense YDC films with accurate Y-doping control. For instance, Balle *et al.* have used β -diketonates precursors (Ce(thd)₄, Y(thd)₃) and ozone for obtaining YDC films *via* ALD on different substrates finding a growth rate for YDC of 0.4 to 0.5 Å/cycle[87]. Fan *et al.* have also used ALD for depositing YDC films using a precursor chemistry based on Y(mcp)₃, (mcp=methylcyclopentadienyl), Ce(thd)₄, and ozone for the fabrication of YDC as electrode interlayers with individual growth rates of 0.75 and 0.53 Å/cycle for CeO₂ and Y₂O₃ respectively [18]. In general, ALD of rare-earth oxides using precursors with cyclopentadienyl– ligands (CP-type) along with water, have shown higher deposition rates than those with the conventional β -diketonate/ozone reaction system[83]. In ALD, growth rate is an important variable for the application of ALD processes as higher growth rates reduce the processing time within the ALD-regime, without compromising the quality or compositional control of the film.

In this chapter, ALD of YDC with potential applications as IT-SOFC electrolyte is presented. Significantly higher ALD growth-rate of YDC films is reported using CP-type precursors tris(isopropyl-cyclopentadienyl)Cerium, tris(isopropyl- $Ce(i-prcp)_3$, and cyclopentadienyl)Yttrium, Y(i-prcp)₃, with water vapor as the oxygen donor. The resulting YDC films are analyzed and discussed in terms of compositional tunability, yttrium thermal diffusivity, interfacial interaction, and chemical stability under intermediate-temperature SOFC environmental conditions. After obtaining reaction conditions for self-limiting growth of individual oxides, CeO2 and Y2O3, a suitable ALD window overlap is found for the codeposition of YDC thin films. X-ray photoelectron spectroscopy (XPS) allows determining that YDC films can be fabricated with atomically-tunable content of yttrium and that there is thermally activated yttrium diffusion in the film. X-ray absorption near edge spectroscopy (XANES) shows that the films are chemically stable under SOFC operation conditions with no reduction of Ce⁺⁴ while extended X-ray absorption fine structure spectroscopy (EXAFS) allows determining that the analyzed film have bulk-like structure.

Since ALD processes using CP-type precursors are capable of producing YDC films with higher deposition rates, good Y-tunability and stable under reducing conditions, this approach becomes a very attractive means to explore the scalability limits of using ultra-thin YDC films in reducing the operating temperature requirements for solid oxide fuel cells.

5.2. Experimental Methods

Yttria doped ceria thin films were deposited on p-type silicon (100) using precursors tris(isopropyl–cyclopentadienyl)Cerium, tris(isopropyl–cyclopentadienyl)Yttrium, (Ce(i-prcp)₃, and Y(i-prcp)₃), (Air Liquide, USA), with water vapor as the oxygen donor in a custom-

designed and built hot wall ALD reactor. The Ce(i-prcp)₃ and Y(i-prcp)₃ precursors were kept in stainless steel vessels at 120 °C and 110 °C, respectively. All lines downstream the precursor vessels were maintained at least 10 °C higher in order to prevent condensation of precursor in the manifold. Deionized water maintained at 0 °C using an ice bath was used to introduce pulses of water vapor into the reactor. Before deposition, silicon (100) substrates were cut into squares of about 1.5 cm X 1.5 cm and cleaned using standard Radio Corporation of America (RCA) SC-1 cleaning method in order to remove organic contamination, followed by a 10 s dip in a 2% HF solution which reduces the native silicon oxide layer below 7 Å as measured by spectral ellipsometry (JA Woollam Co., Inc. model M-44). Each of the cleaning steps was followed by a thorough deionized water rinse and final dry with N₂. Immediately after the cleaning process, the samples were loaded into the reactor chamber and pumped down to a deposition pressure of 180 mTorr.

Both metal precursors were injected into the reactor as pulses by backfilling precursor reservoir with N_2 and evacuating this N_2 with precursor vapor under vacuum into the reactor, each pulse lasting 1 s. The precursor dosage per ALD cycle was controlled by increasing the number of precursor pulses. Detailed information about the reactor set up and operation can be found elsewhere [90, 91].

Once the ALD parameters for the growth of individual oxides were obtained, YDC samples (4 - 15 nm thick, verified using spectral ellipsometry) were deposited at 260 °C with different ALD Cycle ratio (*i.e.*, Y₂O₃/(Y₂O₃+CeO₂)). Next, each sample was cut in half and one of the halves was placed in a three zone annealing furnace (Lindberg/Blue) for 5 min, in a nitrogen environment at furnace temperatures of 600 °C and 1 atm. Prior to placing samples into the

furnace, residual air was removed from the furnace chamber by purging it with N_2 . The other half serves as the as-deposited sample.

X-ray photoelectron spectroscopy (XPS) was performed for investigating the elemental bonding state of the film and interfacial regions. XPS was also used to determine the stoichiometry and thus compositional tunability of the YDC films fabricated via ALD. All XPS spectra were collected using a Kratos AXIS-165 spectrometer. The surface analysis system was equipped with a monochromatic Al K α (1486.6 eV) X-ray source and a concentric hemispherical analyzer coupled with a charge neutralizer operated at 15 kV and 10 mA. High resolution spectra were collected at a take-off angle 90° with pass energy of 20 eV, step size of 0.1 eV, and dwell time of 200 ms. The quantitative elemental analysis was performed by fitting the spectral peak areas with Shirley background correction and applying the appropriate sensitivity factors. The binding energy was referred to the adventitious carbon in the C1s spectra at 284.8 eV.

40 nm-thick CeO₂ and YDC samples were studied under reducing conditions (4% H₂ in He at 700 $^{\circ}$ C at 1 atm) by using X-Ray absorption spectroscopy (XAS) for obtaining film stability, coordination number (N) and bond distance (d). L₃ cerium edge (5723 eV) was collected in fluorescence mode using an ion chamber with Stern Heald geometry at the 10-ID line of the MRCAT at Argonne National Laboratory. Higher harmonic x-rays were rejected using a rhodium coated mirror and the ionization chamber was filled with a mixture of 80 % He and 20 % N₂ for incident monitor, and Ar for fluorescence chamber X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) analyses were performed using WinXAS [92]. The CeO₂ and YDC samples were placed in an air-tight quartz fluorescence cell and then purged for 10 min at room temperature using 200 sccm of Helium. The samples were then annealed at 700 $^{\circ}$ C for 10 min under the same flow of He and

cooled down to room temperature (under continuous He flow) for collecting XAS spectra. The same procedure was repeated using H_2 (200 sccm of 4% H_2 in He at 700 °C). Before collecting the XAS spectra of H_2 treated samples, the samples were cooled down while purging the fluorescence cell with a continuous 200 sccm flow of He. CeO₂ nanoparticles (<25 nm (BET) from Sigma-Aldrich and cerium (III) acetylacetonate hydrate also from Sigma-Aldrich were used as standards for the XANES analysis.

The electrochemical properties of as-deposited and annealed YDC films with 10 and 20 atomic % of yttrium were analyzed by electrochemical impedance spectroscopy. These measurements were carried out under ambient air, using an Bio-Logic SP-240 potentiostat with 10 mV ac dignal amplitude (Δ V) and without dc polarization in the 7 MHz to 10 µHz frequency range (10 points per decade) in a temperature range varying from room Temperature to 400 °C. 2 circles of 3mm diameter using high temperature silver paste (Heraeus C8729-conductor paste) were used as support for pasting platinum wires that worked as working electrode and counter electrode. The obtained impedance diagrams were analyzed using equivalent circuit simulation software EC-Labs commercially available from the potentionstat vendor.

5.3. Results and discussion

ALD growth process variables for individual oxides using Ce(i-prcp)₃, Y(i-prcp)₃ and water are shown in Figures 20 and 21, respectively. The growth rate was measured as function of precursor dosage, water vapor dosage, reactor temperature, and number of ALD cycles. Figures 20(a) and 21(a), show the effect of the precursor dosage on the ALD of CeO₂ and Y₂O₃, respectively. It is observed that 6 and 12 pulses of precursor, respectively, provide sufficient dosage for saturating the substrate surface in this reactor whereby a constant growth rate of ~1.4 Å/cycle is obtained for the deposition of CeO₂ and Y₂O₃ individually. Figures 20(b) and 21(b), show the effect of the water pulse duration. In both cases, a water pulse of 60 ms is required to fully react with the precursor saturated surfaces. A linear regression analysis, Figure 20(c), shows that the growth-rate of CeO₂ is 1.4 Å/cycle, a value that is at least 3 times higher than the growth-rate values reported for the ALD of CeO₂ using β -diketonates precursors and ozone [65, 80, 87]. Similar analysis (Figure 21(c)), shows that the growth-rate of Y₂O₃ is also 1.4 Å/cycle, which is comparable to the growth-rate reported previously by our group for the ALD of Y₂O₃ using other CP-type precursors [90, 91].

Figure 20(d) shows temperature dependence of the CeO₂ growth-rates. At low temperatures, higher growth-rates that monotonically decrease with increasing the reaction chamber temperature were observed; these higher values in the growth rates indicate a non-self-limiting growth behavior possibly resulting from multilayer condensation of the precursor during precursor dosage. At high temperatures (>290 °C), a rapid increase in the growth-rate is observed and it might be attributed to thermal decomposition of Ce(i-prcp)₃.



Figure 20, Growth rate of CeO_2 as a function of precursor pulses (a), water pulse duration (b), number of ALD cycles (c) and reaction temperature (d). The depositions were carried out at a precursor temperature of 120 °C and reactor pressure of 180 mTorr. Data points in Figure 15(c) were obtained using 6 pulses of precursor (1 s long each), a water pulse duration of 60 ms and a reactor temperature of 250 °C. In all cases, the vertical error bars indicate film uniformity across the samples



Figure 21, Growth rate of Y_2O_3 as a function of precursor pulses (a), water pulse duration (b), number of ALD cycles (c) and reaction temperature (d). The depositions were carried out at a precursor temperature of 110 °C and reactor pressure of 180 mTorr. Data points in Figure 16(c) were obtained using 12 pulses of precursor (1 s long each), a water pulse duration of 60 ms and a reactor temperature of 250 °C. In all cases, the vertical error bars indicate film uniformity across the sample

An analogous growth-rate dependence at low temperatures for Y_2O_3 is observed in Figure 21(d), at high reactor temperatures, (>290 °C), low growth-rates of Y_2O_3 are observed and this is most likely due to lower surface adsorption of Y(i-prcp)₃ precursor on the substrate at these temperatures. In the deposition of both CeO₂ and Y₂O₃, a region in which the growth-rate is

independent of the reactor temperature is observed and is taken as the ALD temperature window for each oxide deposition. For growing composite metal oxide films *via* ALD, an overlap of the ALD temperature windows from each binary metal oxide deposition is desirable [124].

Figure 22 shows a sufficient overlap in the individual ALD windows between 240 and 290 °C. This overlap offers a suitable range of temperatures for the ALD of YDC under self-limiting growth conditions and based on these results, 260 °C was selected for the deposition of the YDC films. In order to study the atomic composition tunability of atomic layer deposited YDC thin films, a series of experiments were carried out with different ALD cycle ratios, $[Y_2O_3/(Y_2O_3+CeO_2)]$; e.g., for a cycle ratio of 0.2, four cycles of CeO₂ are alternated with one cycle of Y_2O_3 . Figure 23(a) illustrates the effect of the cycle ratio $[Y_2O_3/(Y_2O_3+CeO_2)]$ on the atomic composition [Y/(Ce+Y)] of 15 nm-thick as-deposited YDC films. As determined from quantitative analyses of XPS spectra, the atomic content of Y increases almost linearly with increasing the ALD cycle ratio thus demonstrating that by controlling this variable, the composition of YDC thin films can be controlled down to the atomic level. Similar atomic composition tunability was also reported in earlier studies of our group with the ALD of other composite metal oxides using CP-type precursors, such as Y₂O₃-doped HfO₂ and Er₂O₃-doped TiO₂ [91, 124]. Figure 23(b) shows the YDC film thickness as function of total ALD cycles for a YDC film with a 20 atom.-Y % (i.e,. an ALD cycle ratio 1:4 - Y:Ce) which demonstrates a linear growth-rate of the YDC films with the total number of ALD cycles corroborating the selflimiting feature of an ALD process. A linear regression analysis of the data shows that the YDC growth rate has a value of 1.3 Å/cycle, a value that is at least 3 times higher than the reported for YDC using β -diketonates precursors and ozone [87]. From the finding presented from figure 20 trough 23, it is possible to say that using this precursor combination in a conventional ALD

process is a very interesting and viable option for scaling the production of Yttria doped Cerium Oxide (YDC) films for diverse applications including solid oxide fuel cell electrolytes as a significant improvement in the growth-rate and appreciable thickness and composition control is achieved. This may allow reduction of the processing time and further tuning of the composition for reaching structural and conductivity requirements therefore making the process more efficient.



