Nanostructured Thin Film Materials for Solid Oxide Fuel Cells by Atomic Layer Deposition

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THESIS
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1 INTRODUCTION

1.1 Introduction to Solid Oxide Fuel Cells

Solid oxide fuel cells (SOFCs) are electrochemical conversion devices that produce electricity directly from oxidizing a fuel without involving the process of combustion\(^1\).

SOFCs offer very high conversion efficiencies because it is not limited by Carnot thermodynamic inherent in combustion-based energy producing processes. 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\(^2\).

The operation of the first ceramic fuel cell at 1000 °C was achieved in 1937 by Swiss scientist E. Baur and H. Preis, using such materials as zirconium, yttrium, cerium, lanthanum and tungsten oxide\(^3\) for the solid electrolyte. In the 1940s, to increase the conductivity and mechanical strength of the electrolyte, a Russian scientist O. Davtyan added monazite sand to a mix of sodium carbonate, tungsten trioxide, and soda glass\(^4\). Research in solid oxide technology began to accelerate at late 1950s. The promise of using a high temperature cell, able to tolerate carbon monoxide and using a stable solid electrolyte continued to draw attention\(^4\).
1.2 **Electrodes and Electrolyte for Solid Oxide Fuels**

Solid Oxide fuel cells (SOFCs) provide direct conversion of chemical energy into electrical energy by means of electrochemical reactions\(^5\). By utilizing direct electrochemical conversion of energy, cells help satisfy the global need for efficient, environmentally safer energy sources. For these reasons, fuel cells attract much interest as a solution for future energy needs.

Electrochemical conversion of chemical fuel to electrical power with any fuel cell technology basically requires an anode and a cathode separated by an ion conducting electrolyte\(^6\). Advantages of the class of fuel cells known as solid oxide fuel cells have very high conversion efficiency, high capability to different fuels, and relatively low cost. The most serious disadvantage of SOFC is the high operating temperature required for efficient electrochemical reactions, which results in longer mechanical and chemical failures of cell components.

![Scheme of a solid oxide fuel cell](image)

**Figure 1** Scheme of a solid oxide fuel cell\(^7\)
The anode reaction is

\[ \text{H}_2 + \text{O}^- \rightarrow \text{H}_2\text{O} + 2\text{e}^- \]

The cathode reaction is

\[ \text{O}_2 + 2\text{e}^- \rightarrow 2\text{O}^- \]

The anode layer of SOFCs is a very porous ceramic layer to allow the fuel to reach the triple phase boundaries and flow to the electrolyte layer. The anode layer also needs to be electronically conductive, with a high ionic conductivity. The most common material used as an SOFC anode is cermet, such as Ni-YSZ, which is made up of nickel with a ceramic material such as yttria-stabilized zirconia. The YSZ can also be used for the electrolyte. The function of the anode material is to allow the oxygen ions that have diffused through the electrolyte from the cathode to oxidize the hydrogen fuel by an electron transfer reaction. The oxidation reaction produces electricity as well as water as product.

The electrolyte layer for SOFCs is a dense layer made up of ceramics that conduct oxygen ions. The electrolyte material must keep a low electronic conductivity to prevent current leakage. Also a high operation temperature of SOFCs is required to allow the oxygen ion transport through the electrolyte. The electrolyte material has a crucial influence on the cell performance.

The cathode is a porous layer where the oxygen reduction electron transfer reaction takes place. The cathode material needs to be both electronically and ionically conductive. Also it needs to have a similar thermal expansion coefficient
with the electrolyte material. In addition, for both the cathode and anode side of the fuel cell, in order to increase the electron-transfer zone of the cathodic and anodic reactions, the triple phase boundary (TPB), that is where the electrolyte, oxidizer and the electrodes meet, should be enlarged.

### 1.3 Challenges to Anode Materials

The anode is the electrode where hydrogen is oxidized and water is formed. The anode should have high electronic conductivity, large triple phase boundary (TPB), high ionic conductivity, and should catalyze the dissociation of hydrogen. The anode material must also have a good thermal expansion coefficient (TEC) match with the adjacent components in the fuel cell assembly to prevent gas leakage.

A composite of Ni-YSZ (yttria-stabilized zirconia) is the most common choice for the anode material for SOFC\(^9\). However, this material is faced with challenges. First, Ni in the anode suffers serious sintering issue over time. Problems associated with nickel coarsening are factors for performance loss in long-term operation\(^10\). Second, the metallic content should be as low as possible. However, no continuous metallic phase will exist when the metallic phase content is too low. Third, commercial Ni-YSZ anodes have various long-term stability problems.