Figure 22, Growth rates of CeO_2 and Y_2O_3 deposited by using Ce(i-prcp)3/Y(i-prcp)3 and H_2O on silicon substrates as a function of reaction temperature. Other deposition conditions were the same as those in Fig 15(c) and 16(c). ALD temperature windows for CeO_2 and Y_2O_3 overlap between 240 and 290 °C



Figure 23, YDC (15 nm-thick) film composition evaluated using XPS as a function of normalized ALD cycle ratio $Y_2O_3/(Y_2O_3 + CeO_2)$ (a). Thickness of YDC films with 20% atom. Y (i.e. ALD cycle ratio 1:4, Y_2O_3 :CeO₂) as a function of the total number of ALD cycles (b). All films were deposited at a reactor temperature of 260 °C. Ce and Y-precursor temperatures were 120 and 110 °C, respectively.

Ce-3d and Y-3d XPS core spectra for 15 nm-thick YDC films with 20 atom.-Y % are shown in Figure 24. Deconvolution of the Ce-3d XPS core spectra for as-deposited and annealed 15 nmthick YDC films is presented in Figures 24(a) and 24(b). A number of satellite peaks (shake ups) resulting from strong hybridization of the O-2p valence band with the intense and localized Ce-4f orbitals are observed [102, 103]. By fitting these spectra, it is possible to obtain the relative amounts of Ce⁺³ and Ce⁺⁴. The fitting was performed based on the procedure presented by Paparazzo[106], and the results indicate that both films have considerable amounts of Ce^{+3} ; *i.e.*, 23 and 11 % for as-deposited and annealed films respectively. This suggests that the YDC films most likely have point defects created by the redox activity of the Ce^{+3}/Ce^{+4} pair which may be beneficial for increased the ionic conductivity [96-98].



Figure 24, Ce-3d XPS core spectra collected for as-deposited YDC sample (a) Ce-3d XPS core spectra collected for annealed YDC sample (b), Y-3d XPS core spectra collected for as-deposited YDC sample (c), Y-3d XPS core spectra collected annealed YDC sample (d). Samples were 15 nm-thick. Deposition conditions were the same as in Figure 18. Annealing was carried out under N₂ for 5 min at 600 °C and 1 atm

Moreover, an apparent decrease on the Ce⁺³ amount of the YDC films is observed after annealing which may likely be due to thermally activated atomic diffusion of yttrium to a vacancy, or lattice place [10, 125]. Y-3d XPS core spectra for the as-deposited sample shown in Figure 24(c), shows a main feature as well as a small shoulder feature located at ~158.2 eV which is likely due to absorbed –OH species on the surface and that is corroborated by its desorption after annealing (Figure 24(d)). Quantitative analysis showed that the total Y-atom. % decreases by about 10-15 % after annealing which may also be attributed to Y migration away from the YDC surface to the bulk of the film or towards the Si interface

In order to determine thermally induced changes at the interface that may contribute to these phenomena, XPS analyses collected at a take-off angle of 90° was performed on 4 nm-thick samples; these can provide information about the YDC/Si interfacial region. The XPS results indicate that yttrium atoms not only diffuse into the bulk of the film (*i.e.*, vacancies or lattice places) but they also diffuse towards the YDC/Si interface where they react with the Si-substrate (Figure 25). The XPS spectra of the Y-3d doublet and the Si-2s core levels collected for as-deposited and annealed YDC 20 Y-atom. % samples, is presented in Figures 25(a) and 25(b), respectively. Even though the first four ALD cycles are CeO₂ cycles, it can be seen that after annealing, (Figure 25(b)), the peak in the Y-3d line at a binding energy of 158.5 eV not only increases in intensity but also shifts towards a lower binding energy indicating that some of the yttrium diffuses through the CeO₂ towards the interface were it may react with the silicon substrate to likely form yttrium silicide; likewise, the significant increase in the Si-2S peak at ~153.5 indicates a change in the Si chemical environment that may be attributed to the yttrium silicide formation [126, 127].



Figure 25, Y-3d and Si-2s XPS core spectra collected for an as-deposited YDC sample (a), Y-3d and Si-2s XPS core spectra collected for an annealed YDC sample (b), Si-2p XPS core spectra collected for an as-deposited YDC sample (c), and Si-2p XPS core spectra collected for an annealed YDC sample (d). Samples were 4 nm-thick. Deposition and annealing conditions were the same as in Figure 19

It is possible to see that the Si-2p XPS core spectra of as-deposited films (Figure 25(c)) display one main feature at ~99 eV which corresponds to the Si $2p^{1/2}-2p^{3/2}$ orbit split. A small feature at a higher binding energy can also be observed, which is most likely due to presence of a thin SiO₂ interfacial layer [89]. After annealing, a new feature at a binding energy of ~103.3 eV is obtained (Figure 25(d)). This feature, indicates a change in the chemical environment of silicon that may be attributed to a reaction between Y and Si to form yttrium silicide [128] or a

more complex interaction such as Y-O-Si [129]. Changes in the Si $2p^{1/2}-2p^{3/2}$ peak ratio shoulder (~99 eV), also supports a change in the chemical environment of Si. While these changes in the Si-2p XPS core spectra are well characterized for Y-Si or Y-Si-O systems there are no reports that indicates a Ce-Si or Ce-Si-O interaction.

Grazing incidence X-ray diffraction patterns for as-deposited and annealed YDC (30 nmthick) samples prepared with an ALD cycle ratio of 0.2 is presented in figure 26. As deposited YDC films appear to be amorphous but a trace presence of a diffraction feature at 28.55° corresponding to cubic phase of ceria (111) is observed (JCPDS-340394). Annealing in an inert environment for 5min, GIXRD pattern reveals that the films appear to become polycrystalline but no preferential orientation is obtained. Stronger peak at 28.55° along with the appearance of vanished features at 33.1, 47.48, 56.33 and 59.08° that were assigned to 002, 220, 311 and 222, respectively. These results are in good agreement with the reported for CeO_{2-x} using TEM that was shown in the previous chapter (figure 5). Calculated lattice parameter with these results is 5.416 \pm 0.001 Å. This calculated value is in good agreement with the reported values of the lattice constant for thin films of YDC with this level of doping deposited by using β-diketonates precursors [87].

Factors that may limit the applications of Ceria-based films as electrolyte for SOFCs are the Ce^{+4} stability under reducing conditions and the mixed ionic electronic conductivity at high temperatures and low oxygen partial pressures, which may increase the local electronic conduction of the film [65, 115]. X-ray absorption near edge spectroscopy (XANES) was used for determining the stability of CeO₂-based films at high temperatures under reducing conditions and the results are displayed in Figure 27.



Figure 26, GIXRD patterns of as-deposited and annealed YDC films deposited with ALD cycle ratio of 0.2;CeO₂ pdf card (JCPDS-340394) is also plotted for reference

Trivalent Ce-materials, Ce⁺³, have a single white line with the leading edge shifted to lower photon energy while tetravalent Ce-materials, Ce⁺⁴, have a pre-edge feature and two peaks in the XANES white line, *i.e.*, interaction between 4f orbitals of the Ce-metal and 2p orbitals of the ligands [116] (Figures 12(a) and 12(b)). By fitting the spectra using the standards, the amount of Ce⁺³/Ce⁺⁴ can be quantified. Figure 27(a) displays the comparison of 40 nm-thick undoped ALD fabricated CeO₂ films with CeO₂ nano-powder standard (<25 nm). There is a slight shift in the edge to a lower energy and a slight change in the ratio of the two peaks for Ce^{+4} possibly indicating a small amount of Ce^{+3} in the as-deposited CeO_2 sample.



Figure 27, XANES comparison of a CeO₂ standard (<25nm) vs: (a) undoped as-deposited CeO₂, (b) undoped CeO₂ after H₂ treatment, (c) as-deposited YDC 20 Y-atom.%, (d) YDC 20 Y-atom. % after H₂ treatment. The H₂ treatment was carried out at 1 atm and 700 °C for 10 min by flowing 200 sscm of 4% H₂ in He. Samples were 40 nm-thick. ALD fabrication conditions were the same as those in figures 1 and 4 for CeO₂ and YDC, respectively

The XANES fitting indicates that there is 5% of Ce^{+3} in the bulk of the as-deposited sample. XANES analysis performed on undoped ALD fabricated CeO_2 samples annealed in an inert environment, *i.e;* 200 sccm of He, at 700 °C for 10 min (dotted spectra in Figure 27(b)), shows that the structure of these ALD fabricated CeO_2 is identical to CeO_2 nano-powder standard. This
indicates the presence of interstitial oxygen in the analyzed films, *i.e.* point defects that can be thermally activated so they occupy a lattice or a vacancy site. The presence of these point defects in the ALD fabricated CeO_2 films is created most likely by the redox activity of the Ce^{+3}/Ce^{+4} pair [96-98]. Figure 27(b) shows that annealing the CeO₂ sample at 700 °C for 10 min and 1 atm in a reducing environment of 200 sccm of 4% H₂ in He, lead to partial reduction of the undoped ALD fabricated CeO_{2-x} films. 30 to 35% of Ce⁺³ was found after the XANES fit was performed in the H₂ treated ALD fabricated CeO₂ samples. Figure 27(c) shows the XANES results of asdeposited YDC samples with 20 Y-atom%. These results indicate that ALD deposited YDC samples are identical, within the noise, to CeO₂ nano-powder standard, *i.e.*, only Ce⁺⁴ features are found in the bulk of the films. Additionally, it was found that annealing these YDC samples in the same reducing environment conditions as undoped CeO_{2-x} did not lead to a change in the oxidation state of the Ce-metal (Figure 27(d)). A preliminary extended X-ray absorption fine structure, EXAFS, analysis performed on Helium annealed YDC films (figure 28) indicates that the films have bond distance and coordination number close to the bulk cubic phase of CeO_2 , *i.e.*, 2.34 Å and N=8, but there are some important differences which are summarized in table 7.

Annealed Sample	Ce-O distance (Å)	Coordination (N)	σ^2	
*CeO _{2-x}	2.336 ± 1E-4	8.247 0.013	$0.002 \pm 4.35 \text{E-5}$	
YDC10	$2.316 \pm 2E-4$	7.961 ± 0.014	$0.003 \pm 3.84 \text{E-5}$	
YDC20	$2.306 \pm 3E-4$	7.852 ± 0.020	$0.004\pm6.31\text{E-5}$	
*Data from table (in abortan 4				

Table 7, Fitting results for the 1st coordination shell of Ce in annealed YDC thin films deposited with different concentration of yttrium (YDC10 indicates 10 atom. % Y and YDC20 indicates 20 atom. % yttrium)

*Data from table 6 in chapter 4



Figure 28, radial distribution function of annealed YDC samples deposited with 10 Y-atom%.(i.e., YDC10) (a) and 20 Y-atom%. (i.e., YDC20) (b). Solid and dotted lines denote experimental and fitted data, respectively. Samples were 40 nm-thick, deposition conditions are the same as in figure 6.

As seen in table 7 and figure 29, the mean interatomic Ce-O distances, calculated from fitting the EXAFS data, are seen to decrease with increasing the yttrium dopant concentration. These phenomena are in good agreement with previous observations performed on doped ceria [130, 131]. The crystal structure of pure ceria has 8 O^{-2} ions around Ce⁺⁴ in the nearest neighbor shell. After doping the CeO₂ with Y₂O₃, some oxygen sites change to a vacancy and some Ce⁺⁴ are substituted by Y⁺³ [132, 133]. The decrease in the mean interatomic Ce-O distance observed

in the fitting of the ALD-YDC EXAFS data as a function of the yttrium content can be attributed to the Ce^{+4} ion shifting away from a vacancy towards its oxygen neighbors.



Figure 29, Calculated Ce-O interatomic distance in YDC ($Ce_{1-x}Y_xO_y$) as a function of the Yttrium amount. EXAFS analysis was collected on 40 nm samples deposited on Si

Although further comprehensive analyses need to be perform in order to determine the interaction of oxygen vacancies with Ce^{+4}/Y^{+3} ion neighbors, the EXAFS studies indicate that the deposited ALD-YDC films have structure that resembles the bulk CeO_2 (*i.e.* N=8, r=2.343). Studies indicate that nanostructured CeO_2 films, N<8, may become electronic conductors even

at high oxygen partial pressures [134], thus having bulk-like structure is of interest for potentiate the applications of Ceria-based materials as electrolytes for IT-SOFC applications.

It seems clear from the experiments presented in this chapter that the use of undoped CeO₂ as IT-SOFC electrolyte can lead to failure of the SOFC stack due to partial reduction of the Ce⁺⁴ phases under low oxygen partial pressure environments increasing in that way the electronic conduction. However, it is important to remark that the ALD-deposited YDC films performed well under reducing conditions (*i.e.*, stable Ce⁺⁴ phases up to 700 °C). This suggest that the use of ALD is a promising way for fabricating YDC films with stable Ce⁺⁴ phases, large concentration of point defects and bulk-like structure that may contribute in increasing the ionic conductivity for applications of these materials as IT-SOFC electrolyte.

Electrochemical impedance spectroscopy (EIS), has become a powerful tool to study the conductivity of solid electrolytes. EIS allows characterizing possible limitations and may give guidance that allows engineering of fuel cells electrolytes with improved performance. Three fundamental sources of voltage loss have been identified as limitation for wide spreading of the fuel cell technology. These losses are related to charge transfer activation as well as losses related to ion and electron transport can be, and finally mass transfer losses. Physiochemical processes occurring within the fuel cell can be represented by a network of resistors, capacitors or constant phase elements, and by correctly fitting the impedance spectra meaningful information, quantitative and qualitative, can be acquired [135].

Complex impedance was collected at different temperatures for as-deposited and annealed YDC samples with 2 doping levels: YDC10 which indicates 10 atom. % of yttrium (deposited using an ALD cycle ratio 0.1 Y/(Ce+Y)) and YDC20 which indicates 20 atom. % of yttrium

(deposited by using an ALD cycle ratio 0.2 Y/(Ce+Y)), and the results are displayed in figures 30 through 33.

Figure 30 displays the complex impedance (Nyquist plot) collected at different temperatures for as-deposited 40 nm-thick YDC10 samples along with the fit of the data which was performed using an equivalent circuit for each data set. It is possible to observe that at 100 and 200 °C (figures 30a and 30b), 2 semicircles can be fitted, one small at high frequency values corresponding to the conductivity of the bulk and a larger one at lower frequency values which has been attributed to grain boundaries [136].



Figure 30, complex impedance plot (Nyquist plot) and fitted simulation of as-deposited 40 nm-thick YDC films deposited with 10 atom. % Y (YDC10) on silicon substrates collected at (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d)



400 °C. The data was collected at ambient atmosphere using a "side by side" electrode geometry and it was modeled using equivalent circuits

Figure 31, complex impedance plot (Nyquist plot) and fitted simulation of annealed 40 nm-thick YDC films deposited with 10 atom. % Y (YDC10) on silicon substrates collected at (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 400 °C. The data was collected at ambient atmosphere using a "side by side" electrode geometry and it was modeled using equivalent circuits



Figure 32, complex impedance plot (Nyquist plot) and fitted simulation of as-deposited 40 nm-thick YDC films deposited with 20 atom. % Y (YDC20) on silicon substrates collected at (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 400 °C. The data was collected at ambient atmosphere using a "side by side" electrode geometry it was modeled using equivalent circuits



Figure 33, complex impedance plot (Nyquist plot) and fitted simulation of annealed 40 nm-thick YDC films deposited with 20 atom. % Y (YDC20) on silicon substrates collected at (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 400 °C. The data was collected at ambient atmosphere using a "side by side" electrode geometry and it was modeled using equivalent circuits

As the temperature increases, (figures 30c and 30d) the effect of the large semicircle (attributed to grain boundaries) decreases and the major contribution to the resistance is due to bulk YDC10 film. It has been reported that, for ionic conductors the grain boundary resistance is higher than the bulk [136, 137], thus this transition from grain boundary dominated to bulk dominated is believe to be due to low crystallinity on as-deposited YDC films.

Figure 31 displays the impedance spectroscopy results for annealed 40 nm-thick YDC10 films. It can be observed that apparently only one semicircle can be used for fitting the results,

however a more complex model in the form R1+Q1/(R2+Q3/R3) needs to be used where R1 is the resistance characteristic to the measurement equipment. This is believed to be due to an intricate contribution of parallel and transverse grain boundaries (*i.e.*, R2 and R3 are a combination of the resistance of bulk, parallel and transversal grain boundaries) that cannot be clearly observed due to the side by side electrode configuration used for collecting the data.

The Nyquist plot for as-deposited YDC20 is displayed in Figure 32. It can be observed that, the grain boundaries have a larger effect even at higher temperatures (figures 32a and 32b) when compared to as-deposited YDC10 (figure 39). Although it was found *via* GIXRD that as-deposited YDC20 films are mostly amorphous, this larger contribution to the impedance of the grain boundaries is attributed to the combination of crystallization and a higher doping concentration of Y in the sample. Figure 33 shows the Nyquist plot for annealed YDC20 films with an initial contribution of grain boundaries (figures 33a and 33b) with features of a Warburg element (*i.e.*, Ionic diffusion or mass transport) [135, 138].

The total activation energies for conduction are calculated by fitting the collected data to an Arrhenius relation for thermally activated conduction plot

$$\sigma T = \sigma_0 e^{-\frac{E_a}{kT}} \qquad (4)$$

Where E_A is the activation energy for conduction, T is the absolute value of the temperature, k is the Boltzmann constant and σ_0 is a pre-exponential factor.

Figure 34 shows the calculation of the total activation energy for all the analyzed films. It can be observed that as-deposited YDC thin films with 10 atom. % (Figure 34a) have an activation energy of 2.82 eV which is close to the values reported for bulk un-doped CeO_{2-x} . [139]. Annealed thin films of YDC10 (figure 34b) appear to have 2 regions in which a linear fit can be performed. There is an interesting evolution in the activation energy at temperatures

higher that 200 °C, where the activation energy increases from -1.04 to 2.11 eV. This may be attributed to the complex interaction of parallel and grain boundaries. Other viable application is a reduction of the total amount of Y in the film after annealing as demonstrated in the analyses performed on figure 25.



Figure 34, total ionic conductivity of as-deposited YDC10 (a), annealed YDC10 (b), as-deposited YDC20 (c) and annealed YDC20 (d) as a function of temperature. Analyzed films were 40 nm thick

The calculation of the total activation energy for as deposited and annealed YDC films with an of Yttrium content of 20 atom % yttrium (*i.e.* YDC20) are shown in figures 34c and 34d, respectively. Both, as-deposited and annealed films display a lower dependence on the temperature at values higher than 300 C as observed by the transition in the activation energy with temperatures higher than 300 °C. This indicates that the resistance of grain boundaries decreases or in other words ionic conductivity of these grain boundaries increases and the ionic conductivity is a dominated by the bulk, as expected for YDC films with higher doping levels [137]. The values of the calculated activation energy of ALD-YDC20 thin films at temperatures higher than 300 °C are lower than the reported values of 50 nm-thick YDC samples with the same doping level deposited by dc reactive co-sputtering at temperatures higher than 500 °C [134].

The combination of analyses presented in this chapter demonstrates that the YDC20 thin films hold promise for being used as electrolytes in IT-SOFC as it was found that these films are stable under reducing condition, present bulk like structure and have low activation energies. Nevertheless, further ionic conductivity analysis needs to be done in order to fully characterize the performance of these materials under actual SOFC operation conditions.

5.4. Summary

In this chapter, yttria doped ceria, YDC, thin films were deposited via atomic layer deposition (ALD) on p-type silicon (100) using novel precursor chemistry based on tris(iso-propylcylopentadienyl)Cerium, Ce(i-prcp)₃, and tris(iso-propylcylopentadienyl)Yttrium, Y(i-prcp)₃, with water vapor as the oxygen donor in a custom built hot wall ALD reactor. Individual binary deposition processes of CeO₂ and Y₂O₃ were characterized and a sufficient ALD

temperature-window overlap was found suitable for the ALD of YDC films under self-limiting growth conditions. The ALD cycle ratio $[Y_2O_3/(Y_2O_3 + CeO_2)]$ was used as control parameter for tuning the composition of the films and the atomic composition was found to change almost linearly with the ALD cycle ratio, indicating excellent tunability. X-ray photoelectron spectroscopy analysis of the ALD films shows that annealing of the YDC films in an inert environment at 600 °C, decreases the total amount of point defects in the surface of the films and produces Y-Si bonds at the Si-YDC interface thus indicating thermally activated yttrium diffusion in the films. Analysis of the YDC films by X-ray absorption spectroscopy shows that the YDC films have bulk-like structure and are chemically stable under reducing conditions up to 700 °C in 4% H₂ in Helium which may potentiate the applications of these films as IT-SOFC electrolyte. It was also found by EXAFS that the mean interatomic distance Ce-O decreases monotonically with increasing the yttrium doping concentration in the film. This can be explained in terms of strain induced not only introduced by the aliovalent dopant (*i.e.* Y^{+3}) but also for the localization of oxygen vacancies next to the Ce^{+4} ion instead of the Y^{+3} which may improve ionic conductivity. Evidence of this is presented in the ionic conductivity analyses which show clear differences between YDC films deposited with a doping level of 10 % Y with those deposited with 20 % atom. Y.

It is then concluded that the results presented in this chapter are of great interest toward improving the design of IT-SOFC stacks with YDC films as the electrolyte. It was shown that the thermal and composition induced structural transformation on the YDC thin films have an impact on the physical properties relevant to stoichiometry stability and ionic conductivity processes. It is also concluded that on the fabrication of YDC not only the films processing but also the precursor selections affect the microstructure of YDC and with this the ionic conductivity. ALD is an effective way of fabricating stable and continuous YDC films with varying thicknesses, from unexplored ultra-thin nanometer levels to bulk-like levels. It is important to remarks that this work is the first to explore ultra-thin YDC20, (*i.e.* deposited with 20 % atom. Y), which showed improved values of the ionic conductivity activation energy, and good stability under reducing condition therefore these YDC films hold promise as intermediate temperature solid oxide fuel cell (IT-SOFC) electrolyte.

6. Atomic Layer Deposition of YSZ and Fabrication of YSZ/YDC Composites

6.1. Introduction

Yttria stabilized zirconia (YSZ) films have been widely studied due to their excellent properties as a ceramic material including low thermal conductivity, good corrosion resistance, relatively low elastic modulus, good optical properties and in view of SOFC because of its high ionic conductivity, low electronic conductivity, and the stability at high temperatures and under operating conditions [44, 50]. The maximum ionic conductivity of YSZ is observed when the concentration of the dopant is close to the minimum necessary to completely stabilize the cubic fluorite-type phase. However, it has been reported that this minimum concentration, and its corresponding conductivity, is dependent on the processing and microstructural features [16, 44].

Up to now YSZ with an yttria concentration of 8 % mol has been used as the state-of-the-art electrolyte material in SOFCs. The doping of zirconia with this level of yttria has been identified as the one that can induce the higher ionic conductivity due to the creation of a considerable amount of oxygen vacancies while simultaneously inducing the cubic fluorite-type crystalline structure in the film. However, further addition of yttria decrease the ionic conductivity due to increasing association of the oxygen vacancies and dopant-cations into complex defects of low mobility [16, 72]

150 μ m-thick YSZ films have been typically fabricated using physical deposition techniques however this rather thick films cannot be used for IT-SOFCs due to inefficient oxygen ion transport below 800 °C [10, 12, 44, 45]. Implementation of ultra-thin films in nanometer scale, (50 – 200 nm), has been widely identified to be an effective means of increasing ionic conductivity of the electrolyte in IT-SOFC [19, 46, 47, 62]. Further improvement of the ionic conductivity on ultra-thin YSZ films has been achieved by using interlayers of YDC. YDC has been recognized as a material with higher oxygen ion incorporation coefficient which may facilitate the charge transfer kinetics at lower temperatures in the IT-SOFC stack, therefore study of YSZ/YDC composites is a current trend in ways of effectively reducing the operating temperature [13, 15, 18, 64, 140]

With the development of thin film fabrication technologies, chemical vapor deposition techniques have been currently considered to be a powerful means of fabricating very thin structures and tailored interfaces of multilayered materials for IT-SOFCs applications due to the ability of depositing films with superior properties (*i.e.*, pinhole free and highly dense ultra-thin films) and also because these methods satisfy additional fabrication criteria, such as fully coverage of three-dimensional features for all needed dimensions.

Metal organic chemical vapor deposition MOCVD was used in 1999. B-diketonates precursors along with ozone were used for depositing YSZ films over alumina and silicon substrates at high temperatures (450-850 °C). For this process and this precursor chemistry, growth-rates as high as $0.7 \,\mu$ m-min⁻¹ were obtained and the resulting films exhibited fine-grained microstructures [73].