As the ideal anode structure, the ceramic phase should both contact with and coat the metallic phase. By coating ceramic film on well distributed nickel porous backbone, anodes utilize significantly lower Ni loading while maintaining good electrical conductivity and continuous triple phase boundaries.
Solid Oxide Fuel Cells (SOFCs) are promising next generation electrochemical energy conversion devices that convert chemical energy in fuel directly into electricity. The anodes used in SOFCs are mostly based on porous composite metals such as Ni, Pt, and Ru and oxygen-ion conducting ceramics such as yttria-stabilized zirconia (YSZ). As a commonly used anode for SOFCs, Ni-YSZ composites have been prepared by several wet chemical and gas phase techniques, such as slurry coating, pulsed laser deposition (PLD) and physical vapor deposition (PVD), resulting in micron particle sizes.

However, the electrochemical performance of Ni-YSZ anodes can be extensively improved when the size of the constituent particles is reduced. By reducing the particle size and improving the electrode’s nanostructure, a better cell performance can be expected. Unfortunately, under SOFC operating environments, nano-sized Ni particles suffer from sintering, causing the Ni-YSZ anodes to undergo severe structure changes, and ultimately degrading cell performance. This degradation effect has consequently constrained the use of nano-scale Ni-YSZ anodes.
understanding and development is needed to prepare Ni-YSZ anodes that have stable nanostructure to reduce sintering and prevent degradation of nanoscale SOFC’s.

To achieve a stable performed nanoscale anode, a careful engineering optimization of the triple phase boundary is required.\textsuperscript{21} A high triple phase boundary (TPB) where the electrode, electrolyte and gas phases meet is required for high electrochemical performance.\textsuperscript{22} Among various deposition techniques, atomic layer deposition (ALD) stands out as a new fabrication technique for preparing the YSZ phase that can potentially optimize the triple phase boundary. Studies have been successfully done depositing YSZ electrolyte layers by ALD,\textsuperscript{23} and it has been shown that ALD is capable of meeting the needs for atomic layer control and conformal deposition to achieve a high triple phase boundary of YSZ electrolyte/electrode layers using sequential, self-limiting surface reactions.\textsuperscript{24} No other thin film technique can approach the conformity achieved by atomic layer deposition on high aspect structures.\textsuperscript{25} Therefore ALD has the capacity of forming and uniform layers of nanoscale YSZ electrolyte phases onto the surface of porous Ni electrode scaffolds. The advantages of the ALD nanoscale approach are three-fold; its flexibility in combining a highly structurally stable and ionic conductive YSZ electrolyte phase with a catalytically active and electrically conductive Ni phase; its controllability in forming nanostructures and defined porosity without the help of a template or pore former; and providing a means of extending of triple phase boundary to a three-dimensional, nanoscale level.

In this work, a nanoscale Ni-YSZ anode was prepared by combining ALD and
glancing angle deposition (GLAD) techniques. GLAD is a technique based on performing physical vapor deposition at oblique angles. The GLAD technique was used to deposit template-free, self-organized, nanoporous, nanorod Ni films as the electrode. The nanorod structure contributes to a lateral surface area, so the surface area is increased to greater than 3 times that of a planar electrode. ALD was the used to uniformly deposit a nanoscale YSZ layer to stabilize the nano-sized Ni, and to provide an ionic conductive phase; which resulted in an increased stability under the elevated temperature compared to uncoated nano-sized Ni. The nano-composite anode was also characterized with respect to morphology, wettability, surface chemistry and conductivity.

The anode is the electrode where hydrogen is oxidized and water is formed. The anode should maintain high electronic conductivity under the SOFC operation conditions. To measure the thin film anode conductivity, anode materials were deposited on low-conductive quartz substrates to avoid any substrate effect on the subsequent conductivity measurements. In this work, we developed a characterization technique to study the thin film electrical properties. A new four point probe method was applied to study the electrical conductivity of the Ni-YSZ thin film electrode materials prepared by atomic layer deposition and glancing angle deposition. In this method, it becomes possible to study the in-situ electrical conductivity of thin film materials on different substrate under different environment. The system has a wide temperature testing range, from room temperature to 800°C. Also it allows multiple
gas phase environments. Consequently, this development is a good supplemental method for studying electrical properties of thin film materials.