ALD as a method for depositing YSZ films was firstly introduced in early 2000's using soda lime glass, silicon as well as Ni-YSZ cermets as substrates and a variety of metal precursors with a variety of ligands including chloride, β -diketonates, and cyclopentadienyl [74, 75]. In 2007, YSZ films were synthesized by ALD using tetrakis-(dimethylamido)-zirconium, Tris(methylcyclopentadienyl)yttrium and water as the oxygen source. A free-standing structure made of 60 nm-thick ALD YSZ sandwiched between sputtered platinum were reported to have a maximum power density of 270 mW/cm² at 350 °C [46]. In 2008, a low temperature SOFC with corrugated electrolyte membrane was developed and tested. 70 nm-thick YSZ membranes were deposited using the same precursor chemistry onto pre-patterned silicon substrates and a maximum power density of 677 mW/cm² at 400 °C was found and attributed to the increased electrochemical active surface area. More recently, in 2013, a 10 nm-thick YSZ layer with a higher yttria doping level was deposited using ALD on a 500 μ m-thick single crystal YSZ. The results indicate that nano-laminates of slightly higher yttria doping level at the electrode/electrolyte interface significantly enhance the oxygen exchange kinetics.

Fan *et al.* used a mixed precursor chemistry based on an yttrium-CP-Type precursor and a cerium- β -diketonate precursor for fabricating YDC films as interlayers for enhancing the properties of traditional YSZ films. The individual growth rates reported for this process is 0.75 and 0.53 Å/cycle for CeO₂ and Y₂O₃ respectively. Their films presented excellent tunability of the yttrium doping with the ALD cycle ratio and electrical measurements show that using YDC as an interlayer between the cell performance is enhanced and depends on the interlayer film thickness [18, 64, 65]

Decreasing the thickness of YSZ films to several tens of nanometers, as wells as nanoengineered interfaces is therefore confirmed as effective routes for enhancing O^{-2} transport. However, it is of importance to further understand the properties of the film grown *via* ALD using different precursor chemistries and how the film processing affects not only the microstructure but also the physical properties related to electrochemistry processes in IT-SOFCs. This fundamental understanding can be applied for optimizing the construction and working conditions of IT-SOFCs.

In this chapter, novel precursor chemistries based on CP-type precursors tris(dimethylamino)cyclopentadienyl-Zirconium, ZyALD, Y(i-prcp)₃, and Ce(i-prcp)₃, along

with water vapor as the oxygen donor were used for the deposition of ultra-thin YSZ and YSZ/YDC films using ALD on p-type silicon (100) substrates in a custom-designed and built hot wall ALD reactor in order to explore the potential applications of ultra-thin YSZ films as IT-SOFC electrolytes and to investigate scalability of ALD process capable of continuously process multilayer films under optimized ALD conditions.

First, the ALD process variables for self-limiting growth of ZrO₂ were characterized by measuring the growth rate as a function of precursor dosage, water vapor dosage, reactor temperature and number of ALD cycles. A suitable ALD window overlap is found for the co-deposition of YSZ, YDC and YSZ/YDC composites using the same reactor in a continuous process. The resulting YSZ films are analyzed and discussed in terms of compositional tunability, and crystalline structure variation with increasing the doping level.

The ALD cycle ratio $[Y_2O_3/(Y_2O_3 + (ZrO_2)]$ was used for tuning the YSZ composition which was found to increases linearly with the cycle ratio. Characterization shows that ratio, compared to YSZ films deposited with other precursor chemistries, as-deposited films are polycrystalline and the crystalline structure depends on the yttrium concentration. After carefully tuning the yttrium composition and annealing, it is possible to obtain YSZ films display the cubic phase and the calculated value of the lattice parameter is lower than that estimated for cubic YSZ single crystals at the same composition, which indicates that not only the processing technique but also the precursor selections plays an important role on the YSZ microstructure.

YSZ/YDC were fabricated under optimized ALD condition in the same reactor and using novel precursor chemistries that allow lower processing times. YSZ/YDC Films are analyzed in term of composition at each interface and crystalline structure variation with annealing. It was found that YDC section of the composite present an oxygen deficiency gradient which can progressively provide exchange of oxygen ions among the YDC surface, the YDC lattice and most importantly improve the kinetics at the YSZ/YDC interface at low temperatures (*i.e.*, 600 to 800 °C). Electrochemical impedance spectroscopy analyses show that, in the range of 100 to 400 °C, ultra-thin YSZ (40 nm) deposited with the procedure presented in this chapter have total activation energy compared to bulk YSZ calculated at temperatures higher than 500 °C. Electrochemical impedance spectroscopy analyses performed on YDC/YSZ interlayers show clear trend induced by the enhanced properties of the YDC layer which are related to a better oxygen ion incorporation induced by the oxygen deficiency gradient.

6.2. Experimental Methods

ZrO₂, YSZ and YSZ/YDC films were deposited on p-type silicon (100) using precursors tris(dimethylamino)cyclopentadienyl-Zirconium, tris(isopropyl–cyclopentadienyl)Yttrium tris(isopropyl–cyclopentadienyl)Cerium, (ZyALD, Y(i-prcp)₃ and Ce(i-prcp)₃), (Air Liquide, USA), with water vapor as the oxygen donor in a custom-designed and built hot wall ALD reactor. The ZyALD, Y(i-prcp)₃ and Ce(i-prcp)₃ precursors were kept in stainless steel vessels at 55, 110 and 120 °C, respectively. All lines downstream the precursor vessels were maintained at least 10 °C higher in order to prevent condensation of precursor in the manifold. Deionized water maintained at 0 °C using an ice bath was used to introduce pulses of water vapor into the reactor. Before deposition, silicon (100) substrates were cut into squares of about 1.5 cm X 1.5 cm and cleaned using standard Radio Corporation of America (RCA) SC-1 cleaning method in order to remove organic contamination, followed by a 10 s dip in a 2% HF solution which reduces the native silicon oxide layer below 7 Å as measured by spectral ellipsometry (JA Woollam Co., Inc. model M-44). Each of the cleaning steps was followed by a thorough deionized water rinse and

final dry with N_2 . Immediately after the cleaning process, the samples were loaded into the reactor chamber and pumped down to a deposition pressure of 180 mTorr.

Metal precursors were injected into the reactor as pulses by backfilling precursor reservoir with N_2 and evacuating this N_2 with precursor vapor under vacuum into the reactor, each pulse lasting 1 s. The precursor dosage per ALD cycle was controlled by increasing the number of precursor pulses. Detailed information about the reactor set up and operation can be found elsewhere [90, 91].

Once the ALD parameters for the growth of individual oxides were obtained, YSZ samples (15 nm thick, verified using spectral ellipsometry) were deposited at 280 °C with different ALD Cycle ratio (*i.e.*, $Y_2O_3/(Y_2O_3+ZrO_2)$). Next, each sample was cut in half and one of the halves was placed in a three zone annealing furnace (Lindberg/Blue) for 5 min, in a nitrogen environment at furnace temperatures of 600 °C and 1 atm. Prior to placing samples into the furnace, residual air was removed from the furnace chamber by purging it with N₂. The other half serves as the as-deposited sample.

X-ray photoelectron spectroscopy (XPS) was performed for investigating the elemental bonding state of the film and interfacial regions. XPS was also used to determine the stoichiometry and thus compositional tunability of the YSZ films fabricated via ALD. All XPS spectra were collected using a Kratos AXIS-165 spectrometer. The surface analysis system was equipped with a monochromatic Al K α (1486.6 eV) X-ray source and a concentric hemispherical analyzer coupled with a charge neutralizer operated at 15 kV and 10 mA. High resolution spectra were collected at a take-off angle 90° with pass energy of 20 eV, step size of 0.1 eV, and dwell time of 200 ms. The quantitative elemental analysis was performed by fitting the spectral peak areas with Shirley background correction and applying the appropriate sensitivity factors. The binding energy was referred to the adventitious carbon in the C1s spectra at 284.8 eV.

50 nm-thick YSZ samples with different ALD-cycle ratio were prepared for transmission electron microscopy TEM analysis. The TEM analysis was performed using a JEOL JEM-3010 with Gatan digital cameras and Thermo-Noran XEDS microscope in order to obtain detailed information of the crystalline structure dependence with the yttrium content. . Energy loss spectroscopy (EELS) was performed in a JEM-ARM200CF STEM/TEM with a cold field emission source, equipped with a Gatan Enfina EELS detector with 0.35 eV energy resolution to confirm the stoichiometry obtained with XPS.

70-nm thick YSZ/YDC (YSZ 40 nm, YDC 30 nm) composites were prepared in the reactor using desired ALD cycle ratios for both YSZ and YDC one after the other. TEM along with EELS was used for characterizing the YSZ/Si interface as well as the YSZ/YDC interface.

The electrochemical properties of annealed YSZ and YSZ/YDC were analyzed by electrochemical impedance spectroscopy. These measurements were carried out under ambient air, using an Bio-Logic SP-240 potentiostat with 10 mV ac dignal amplitude (Δ V) and without dc polarization in the 7 MHz to 10 μ Hz frequency range (10 points per decade) in a temperature range varying from room Temperature to 400 °C. 2 circles of 3mm diameter using igh temperature silver paste (Heraeus C8729-conductor paste) were used as support for pasting platinum wires that worked as working electrode.and counter electrode The obtained impedance diagrams were analyzed using equivalent circuit simulation software EC-Labs commercially available from the potentionstat vendor

6.3. Results and discussion



Figure 35, Growth rate of ZrO₂ as a function of precursor pulses (a), water pulse duration (b), number of ALD cycles (c) and reaction temperature (d). The depositions were carried out at a precursor temperature of 55 °C and reactor pressure of 180 mTorr. Data points in Figure 35(c) were obtained using 6 pulses of precursor (1 s long each), a water pulse duration of 60 ms and a reactor temperature of 260 °C. Data points in figures 35(a), (b), and (d) were obtained using 50 ALD cycles. In all cases, the vertical error bars indicate film uniformity across the samples

Characterization of the ALD variables for the fabrication of ZrO_2 using ZyALD and water is shown in Figure 35. The growth rate was measured as function of precursor dosage, water vapor dosage, number of ALD cycles and reactor temperature. As seen in Figure 35(a), 6 pulses of precursor are enough for saturating the surface on which a constant growth rate of ~0.45 Å/cycle is obtained. Figure 35(b), shows the effect of the water pulse duration on the growth rate. It is possible to see that water pulse of 60 ms is required to fully react with the saturated surface. The variation of the ZrO_2 film thickness with the total number of ALD cycles is presented in figure 35(c). It is possible to appreciate that at a low number of cycles (<60) the growth rate has a value of 0.45 Å/cycle. At higher number of cycles, the obtained value for the growth rate of ZrO_2 stabilizes at 0.6 Å/cycle. All data points presented in figure 35(c) were obtained using 6 pulses of precursor (with duration of 1 s each), water pulse duration of 60 ms and a reactor temperature of 260 °C. A linear regression analysis using minimum least squares, using all data points, shows that the growth-rate is 0.58 Å/cycle, a value that is in the same order of those reported using mixed CP-type precursors and ozone [141].

Figure 35(d) shows a relatively wide ALD temperature window ranging from 220 to 280 °C. Below this region, lower values of the growth-rate are observed which is likely due to the insufficient deposition temperature impeding surface chemisorption and/or chemical reaction between the metal precursor and water. At high reactor temperatures, (>280 °C), low growth-rates of Y_2O_3 are also observed and this is most likely due to lower surface adsorption of ZyALD precursor on the substrate at these temperatures.

Zr-3d and O-1s XPS core spectra for as-deposited samples were collected for the determination of the ZrO_2 film stoichiometry and the results are presented in Figures 36. Figure 36(a) shows the deconvolution of the Zr-3d XPS core spectra. In this figure the Zr-3d^{5/2} contribution located at 182.4eV with a 2.39eV split separation which in good agreement with Zr⁺⁴-O interaction [142]. Figure 36(b) shows the O-1s XPS core spectra which reveals two

peaks: the dominant one, located at 530.3 eV, consistent with a Zr-O bonding of ZrO_2 [142, 143], while a small shoulder peak at 531.85 eV appears after spectral peak deconvolution and this is likely due to -OH species from absorbed moisture on the surface [111].



Figure 36, Zr-3d (a) and O-1s (b) XPS core spectra of a 15 nm-thick ZrO_2 sample. Deposition conditions were the same as in figure 35(c).

Quantitative analysis shows that the as-deposited ZrO_2 films are nearly stoichiometric giving an oxygen to zirconium ration (O:Zr) of 1.94. Figure 37 shows C-1s XPS core spectra in which the carbon content is quantified. Before sputtering, the superficial carbon content was determined to be ~5 % which decreases to a value below detectable level after 5 min of Ar⁺ sputtering.



Figure 37, C-1s XPS core spectra of a 15 nm-thick ZrO2 sample after collected after 5 min Ar^+ sputtering. Deposition conditions were the same as in figure 35(c).



Figure 38, Growth rates of ZrO_2 and Y_2O_3 deposited by using $ZyALD/Y(i-prcp)_3$ and H_2O on silicon substrates as a function of reaction temperature. Other deposition conditions were the same as those in Fig 35(c) and 21(c). ALD temperature windows for ZrO_2 and Y_2O_3 overlap between 250 and 280 °C

Figure 38 shows a combination of figures 21(d) and 35(d) in which a sufficient overlap in the individual ALD temperature windows of Y_2O_3 and ZrO_2 is observed between 250 and 280 °C. This overlap offers a suitable range of temperatures for the ALD of YSZ under self-limiting growth conditions and based on these results, 260 °C was selected for the deposition of the YSZ films. In order to study the atomic composition tunability of atomic layer deposited YSZ thin films, a series of experiments were carried out with different ALD cycle ratios,

 $[Y_2O_3/(Y_2O_3+ZrO_2)]$; *e.g.*, for a cycle ratio of 0.2, four cycles of ZrO_2 are alternated with one cycle of Y_2O_3 . Figure 39 illustrates the effect of the cycle ratio $[Y_2O_3/(Y_2O_3+ZrO_2)]$ on the atomic composition [Y/(Zr+Y)] of 15 nm-thick as-deposited YSZ films. As determined from quantitative analyses of XPS spectra, the atomic content of Y in $Y_xZr_{1-x}O_y$ films increases almost linearly with increasing the ALD cycle ratio thus demonstrating that by controlling this variable, the composition of YSZ thin films can be controlled down to the atomic level.



Figure 39, YSZ film composition evaluated using XPS as a function of normalized ALD cycle ratio $Y_2O_3/(Y_2O_3 + ZrO_2)$. YSZ films were 15 nm-thick and were prepared at 260 °C. Other deposition conditions were the same as in figure 21(c) for the Y_2O_3 cycles and figure 35(c) for the ZrO_2 cycles

The calculation of the total mol % of yttia (Y_2O_3) in the YSZ films is presented in table 8. Since yttria is Y_2O_3 and not just Y, the equation x=2y/(1+y) must be used to convert from Y % in $Y_xZr_{1-x}O_y$ (*i.e.* x in the equation) to mol % Y_2O_3 in $(ZrO2)_{1-y}(Y_2O_3)_y$.

Table 8, composition tunability of the ALD deposited YSZ films. Increasing the ALD cycle ratio monotonically increases the vttrium amount in the film

ALD Cycle Ratio (Zr:Y)	Target Y-atom. % in the sample based in normalized cycle ratio	Measured Y-atom % atom via XPS	$\frac{Y_{2}O_{3} \text{ Mol \%.}}{Y_{atom} \%}$ $\frac{Y_{atom} \%}{(2 + Y_{atom} \%)}$
11:1	$\frac{Y_2O_3}{Y_2O_3 + ZrO_2} = \frac{1}{12} = 0.083$	8.9 %	4.26 %
4:1	$\frac{Y_2O_3}{Y_2O_3 + ZrO_2} = \frac{1}{5} = 0.20$	23 %	10.3 %
1:1	$\frac{Y_2 O_3}{Y_2 O_3 + Zr O_2} = \frac{1}{2} = 0.50$	53 %	20.9 %

Figure 40 shows XPS analyses on the Y-3d core spectra performed on 15 nm-thick YSZ. These XPS analyses reveal a shift towards a lower binding energy of the Y-3d^{5/2} of about 1.15 eV. This shift has been related to alteration in the yttrium chemical environment that may be introduced by changes in the crystalline structure of the YSZ induced by the amount of yttrium [48, 144]. Transmission electron microscopy studies were performed on 100 nm-thick YSZ samples with ALD cycle ratio of 1:12, 1:5 and 1:2 [Y/(Y+Zr)] (*i.e.*, 4, 8, and 20 % mol Y₂O₃) and the results are displayed in figures 41 to 43.



Figure 40, Y-3d XPS core spectra collected from 15 nm-thick as-deposited YSZ samples with ALD cycle ratio 1:5 $Y_2O_3 / (Y_2O_3 + ZrO_2)$ (solid line) and 1:12 $Y_2O_3 / (Y_2O_3 + ZrO_2)$ dotted line Other deposition conditions were the same as in figure 21(c) for the Y_2O_3 cycles and figure 35(c) for the ZrO_2 cycles.



Figure 41, TEM micrograph of a 100 nm-thick YSZ sample with 4 % mol Y_2O_3 (ALD cycle ratio 1:12 Y_2O_3 /($Y_2O_3+ZrO_2$)). Other deposition conditions were the same as in figure 21(c) for the Y_2O_3 cycles and figure 35(c) for the ZrO_2 cycles



Figure 42, TEM micrograph of a 100 nm-thick YSZ sample with 8 % mol Y_2O_3 (ALD cycle ratio 1:6 Y_2O_3 /($Y_2O_3+ZrO_2$)). Other deposition conditions were the same as in figure 21(c) for the Y_2O_3 cycles and figure 35(c) for the ZrO_2 cycles



Figure 43, TEM micrograph of a 100 nm-thick YSZ sample with 20 % mol Y_2O_3 (ALD cycle ratio 1: 2 Y_2O_3 /($Y_2O_3+ZrO_2$)). Other deposition conditions were the same as in figure 21(c) for the Y_2O_3 cycles and figure 35(c) for the ZrO_2 cycles

It is possible to appreciate that figures 42 and 43 display some darker areas than figure 41 and this is attributed to a non uniform polishing of the samples when they were being prepared for TEM analysis. However, it is clear from these 3 figures (figures 41 to 43) that the deposited ALD-YSZ films are polycrystalline with crystal size of several nanometers at deposition conditions.





Figure 44, TEM electron diffraction analyses showing a mixture of monoclinic and tetragonal structures in asdeposited YSZ 4 % mol Y_2O_3 . Deposition conditions are the same as in figure 41.



Figure 45, TEM electron diffraction analyses showing a mixture of tetragonal and cubic structures in as-deposited $YSZ \ 8 \ \% \ mol \ Y_2O_3$. Deposition conditions are the same as in figure 42





Figure 46, TEM electron diffraction analyses showing the cubic structure in as-deposited YSZ 20 % mol Y_2O_3 . Deposition conditions are the same as in figure 43

In order to identify the crystalline structure of the YSZ films and its relation with the shift in the Y-3d binding energy observed in figure 40, TEM images using diffraction mode were collected for the YSZ samples with ALD cycle ratio 1:12, 1:6, and 1:2 (Y/(Y+Zr)). It has been reported that pure ZrO_2 undergoes two crystallographic transformations between room temperature and its melting point: monoclinic to tetragonal at ~1170 °C and tetragonal to cubic at ~2350 °C, however the cubic phase of ZrO_2 , which has the larger ionic conductivity, can be stabilized at lower temperatures by doping with oxides of di, tri, and tetravalent metals such as calcium, magnesium, ytterbium and yttrium [144-146].

The diffraction pattern collected via TEM of as-deposited YSZ films deposited with ALD cycle ratio of 1:12 (*i.e.*, 8.33 Y-atom % or 4 % mol Y₂O₃) and its analysis is presented in figure 44. It is possible to see that this film is polycrystalline with no preferential orientation. Diffraction analyses indicate that this film has the monoclinic crystal structure with dominant phases 100, 101, 111, 122 and 131. Some small traces of the tetragonal structure specially 101, 200, 103, and 202 are also observed. The calculated lattice parameters for the monoclinic structure are a = 5.151 Å, b = 5.212 Å, c = 5.317 Å and β = 99.23. It has been reported that that ZrO₂ films crystallize in a mixture of monoclinic-cubic structure when using CP-Type precursors [141]. However, tetragonal and cubic structures of ZrO₂ are very similar which make it difficult to differentiate the tetragonal from the cubic crystalline structure [120].

Analyses of the TEM collected diffraction pattern of YSZ deposited with ALD cycle ratio 1:6 (*i.e.*, 16.7 Y-atom % or 8 % mol Y_2O_3) are presented in figure 45. This film is polycrystalline with no preferential orientation and a combination of tetragonal and cubic phases are observed. Diffraction analyses indicate that this film has tetragonal phases 002, and 103 with lattice parameters a = 5.037 Å and b = 5.202 Å. The cubic phases that were found are 111, 022 and 222. The calculated lattice parameter using the cubic structure is 5.135 ± 0.022 Å which is in good agreement with the values of the lattice constant reported for bulk and thin films of cubic YSZ with 8% Y₂O₃ [75, 147]

Crystalline structure analyses of YSZ with 20 % mol Y_2O_3 (*i.e.*, deposited with ALD cycle ratio 1:2 Y/(Y+Zr)) is presented in figure 46. Cubic structure with orientations 111, 002, 022, 113 and 222 were found through the TEM analyses. Although it is possible to label some tetragonal phases, such as 002, they were not considered and the films were labeled as pure cubic. The calculated lattice parameter was 5.156 ± 0.008 Å which correspond to cubic YSZ with ~18 % mol Y_2O_3 doping. This apparent expansion in the lattice parameter value is related to the addition of Y and is also in good agreement with the reported lattice parameter for bulk and thin films of cubic YSZ with this level of doping [75, 147].

Diffraction analyses on vacuum-annealed 8 % mol YSZ (*i.e.*, sample prepared with ALD cycle ratio 1:6 Y/(Y+Zr)) is presented in figure 47. The TEM sample was annealed at 400 °C for 30 minutes under vacuum conditions. Polycrystalline cubic structure with orientations 111, 022, 113 and 133 was found after performing the diffraction analysis. The calculated lattice parameter was 5.124 ± 0.024 Å which correspond to cubic YSZ with 4–7 % mol Y₂O₃ doping [75, 147]. This indicates a reduction in the total amount of yttrium in the bulk of the sample. This phenomenon was investigated using energy dispersive X-ray spectroscopy (EDS) and the analysis is displayed in figure 48. Quantification performed on the analyzed area of this annealed sample allowed to determine that the atomic percentage of Y in Y_xZr_{1-x}O_y is 0.11 which correspond to 5.3 % mol Y₂O₃. Compositional and structural analyses of YSZ single crystals, report that this concentration of yttria in the samples is below the limit for stabilizing the cubic YSZ structure, thus a mixture of cubic and tetragonal phases, with a prevalence of the cubic one
should be present in the vacuum annealed YSZ film [148]. We can conclude that the deposited cubic YSZ film has a lattice parameter even lower than that estimated for cubic YSZ single crystals at the same composition. Similar effects has been reported for YSZ thin films deposited by laser ablation and these are noticeable result because that thin films generally exhibit an opposite behavior [149, 150]. Although it was possible to obtain cubic YSZ after annealing, there is evidence that points out possible thermally activated Yttrium mobility, most likely toward the silicon substrate due to the higher chemical affinity of Y-Si formation, thus decreasing the Y_2O_3 amount in the bulk of the films [126, 127] or other surface effects that are induced by annealing the TEM sample under vacuum [145].



Figure 47, TEM electron diffraction analyses showing the cubic structure in annealed YSZ 8 %mol. Sample was annealed in vacuum for 30 minutes at 400 °C. Deposition conditions are the same as in figure 42



Figure 48, EDS spectrum of annealed YSZ 8 %mol. Sample was annealed in vacuum for 30 minutes at 400 °C. Deposition conditions are the same as in figure 42.

Figure 49 shows a sufficient overlap in the individual ALD windows of CeO_2, Y_2O_3 and ZrO_2 between 230 and 280 °C. This overlap offers a suitable range of temperatures for exploring

the ALD of YSZ/YDC under self-limiting growth conditions in the same reaction system. Based on these results, YSZ/YDC composites were deposited at 280 C in order to favor crystallinity [141].



Figure 49, Growth rates of ZrO₂, CeO₂ and Y₂O₃ deposited by using ZyALD/Ce(i-prcp)₃/Y(i-prcp)₃ and H₂O on silicon substrates as a function of reaction temperature. Other deposition conditions were the same as those in Figures 35 (c), 21(c) and 20(c) for ZrO₂, Y₂O₃ and CeO_{2-x}, respectively.. ALD temperature windows for ZrO₂ CeO₂ and Y₂O₃ overlap between 230 and 280 °C

Since the atomic composition tunability of atomic layer deposited YSZ and YDC thin films was characterized using the ALD cycle ratio $[Y_2O_3/(Y_2O_3 + (ZrO_2,CeO_2))]$, this

parameter was again used for controlling the composition of both YSZ and YDC in the composite. A slightly higher composition for YSZ using ALD cycle ratio of 2/11 $Y_{cycles}/(Y_{cycles}+Zr_{cycles})$ (*i.e.*, 18.2 Y-atom %) was selected. The ALD cycle ratio selected for depositing the YDC films was 0.2 (1:5 $Y_{cycles}/(Y_{cycles}+Ce_{cycles})$). 70 nm samples (40 nm YSZ and 30 nm YDC) were deposited at 280 °C on p-type silicon. TEM images were collected on annealed samples and these TEM studies allowed evidencing the local crystalline structure of the samples and their results are in a general agreement with previous measurements.