In the study of electrochemical properties of atomic layer deposition prepared thin film electrolyte materials, we also have developed a method of characterizing the ionic conductivity. Silicon wafer was used as a substrate and silver paste was applied as current collectors. In this method, the impedance spectra was successfully taken and the ionic conductivity was evaluated to up to 500 °C. The ionic conductivity of ceria prepared by atomic layer deposition was also measured electrochemical impedance spectroscopy with the new characterization method. Compared with literature data, the ceria deposited by atomic layer deposition achieved a higher ionic conductivity under 300 °C. However, the activation energy is lower than reported data. With the effort of exploring a new method characterizing thin film materials’ electrochemical performance, it opens a new way to researching the electrochemical thin film material.
2 Applied Thin Film Deposition Techniques and Post Processing Techniques

2.1 Custom Designed and Constructed ALD System

ALD is an advanced type of chemical vapor deposition (CVD). During ALD process, precursor and the second reactant are pulsed into the reactor sequentially with inert gas purging between each reactant. The atomic layer deposition of composite metal oxide thin films is performed in the customer-made hot-wall reactor. The scheme of the customer-made ALD system is shown in Fig(3)

![Scheme of custom-made atomic layer deposition system](image)

**Figure 3** Scheme of custome-made atomic layer deposition system

The ALD system used is using a horizontal hot-wall tubular ALD reactor consisting of a high purity quartz tube (38 mm in diameter and 480 mm in length). The quartz tube can withstand temperature over 1000 ºC and typical depositions can
be carried out in the temperature range of 25-450°C. A quartz boat is used to hold substrate wafers. The manifold is made up of two separate lines for moisture and precursor leading into the reactor. The precursor vapor and moisture are pulsed into the reactor chamber alternatively through N₂ carrier gas. N₂ gas is purged in between to make sure of the formation of a monolayer of each ALD cycle reaction. The reactant moisture was provided by DI water kept in ice bath, carried by N₂ gas.

A typical atomic layer deposition cycle consists of 4 steps (1) pulse the first precursor (commonly metal organic precursor); (2) purge the first precursor with inert gas; (3) pulse the second reactant (comely oxidizer or reductant); (4) purge the second reactant. The scheme is illustrated in Fig(4).

![Figure 4](image.png) Schematic illustration of the four steps of atomic layer deposition

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2.2 Electron Beam Evaporation System

Electron beam evaporation is one type of physical vapor deposition. An electron beam is given off by a tungsten filament under high vacuum. The atoms from the target source become gaseous phase under the electron beam. The physical vapor precipitates onto the substrate and become solid thin film in the vacuum chamber.

![Diagram of electron beam evaporation](image.png)

**Figure 5** Scheme of electron beam evaporation

In an electron beam physical vapor deposition system, the chamber must be evacuated to a $10^{-5}$ Torr, so that the electrons can move from the electron gun evaporation target. Multiple types of evaporation targets and electron guns can be used. The generated electron beam is accelerated to a high kinetic energy and directed to towards the evaporation target. The kinetic energy of the electrons is
converted into the energy through interactions with the evaporation target, which cause the evaporation material, melt or sublimate. The vapor can then be used for coating surfaces. The scheme of the electron beam evaporation system is illustrated in Fig(5).

2.3 Glancing Angle Deposition Technique

Glancing angle deposition (GLAD) is a physical vapor deposition (PVD) technique based on deposition at oblique angles. We applied GLAD technique to deposit template free, self-organized, nanoporous nanorod-structured Ni films as electrode.

Physical vapor deposition under conditions of obliquely incident flux and limited atom diffusion results in a film with a columnar microstructure. These columns will be oriented toward the vapor source and substrate rotation can be used to sculpt the columns into various morphologies. This is the basis for glancing angle deposition (GLAD), a technique for fabricating porous thin films with engineered structures. As deposition continues, the columnar structures are influenced by atomic-scale ballistic shadowing and surface diffusion.

Due to the porous nature of the films and the increased surface area, a variety of applications are possible. Because the GLAD process provides precise nanoscale control over the film structure, GLAD nickel film can be engineered as SOFC electrode metal phase.
Figure 6 Illustration of the growth of nano-columns on a substrate, during oblique-angle deposition. (a) Initially, material islands form in random locations on the substrate. (b) Due to the non-normal deposition angle, shadowing occurs behind the islands, causing columnar growth.31

2.4 Three-Zone Post-Deposition Annealing Furnace

In this work, Lindberg Blue three-zone furnace was used to do post-deposition annealing of thin films on different substrates. The furnace can be operated in the temperature range of 200-1100°C in different gas such as N₂, low concentration H₂, O₂ and air under ambient pressure.