Figure 50 shows the TEM studies performed on the YSZ layer of the YSZ/YDC composite. Top-left part of the image shows that a majority of the analyzed area display the cubic 111 structure but there are some areas that present polycrystallinity mainly the cubic 002 and 022 (top-right part of the image). Diffraction analyses performer using the fast Fourier transform (FFT) on YSZ layer of the composite reveal that the YSZ is polycrystalline with dominant 111 direction. The calculated lattice parameter is 5.131 ± 0.010 Å. The apparent expansion of the lattice parameter is due to a higher amount of the Y dopant introduced by increasing the ALD cycle ratio. Once again, the value of the calculated lattice constant is lower that the reported for cubic YSZ single crystals with this composition of yttria (*i.e.*, 8.33 % mol by using ALD cycle ratio 2:11 Y/(Y+Zr)) [148]. Therefore, as stated before, we can conclude that the deposited cubic YSZ film has a lattice parameter even lower than that estimated for cubic YSZ single crystals at the same composition.



Figure 50, TEM images and electron diffraction analysis using FFT intensity of the YSZ portion of annealed YSZ/YDC composite. Annealing was performed at 600 C for 5 minutes in a nitrogen environment. Other deposition conditions were the same as in figure 42 for YSZ and 23 (b) for YDC



Figure 51, TEM images and electron diffraction analysis using FFT intensity of the YDC portion of annealed YSZ/YDC composite. Annealing was performed at 600 C for 5 minutes in a nitrogen environment. Other deposition conditions were the same as in figure 42 for YSZ and 23 (b) for YDC

Figure 51 shows the analyses of the local crystalline structure of the YDC layer of the composite. The YDC layer of the annealed composited was polycrystalline and the phases formed were the cubic 111, 002, 022, and 113. The lattice constant parameter was calculated using the same procedure as before and an estimated value of 5.405 ± 0.030 Å was obtained. This value of the lattice parameter for YDC is very close to the reported value for this concentration of yttria (*i.e.*, 9.1 % mol Y₂O₃ by using an ALD cycle ratio of 0.2 or 1:5 Y/(Y+Ce)) [87, 151].



Figure 52, EDS analyses of as-deposited YSZ/YDC composite. YSZ and YDC sections of the composite were deposited with ALD cycle ratio 2:11 and 1:5 respectively. Other deposition conditions were the same as in figure 42 for YSZ and 23 (b) for YDC



Figure 53, EDS analyses of annealed YSZ/YDC composite. YSZ and YDC sections of the composite were deposited with ALD cycle ratio 2:11 and 1:5 respectively. Annealing was performed at 600 °C in an N_2 environment. Other deposition conditions were the same as in figure 42 for YSZ and 23 (b) for YDC

Energy dispersive X-ray spectroscopy was performed on as-deposited and annealed YSZ/YDC composites and the results are displayed in figures 52 and 53, respectively. It is possible to observe 2 distinctive zones, one cerium rich (*i.e.*, the YDC portion of the composite) and one zirconium rich (*i.e.*, the YSZ portion of the composite). Some cross contamination that most likely come from ion-milling of the samples can also be observed in each section.

In both cases, as-deposited and annealed, it is possible to perceive 2 phenomena. The first one is a slight increase of the yttrium signal close to the YSZ/Si interface and the second one is a reduced signal of oxygen in the YDC area. Complimentary EDS analysis using a line-scan on both as-deposited and annealed YSZ/YDC composites is presented in figures 54 and 55 respectively. These figures show that a more intense signal of Yttrium is obtained near the YSZ/Si interface which validates the results obtained previously when analyzing YSZ alone. Also, it is observed that the signal of oxygen, in the analyzed area, decreases while going away from the YSZ/YDC interface towards the YDC surface



Figure 54, EDS analysis using a line-scan of as-deposited YSZ/YDC composite. YSZ and YDC sections of the composite were deposited with ALD cycle ratio 2:11 and 1:5 respectively. Other deposition conditions are the same as in figure 42 for YSZ and 23 (b) for YDC



Figure 55, EDS analysis using a line-scan of annealed YSZ/YDC composite. YSZ and YDC sections of the composite were deposited with ALD cycle ratio 2:11 and 1:5 respectively. Other deposition conditions are the same as in figure 42 for YSZ and 23 (b) for YDC

This reduction on the signal of oxygen was studied qualitatively by using electron energy loss spectroscopy (EELS). Figure 56 shows the EELS spectra collected on the YDC portion of the ALD fabricated YSZ/YDC composite. It is possible to see two sharp peaks close to the ionization threshold called "white-line" that are characteristic to the M_4 (around 880 eV) M_5 (above 900 eV) edges of rare earths. The energy separation of these peaks reflects the spin-orbit splitting of the 3d initial states in the transition and their relative intensity is expected to change with the occupancy of the 4f final state orbital *i.e.*, is expected to change with changing the oxidation state of the rare earth, in this case cerium [101, 152]. Thus, by using spatial resolved EELS it is possible to examine directly the local variations, such as bulk vs surface regions, in order to determine the Ce^{+4}/Ce^{+3} ratios within the YDC portion of the YSZ/YDC composite.



Figure 56, EELS spectra collected on the YDC side of as-deposited YSZ/YDC sample. (a) near the YSZ/YDC interface, (b) middle of YDC portion, and (c) close to the surface. YSZ and YDC sections of the composite were deposited with the conditions shown in figure 42 for YSZ and 23 (b) for YDC

It is possible to see in figure 56 that the M_5/M_4 ratio, collected from the second derivative spectra, decreases gradually from the YSZ/YDC interface to the surface. This indicates an oxygen deficient area near de surface of the film caused by to the formation of point defects such as oxygen vacancies created by the redox activity of the Ce⁺³/Ce⁺⁴ pair near the surface of the YDC/YSZ composite [153]. It is believed that the reported enhanced ionic conductivity of YSZ/YDC composites, [18, 154, 155], is largely due to the formation of this oxygen vacancy concentration gradient from the bulk of the YDC portion to the surface. This gradient can progressively provide exchange of oxygen ions among the surface, the lattice and

most importantly improve the kinetics at the YSZ/YDC interface thus improving the uptake of oxygen ions from the air side, or cathode and the transport to the anode, or fuel side.

Electrochemical impedance spectroscopy (EIS), has become a powerful tool to study the conductivity of solid electrolytes. EIS allows characterizing possible limitations and may give guidance that allows engineering of fuel cells electrolytes with improved performance. Three fundamental sources of voltage loss have been identified as limitation for wide spreading of the fuel cell technology. These losses are related to charge transfer activation as well as losses related to ion and electron transport can be, and finally mass transfer losses. Physiochemical processes occurring within the fuel cell can be represented by a network of resistors, capacitors or constant phase elements, and by correctly fitting the impedance spectra meaningful information, quantitative and qualitative, can be acquired [135].

Complex impedance was collected at different temperatures on annealed YSZ samples with 8 mol Y_2O_3 (ALD cycle ratio 2/11 Y/(Y+Zr)) and fitted using equivalent circuits. Figure 57 displays the complex impedance (Nyquist plot) collected at different temperatures for annealed 40 nm-thick YSZ samples along with the fit of the data which was performed using equivalent circuit for each data set. It is possible to observe that there are 2 distinctive regions, one at high frequency values corresponding to the conductivity of the bulk and a larger one at lower frequency values which can be attributed to grain boundaries [136]. It is possible to conclude that the grain boundaries in this YSZ system have a considerable impact in the ionic conductivity at the analyzed temperature range. The total activation energy for conduction is calculated using the same procedure presented for YDC in chapter 5 and the results are displayed in figure 58. In this figure, 2 different slopes have been traced, one including the four data points corresponding to the whole analyzed temperatures range, and other using temperatures from 200 to 400 °C.



Figure 57, complex impedance plot (Nyquist plot) and fitted simulation of annealed 40 nm-thick YSZ films deposited with 8 % mol Y₂O₃ (ALD cycle ratio 2:11 Y/(Y+Zr)) on silicon substrates collected at (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 400 °C. The data was collected at ambient atmosphere using a "side by side" electrode geometry and it was modeled using equivalent circuits



Figure 58, total ionic conductivity of annealed YSZ film with 8 % mol Y_2O_3 as a function of temperature. Analyzed films were 40 nm thick

By fitting the data from 200 °C, it is possible to find activation energy of 0.95 eV which is in good agreement with the reported values for the activation energy of thin films and bulk YSZ with the same doping concentration level [155, 156]. Even though the calculated activation energy resemble reported values close to the reported in the literature, a comparison with the obtained values for the conductivity of YDC (Chapter 5) indicate that the conductivity of ALD-YSZ is 2 orders of magnitude lower.

Using thin films of YDC as interlayers between the electrolyte and the cathode has been accepted as an effective way of overcoming these limitations [18, 64, 65]. In this chapter we have use a combination of ALD processes for the fabrication of these hybrid YSZ/YDC

interlayers in the same ALD reactor under optimized conditioned that allow precise control of composition and thickness.

Figure 59 show the complex impedance collected on an annealed hybrid YDC/YSZ/Si composite with the electrodes connected "side by side" on the top of the composite (*i.e.*, YDC portion of the hybrid film)



Figure 59, complex impedance plot (Nyquist plot) and fitted simulation of annealed hybrid YDC/YSZ/Si composite collected at (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 400 °C. The data was collected at ambient atmosphere using a "side by side" electrode geometry and it was modeled using equivalent circuits. The YDC portion of the composite was 30 nm-thick and was deposited with a cycle ratio 1:5 (Y/(Y+Ce)). The YSZ portion was 40 nm thick and was deposited using an ALD cycle ratio of 2:11(Y/(Y+Ce)).

Although the selected electrode geometry used for the analyses is not optimal for analyzing the contribution of all the elements to the total conductivity (*i.e.* YDC bulk and grain boundaries, YDC/YSZ interface and YSZ bulk and grain boundaries), a clear trend is observed in figure 59. There is a semicircle at higher frequency values which can be attributed to YDC (YDC bulk and grain boundaries) followed by a larger semicircle attributed to the YSZ portion of the hybrid composite (YDC/YSZ interface and YSZ bulk and grain boundaries). While temperature increases, the semicircle region attributed to the YDC decreases more rapidly than the YSZ section indicating that using thin YDC layers may in fact help in the incorporation of oxygen ions into the YSZ portion of the film, thus improving the performance of these composites in the IT-SOFC region. In order to verify this, further impedance experiments with a different electrode configuration and under real SOFC condition need to be performed in order to investigate the improvement regarding oxygen incorporation of the composites.

6.4. Summary

In this chapter ZrO_2 , Yttria Stabilized Zirconia (YSZ) and YSZ/YDC, thin films composites were fabricated via atomic layer deposition (ALD) on p-type silicon (100) using novel precursor chemistry tris(dimethylamino)cyclopentadienyl-Zirconium, tris(isopropylcylopentadienyl)Yttrium, and tris(iso-propylcylopentadienyl)Cerium, (ZyALD, Y(iprcp)₃, and Ce(i-prcp)₃), with water vapor as the oxygen donor in a custom built hot wall ALD reactor. Individual binary deposition processes were characterized and a sufficient ALD temperature-window overlap was found suitable for exploring the ALD fabrication of YSZ and YSZ/YDC composites under self-limiting growth and using the same ALD reactor. The ALD cycle ratio $[Y_2O_3/(Y_2O_3 + (ZrO_2,CeO_2))]$ was used as control parameter for tuning the composition of the YSZ films as well as the composition of YSZ/YDC composites. The atomic composition of YSZ was found to change almost linearly with the ALD cycle ratio, indicating excellent tunability. The growth rate for YSZ was 1 Å/cycle whereas the growth rate for YDC was 1.3 Å/cycle. Compared to YSZ films deposited using other precursor chemistries, it was found that as-deposited YSZ films are polycrystalline and the crystal structure of was found to be dependent on the yttria (*i.e.*, Y_2O_3) content ranging from monoclinic (4% yttria) to cubic (20% yttria). Upon annealing, YSZ films with 8 % mol yttria became cubic with a lattice parameter lower than that estimated for cubic YSZ single crystals at the same composition. This indicates that not only the processing but also the selection of the precursor chemistry have an impact in the YSZ microstructure.

The activation energy for conduction of ultra-thin YSZ films (40 nm) calculated from 100 to 400 °C was found to similar to that calculated for bulk YSZ films at temperatures higher than 500 °C. This indicates that the ultra-thin YSZ films, at unexplored thickness levels, prepared and analyzed by the procedure presented in this chapter hold promise as IT-SOFC electrolyte. The ionic conductivity of ultra-thin YSZ films was found to be at least 2 orders of magnitude lower that the YDC (chapter 5) when the analyses were performed in the same temperature range. Advantages of using a YDC interlayer were explored and the results indicate that the YDC layer of the YSZ/YDC composite to have an oxygen vacancy gradient as determined by energy dispersive X-ray spectroscopy and electron energy loss spectroscopy. This gradient can progressively provide exchange of oxygen ions among the surface, the lattice and most importantly improve the kinetics at the YSZ/YDC interface. Impedance spectroscopy analyses performed on these composites show that the YDC portion of the film has a rapid decrease in the

resistance, compared to the YSZ portion, which may help in the uptake of oxygen ion during SOFC operation.

It is then concluded that ALD is an effective way of fabricating stable and continuous YSZ films as well as more complex YDC/YSZ structures with atomically defined interfacial regions and with precise atomic composition control and varying thicknesses, from unexplored ultra-thin nanometer levels to bulk-like levels. ALD allowed extending the applications of YSZ to even thinners unexplored layers of YSZ (40 nm) with activation energies for conduction similar to bulk films. It is important to remarks that this work is the first to explore 40 nm-thick YSZ and that the activation energy values (similar to the reported in the literature for bulk YSZ) were obtained at a low temperature range (100 to 400 °C). Also this thesis, to the best of my knowledge, is the first that show the combination of optimized ALD processes for the fabrication of YDC/YSZ composites within the same reactor as one deposition processes.

7. Conclusions

7.1. Use of a Cyclopentadienyl-Precursor for Atomic Layer Deposition of CeO2-x Films with High Concentration of Point Defects. Stability and Photo-catalytic Properties

In this chapter, the characterization of the ALD process variables for the growth of CeO_{2-x} thin films using cerium precursor $Ce(i-prcp)_3$ and water as the oxygen donor was presented and this is the first time that the ALD variables for the fabrication of CeO_{2-x} thin films using this precursor chemistry are fully characterized. The growth rate of CeO_{2-x} under optimized ALD conditions was found to be 1.4 Å/cycle, a value that is 3 times higher than those reported for similar processes using β -diketonate precursors and ozone and those reported using the same cerium precursor via PE-ALD. From these findings, it is possible to say that using this precursor combination in a conventional ALD process is a very interesting and viable option for scaling the production of CeO_{2-x} films for diverse applications as a significant improvement in the growth-rate and appreciable thickness control is achieved. This may allow reduction of the processing time therefore making the process more efficient.

TEM shows that the as-deposited films are mostly amorphous with negligible creation of interfacial SiO₂ layer. After annealing at 600 °C in nitrogen, the films are found to be polycrystalline with no preferred orientation and a 2 nm-thick interfacial SiO₂ layer is formed. It was found that the lattice parameter for cubic CeO_{2-x} films are larger than the theoretical value. This apparent expansion in the lattice parameters was attributed to point defects in the film (*i.e.*, oxygen vacancies, interstitial oxygen).

XPS shows that the surface deposited films are oxygen deficient, i.e., CeO_{2-x} , with Ce^{+3} values ranging between 10 and 30%. (*i.e.*, 0.05<x<0.13). XPS also help to validate the TEM

analysis. By analyzing the oxygen XPS core spectra (O-1s) it is suggests, that the shift between Ce^{+3} to Ce^{+4} oxidation states at the films surface, leads to incorporation of oxygen available from the hydrolysis reaction into interstitial places and stored as the films grows. Post-deposition analyses indicates that the mobility of these point defects is thermally activated. It was observed that thermal processing in an inert environment improves the film stoichiometry (O:Ce ratio) which might be due to migration of interstitial oxygen may be migrating to the interface to form a thin SiO_2 thin layer. Ar⁺ sputtering treatment of the samples indicates that annealed samples are likely more stable under reduction conditions than as-deposited samples and they also suggest that the presence of the point defects is not just superficial but these defects are progressively introduced as the film grows.

XANES analysis help to verify that there is a higher non-stoichiometry on as-deposited CeO_{2-x} films with 5 % of Ce^{+3} in the bulk. These higher values of non-stoichiometry for asdeposited films may generate expansion in the lattice due to the larger size of the Ce^{+3} ion and a reduction in the oxygen vacancies formation. XANES experiments also showed that undoped CeO_{2-x} films (as-deposited and annealed) are unstable under reducing conditions (*i.e.*, they reduce easily from Ce^{+4} to Ce^{+3}), which limits the application as IT-SOFC electrolyte.

EXAFS fitting showed that ALD-CeO_{2-x} thin films resemble the bulk structure with coordination number close to theoretical values. EXAFS simulation results also shows that the mean Ce-O bond distance is smaller than the theoretical values which may implies induced stressed by oxygen vacancies which pushes Cerium atoms closer to its oxygen nearest neighbor thus indication the presence of point defects in the film (*e.g.*, oxygen vacancies)

The characterization of as-deposited and annealed films using surface and bulk characterization techniques suggest that CeO_{2-x} thin films deposited with the procedure presented in this chapter have a density of point defects that may favor oxygen mobility and improve catalytic properties which might be of importance in several technological areas. For instance, it was shown that the thermally induced structural transformation on the CeO_{2-x} thin films have an impact on the physical properties relevant to photocatalytic processes. Prove of this are the results of the photocatalytic activity of as-deposited and annealed ALD-CeO₂. It was found that thin CeO_{2-x} films (14 nm-thick) are suitable for photodegradation under UV light irradiation (λ =254 nm) and the photocatalytic activity can be attributed to both, surface and bulk point defects. It is important to remark that this is the first time that ALD-CeO_{2-x} thin films deposited with the procedure presented in this chapter are studied in the photodegradation of organic contaminants.

It is then concluded that the results presented in this chapter are of great interest toward better understanding the formation and mobility of point defects in ALD fabricated CeO_{2-x} thin films which may be beneficial for the improvement of ceria-based electrolyte materials but also may generate an impact in other technological fields such as catalysis and photo-catalysis. ALD is an effective way of fabricating stable and continuous CeO_{2-x} films with varying thicknesses, from unexplored ultra-thin nanometer levels to bulk-like levels, and it is possible to introduce a large density of defects into the CeO_{2-x} lattice which are mobile and may favor oxygen mobility and/or improve catalytic properties.

Though, the analyzed CeO_{2-x} films have their limitation for SOFC, the development of this ALD process can be used for exploring new applications of CeO_2 -based materials that take advantage of the improved cost-benefit introduced by reducing the processing time, the

possibility of fabricating CeO_{2-x} films in a diverse thickness range and also the film properties related to the non-stoichiometry and point defects that can enhance ionic and catalytic transport.

7.2. Atomic Layer Deposition of Yttria Doped Ceria Using Cyclopentadienyl-ligand Precursors and Water Vapor. Composition Tunability, Post-deposition Annealing Behavior and Stability Analysis

The results summarized in this chapter shown that a combination of two ALD processes using novel precursor chemistry based on CP-type precursors can be used for the fabrication of YDC films with thickness and composition control down to the atomic level, which became a very attractive way for scaling down the dimensions of SOFCs stacks towards cost-effective setups. This is the first study that demonstrates the effectiveness of using Ce(i-prcp)3/Y(i-prcp)3 along with water vapor for developing the fabrication of YDC films with varying thicknesses, from unexplored ultra-thin nanometer levels to bulk-like levels via ALD. The growth-rate of CeO₂ and Y₂O₃ were ~1.4 Å/cycle and a sufficient ALD window overlap of individual CeO₂ and Y₂O₃ ALD processes was found for the deposition of YDC films under self-limiting growth conditions. The growth rate of YDC (20 Y-atom. %) under optimized ALD conditions was found to be 1.33 Å/cycle, a value 3 times higher than the reported for YDC using β-diketonates precursors and ozone.

The atomic percentage of yttrium in the YDC samples was found to increase linearly with increasing the ALD cycle ratio $[Y_2O_3/(Y_2O_3+CeO_2)]$ indicating excellent tunability of the film composition at the atomic level. XPS analysis suggests a thermally activated yttrium diffusion that can be observed by the decrease in the total amount of point defects (*i.e.*, non-stoichiometry)

in the cerium structure due to lattice migration and also the formation of interfacial yttrium silicide, as observed through interfacial analyses.

It was shown *via* XANES that, compared to undoped CeO_{2-x} films (chapter 4), the YDC films deposited with the procedure presented in this chapter appear to be stable under reducing conditions up to 700 °C. YDC has mainly Ce^{+4} and is stable; it also performed well under reducing conditions, *i.e.*, no reduction from Ce^{+4} to Ce^{+3} .

EXAFS fitting shows that YDC films display a bulk-like crystalline structure, *i.e.*, coordination number of 8. It was also show by using EXAFS that the mean interatomic distance Ce-O decreases monotonically with increasing the yttrium doping concentration in the film. This can be explained in terms of strain induced not only introduced by the aliovalent dopant (*i.e.* Y^{+3}) but also for the localization of oxygen vacancies next to the Ce⁺⁴ ion instead of the Y^{+3} which may improve ionic conductivity. Evidence of this is presented in the ionic conductivity analyses which show clear differences between YDC films deposited with a doping level of 10 % Y with those deposited with 20 % atom. Y.

Ionic conductivity analyses show that YDC films with 10 Y-atom. % have higher values of the activation energy than the reported for the YDC10 films deposited with other methods but close to the values reported for non-stoichiometric CeO_2 (*i.e.*, CeO_{2-x}). This may be evidence that YDC10 films deposited with the procedure described in this chapter have a different mechanism for the formation of oxygen vacancies used in the transport of oxygen ion during SOFC operation.

YDC20 thin films showed improved activation energy for conduction, at the analysed temperatures, when compared to YDC films with the same doping level deposited by other thin film fabrication methods and analysed at higher temperatures. This might be induced by

localization of oxygen vacancies next to the Ce^{+4} ion instead of the Y^+ and exploration of these features may help increase the potential use of ALD YDC films as IT-SOFCs electrolytes.

It is then concluded that the results presented in this chapter are of great interest toward improving the design of IT-SOFC stacks with YDC films as the electrolyte. It was shown that the thermal and composition induced structural transformation on the YDC thin films have an impact on the physical properties relevant to stoichiometry stability and ionic conductivity processes. It is also concluded that on the fabrication of YDC not only the films processing but also the precursor selections affect the microstructure of YDC and with this the ionic conductivity. ALD is an effective way of fabricating stable and continuous YDC films with varying thicknesses, from unexplored ultra-thin nanometer levels to bulk-like levels. It is important to remarks that this work is the first to explore ultra-thin YDC20, (*i.e.* deposited with 20 % atom. Y), which showed improved values of the ionic conductivity activation energy, and good stability under reducing condition therefore these YDC films hold promise as intermediate temperature solid oxide fuel cell (IT-SOFC) electrolyte.

7.3. Atomic Layer Deposition of YSZ and Fabrication of YSZ/YDC Composites

In this chapter the combination of ALD processes using novel precursor chemistry based on CP-type precursor for the fabrication of ZrO_2 and YSZ has been shown. Also the combination of 2 ternary ALD processes, (*i.e.*, YSZ and YDC), for the fabrication of YSZ/YDC composites using the same ALD reactor under stable self-limiting growth conditions was presented. It was shown that by using the ALD cycle ratio as control parameter, the composition of the YSZ films can be controlled down to the atomic level, which became a very attractive way for scaling down the dimensions of SOFCs stacks towards cost-effective set-ups. This is the first study that

demonstrates the effectiveness of using ZyALD/Y(i-prcp)3 and Ce(i-prcp)₃/Y(i-prcp)₃ with water vapor for developing the fabrication of ultra-thin YSZ films and YSZ/YDC composites via ALD with precise doping and film thickness control. A sufficient ALD window overlap of individual growth rate was found for developing $ZrO2/Y_2O_3$ and CeO_2/Y_2O_3 using the same ALD reactor. The growth rate of YSZ under optimized ALD conditions was found to be 1 Å/cycle, while for YDC was found to be 1.3 Å/cycle a value 3 times higher than the reported for YDC using β-diketonates precursors and ozone.

It was determined using XPS that the atomic percentage of yttrium $Y_xZr_{1-x}O_y$ (YSZ) increases almost linearly with increasing ALD cycle ratio $[Y_2O_3/(Y_2O_3+(ZrO_2,CeO_2)]$ indicating excellent tunability of the film composition at the atomic level. By using TEM it was possible to determine that, compared to YSZ films deposited with other precursors chemistries, all the as-deposited YSZ films presented in this chapter were polycrystalline and that the crystalline structure depends on the amount of yttrium in the sample. TEM analyses performed on as-deposited samples of YSZ fabricated using ALD cycle ratio 1:6 $[Y_{cycles}/(Y_{cyces}+Zr_{cyles})]$ indicate that these samples have a mixture of tetragonal and cubic phases while TEM analyses on vacuum-annealed samples (with the same ALD cycle ratio) indicate the stabilization of the cubic phase.

The lattice constant for the annealed YSZ 8 % mol Y_2O_3 sample (deposited with ALD cycle ratio 1:6 $Y_{cycles}/(Y_{cyces}+Zr_{cyles})$ and that displayed the cubic structure) was 5.124 ± 0.024 Å. It can conclude then that the cubic ALD-YSZ film has a lattice parameter lower than that estimated for cubic YSZ single crystals at the same composition. It is conclude then that, this structural changes may have a positive impact on the physical properties of ultra-thin YSZ (40 nm) that are relevant to the activation energy for conductivity.

EDS analysis indicate that there is migration of Yttrium towards the YSZ/Si interface which may decrease the total amount of yttrium ion in the YSZ thin film which can affect the long term performance of the cell at this thickness levels. However, further experiments with substrates that display less chemical affinity with yttrium need to be performed.

ALD allowed extending the applications of YSZ to even thinners unexplored layers of YSZ (40 nm) with activation energies for conduction similar to bulk films. It is important to remarks that this work is the first to explore reducing the YSZ electrolyte to 40 nm-thick and that the activation energy values (similar to the reported in the literature for bulk YSZ) were obtained at a low temperature range (100 to 400 °C).

ALD is an effective way of fabricating stable and continuous YSZ films as well as more complex YDC/YSZ structures with atomically defined interfacial regions and with precise atomic composition control and varying thicknesses, from unexplored ultra-thin nanometer levels to bulk-like levels. Also this thesis, to the best of my knowledge, is the first that show the combination of optimized ALD processes for the fabrication of YDC/YSZ composites within the same reactor as one deposition processes.

Characterization of these composites using EDS along with EELS allow to verify that there is a decrease in the oxygen signal on the YDC layer of YSZ/YDC composites. These results show that there is an oxygen vacancies gradient created by non-stoichiometry. It is believe that this gradient can progressively provide exchange of oxygen ions among the surface, the lattice and most importantly improve the kinetics at the YSZ/YDC interface thus improving the uptake of oxygen and overall performance of the cell.

Impedance spectroscopy results show that ultra-thin YSZ films fabricated with the procedure shown in this chapter, show that the activation energy for conduction calculated from

100 to 400 °C was found similar to that calculated for bulk YSZ films at temperatures higher than 500 °C, proving that the use of ALD for fabrication of YSZ is an effective tool in scaling down SOFCs stacks towards more cost effective set-ups allowing the applications of YSZ to even thinners unexplored layers of YSZ (40 nm) with activation energies for conduction similar to bulk films.

Though the selected electrode configuration for measuring the performance of YDC/YSZ composites make it difficult to separate different contribution in the impedance spectra. there is a clear trend in the impedance spectroscopy results collected on YDC/YSZ composites from 100 to 400 °C. It is observed that the contribution related to the YDC decreases faster than the contributrion related to YSZ. This can be related to enhanced properties of the YDC such as best oxygen ion incorporation and the oxygen non-stoichiometry gradient found trough EELS.

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9. Appendix A



9.1. XPS and XRD analyses of CeO₂ nanopowder as standard

Figure 60, Ce-3d XPS core spectra of a CeO2 standard. The standard isCeO2 nanopowder, <25 nm particle size bought from Sigma-Aldrich.

The peak position of the several u-v duplets as well as the values for the full width of half maximum (FWHM) obtained for the Ce-3d XPS core spectra collected for the standard match the results obtained for the CeO_{2-x} films as wells the reported values in the literature (see table 4). The calculation of the Ce⁺³ amounts was performed using the same procedure presented in chapter 4. Table 9, lists the obtained values for the CeO_{2-x} films obtained via ALD

Table 9, Experimentally determined binding energies and film stoichiometry (via XPS) of a CeO_2 standard and asdeposited and annealed CeO_{2-x} films grown via ALD

Ce-3d Binding energy (eV) and stoichiometry analysis obtained experimentally via XPS for					
CeO2 standard and CeO2-x films obtained via ALD					
Peak I.D	as-deposited	Annealed	Standard		
v ₀	880.50	880.52	880.53		
v	882.20	882.40	882.14		
v'	883.87	884.60	883.96		
V''	888.36	888.83	888.53		
V'''	898.16	898.31	898.2		
u ₀	898.64	898.77	898.7		
u	900.72	900.92	901		
u'	902.10	902.99	903.3		
u''	907.11	907.37	907.44		
u'''	916.60	916.70	916.6		
stoichiometry by XPS	$Ce^{+3} = 25 \pm 2\%$ (CeO _{1.875})	$Ce^{+3} = 20 \pm 2\%$ (CeO _{1.90})	$Ce^{+3} = 20 \pm 3\%$ (CeO _{1.90})		

Figure 61 shows the O-1s XPS core spectra collected for the CeO_2 standard, 4 main features can be identified. Features located at 526.7 and 530.58 eV are related to carbon contamination (See figure 62). Features located at 529.5 and 531.1 eV are related to Metal-Oxigen interaction at a lattice place, and to the presence of point defects, respectively.



Figure 61, O-1s XPS core spectra of a CeO_2 standard. The standard is CeO_2 nanopowder, <25 nm particle size bought from Sigma-Aldrich



Figure 62, C-1s XPS core spectra of a CeO2 standard. The standard isCeO2 nanopowder, <25 nm particle size bought from Sigma-Aldrich

The calculated ratio of areas for the peaks located at 529.5 and 531.1 eV is 0.41, which is in good agreement of the calculated ratio of areas presented in chapter 4.

$$\frac{Area \ Peak \ at \ 529.5 \ eV}{Area \ Peak \ at \ 531.1 \ eV} = \frac{1658.4}{3993.7} = 0.41$$

As the CeO₂ standard was also found to be nonstoichiometric (*i.e.*, CeO_{2-x} with x=0.1), it is possible to say that the presence of the lateral peak at 531.1 eV can be attributed to a combination of contamination and surface defects that are related to the nonstoichiometry.



Figure 63, XRD patterns of CeO2 nanopowder (>25 nm particles bought from Sigma-Aldrich). Cubic CeO₂ pdf card (JCPDS-340394) is also plotted for reference

Figure 63 shows the XRD pattern collected for the CeO_2 nanopowder. It was found that the crystal structure is consistent with the bulk values reported in the literature for cubic CeO_2 , further analysis performed in Argonne National lab shows that the average size of the particles is 33 nm and the lattice constant is 5.411 Å. The author wishes to express his most sincere gratitude to Dr. Tomohiro Shibata and Dr. Jim Kaduk from Argonne National laboratory for their help in collecting and analyzing the XRD data presented above.



9.2. Angle resolved XPS analyses of ALD fabricated CeO_{2-x}

Figure 64, Ce-3d XPS core spectra of an asdeposited CeO2-x sample collected at 90° (a) and at 60° (b). These samples were 15 nm-thick and were prepared via ALD. Deposition conditions were the same as in Figure 4(d). Samples were stored for 12 months previous angle resolved analysis



Figure 65, Ce-3d XPS core spectra of an annealed CeO_{2-x} sample collected at 90° (a) and at 60° (b). These samples were 15 nm-thick and were prepared via ALD. Deposition conditions were the same as in Figure 4(d). Annealing was carried out in N2 for 5 min at 600 °C and 1 atm. Samples were stored for 12 months previous angle resolved analysis

Figures 64 and 65 show the Ce-3d XPS core spectra of as-deposited and annealed CeO_{2-x} samples respectively. These XPS core spectra were collected at a normal takeoff angle of 90 ° (Figure 64(a) and 65(a)) and at a takeoff angle of 60 ° (figure 64(b) and 65(b)). Peak labeling was performed using the similar procedure as presented in chapter 4 and the calculated binding energy of the peaks closely match those presented in tables 4 and 9. Using the same procedure presented in chapter 4 for calculating the film stoichiometry it was possible to observe that by changing the collection angle the surface amount of Ce⁺³ increases. These experiments not only validate the assumption of increased surface sensitivity by decreasing the collection angle but

also suggest that the deposited CeO_{2-x} have a concentration gradient were x in CeO_{2-x} increases close to the film surface. Table 10 summarizes the increase in Ce^{+3} observed by changing the collection angle.

Table 10, variation of the amount of Ce^{+3} obtained for as-deposited and annealed CeO_{2-x} films at different XPS collection angles

Analized film	XPS spectra collection angle	% of Ce^{+3}	
as-deposited	90	25	
as-deposited	60	32	
Annealed	90	20	
Annealed	60	28	

The ability of enhancing surface sensitivity by changing the collection angle was used for investigating the nature of the lateral peak observed in the O-1s XPS core spectra and determine if this peak arises from the existence of surface species. Figure 66(a) shows the O-1s XPS core spectra collected at a takeoff angle of 90 ° while Figure 66(b) shows the same spectra collected at a takeoff angle of 60 ° for an annealed CeO_{2-x} sample. The samples were stored for a year previous these experiments. It is possible to see in the O-1s XPS core spectra collected at 90 and 60 ° (Figure 66 (a) and (b)) 3 features in which the one, located at 529.6 eV, can be attributed to the presence of oxygen in the lattice structure of the oxygen deficient CeO_{2-x} films [109]. The shoulder feature located at 532.3 eV in Figure 66(a) is likely due to –OH species from absorbed moisture on the surface from the large time that the sample was exposed to ambient atmosphere and the one located at 531.5 eV has been attributed to the presence of point defects in the film. It is possible to see that even with changing the XPS spectra collection angle there is no variation on the intensity of the peaks located at 532.3 eV(attributed to –OH) and the one located 531.5

eV previously attributed to the presence of point defects in the film. The calculated ratio of areas for the peaks located at 529.6 and 531.3 eV is 0.48 and 0.49, for spectra collected at 90 and 60 $^{\circ}$ takeoff angle, respectively. These values are in good agreement of the calculated ratio of areas presented in chapter 4 and in appendix A section 9.1.



Figure 66, O-1s XPS core spectra of an annealed CeO_{2-x} sample collected at 90° (a) and at 60° (b). These samples were 15 nmthick and were prepared via ALD. Deposition conditions were the same as in Figure 4(d). Annealing was carried out in N2 for 5 min at 600. Samples were stored for 12 months previous angle resolved analysis

Argon sputtering was used in order to remove absorbed surface contaminants that may be interfering with the measurements. Figures 67 and 68 show the O-1s XPS core spectra collected

after 5 and 10 minutes of Argon sputtering, respectively. Figures 67(a) and 68(a) display the spectra collected at a takeoff angle of 90 ° while figures 67(b) and 68(b) show the spectra collected at 60° .



Figure 67, O-1s XPS core spectra of an annealed CeO_{2-x} sample collected at 90° (a) and at 60° (b) after 5 min Ar+ sputtering. These samples were 15 nm-thick and were prepared via ALD. Deposition conditions were the same as in Figure 4(d). Annealing was carried out in N2 for 5 min at 600.



Figure 68, O-1s XPS core spectra of an annealed CeO2-x sample collected at 90° (a) and at 60° (b) after10 min Ar+ sputtering. These samples were 15 nm-thick and were prepared via ALD. Deposition conditions were the same as in Figure 4(d). Annealing was carried out in N2 for 5 min at 600.

Although there is an increase in the calculated area ratio of the analyzed peaks after 5 and 10 min argon sputtering (figures 67(a) and 68(a)), this increase is attributed to selective removal of surface oxygen and the appearance of reduced Cerium oxide phases, *i.e.*, Ce_2O_3 .

Figures 67(b) and 68(b) validate the results obtained when analyzing Figure 66. Even increasing the surface sensitivity by using an XPS collection angle of 60 °, there is little to no variation in the calculated area ratio of the analyzed peaks after 5 and 10 min argon sputtering. A

new feature was obtained in the O-1s XPS core spectra after sputtering. This feature was attributed to reduced phases of CeO₂, *i.e.*, Ce₂O₃. It was observed by using a collection angle of 60 ° that the intensity if this peak increases which suggests that these are superficial phases. As seen in figure 69, as the argon sputtering time increases, the duplets that are related to Ce⁺³ phases, *i.e.*, u_0 - v_0 and u'-v', progressively increase in intensity.



Figure 69, Ce-3d XPS core spectra of an annealed CeO_{2-x} sample collected at 90° as inserted (a), after 5 min Ar+ sputtering (b) and after 10 min Ar+ sputtering. These samples were 15 nm-thick and were prepared via ALD. Deposition conditions were the same as in Figure 4(d). Samples were stored for 12 months previous XPS analyses

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10. VITA

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EDUCATION

Ph.D in Chemical Engineering, University of Illinois, Chicago - Illinois, USA 2014
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PUBLICATIONS AND CONFERENCES

BOOK CHAPTERS

Sánchez, O.J., Rossero, J.I., Cardona, C.A., Higuita, J.C. Developments in bioethanol and biodiesel production, 2008, chapter 7: Effluent Treatment During Fuel Ethanol Production. ISBN 978-958-44-2787-8.

PAPERS

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HONORS / AWARDS

Tuition fee waiver 3rd highest GPA (4.3/5) among all MSc students in the Chemical engineering department, Universidad Nacional de Colombia, 2006.

BSc and MSc sponsored Fellowship by the Colombian Institute for the development of science and technology (COLCIENCIAS)

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