The scheme of the three zone furnace is illustrated in Fig (7). Each zone has a length of 8 inch. The temperature of each zone is controlled by independent
temperature controller and maintained at the same temperature to make sure the whole furnace is heated uniformly. Prior to thermal treatment of samples, the furnace is purged with the gas for 30 min. We use a quartz boat to hold the samples.

Figure 7 Scheme of three zone furnace
3 Characterization Techniques

3.1 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material\textsuperscript{32}.

XPS is also known as ESCA (Electron Spectroscopy for Chemical Analysis). Theoretically, XPS is able to detect all elements exist. However, with laboratory-scale X-ray sources, XPS only detects elements with an atomic number of more than 3.\textsuperscript{33} The high-resolution XPS enables the studies on oxidation, corrosion, adsorption, catalysis, adhesion behavior, and thin film growth\textsuperscript{34}.

![Figure 8](image_url) Basic components of a monochromatic XPS system.\textsuperscript{32}
As shown in Figure 8, in XPS systems, X-ray photons are generated by bombarding metal target with electrons. XPS spectra are obtained by irradiating the sample with a beam of X-rays and measure the kinetic energy and number of electrons that escape from the top 0 ~ 10 nm of the material.

XPS instruments use either a focused 20- to 500-micrometer-diameter beam of monochromatic aluminum Kα X-rays, or a broad 10- to 30-mm-diameter beam of non-monochromatic (polychromatic) aluminum Kα X-rays or magnesium Kα X-rays.

The energy of an X-ray is known, the emitted electrons' kinetic energies are measured; the electron binding energy of each of the emitted electrons can be calculated.

\[ E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \varphi) \]

where \( E_{\text{binding}} \) is the binding energy of the electron, \( E_{\text{photon}} \) is the X-ray photons’ energy, \( E_{\text{kinetic}} \) is the kinetic energy of the electron as measured and \( \varphi \) is the work function of the spectrometer.

3.2 Spectroscopic Ellipsometry (ES)

Spectroscopic Ellipsometry is a very useful and non-destructive technique to characterize thin film thickness (typically, in 1-1000 nm) and thin film optical properties. Ellipsometry uses the change in polarization of light upon reflection from a thin film material to determine the real part (refractive index), \( n(\lambda) \) and the imaginary part (extinction coefficient), \( k(\lambda) \) of the complex refractive index, of a
material, \( N(\lambda) = (n(\lambda)+ik(\lambda)) \) where \( \lambda \) is the wavelength of the electromagnetic radiation. And the schematic image is shown below.\(^{36}\)

![Schematic setup of an ellipsometry experiment](image)

**Figure 9** Schematic setup of an ellipsometry experiment\(^{36}\)

The light source emits the electromagnetic radiation and polarizes it linearly by a polarizer. The angle of incidence from the light source equals the angle of reflection from the sample.

Ellipsometry measures the complex reflectance ratio, \( \rho \) which is the ratio of \( \gamma_p \) over \( \gamma_s \), follows this equation\(^{37}\):

\[
\rho = \frac{\gamma_p}{\gamma_s} = \tan(\Psi) e^{i\Delta}
\]

Thus, \( \tan(\Psi) \) is the amplitude ratio upon reflection, and \( \Delta \) is the phase shift.

The thickness of the thin films is determined by the interference of light reflected from the sample surface and light travelling through the film thickness.\(^{38}\)
Ellipsometry has the following advantages in study film thickness and optical properties\textsuperscript{38}: it measures at least two parameters at each wavelength of the spectrum; it measures an intensity ratio instead of pure intensities; no reference measurement is necessary and both real and imaginary part of the dielectric function can be extracted.

### 3.3 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that images a sample surface by scanning it with a focused beam of electrons. The electrons produce various signals by interacting with atoms in the sample to show information about the sample's surface topography and composition.\textsuperscript{39}

![Figure 10 SU8030 SEM working station](image_url)
A SU8030 SEM in Nuance Center in Northwestern University was used for thin film imaging. The image is as below. The system is using cold field emission technology. The double condenser optics ensures not only the highest resolution; It has a large specimen chamber and equipped with the triple detector super ExB system and Oxford X-max 80 SDD EDS detector. The spatial resolution can reach 1.0 nm at 15kV and 1.3 nm at 1kV. The vibration isolation table secures the image quality.

![Schematic of an SEM](image)

**Figure 11** Schematic of an SEM

The scanning process and image formation is illustrated in Fig(11). An electron beam is emitted from an electron gun fitted with a tungsten filament cathode. The electron beam is focused by one or two condenser lenses. The electrons lose energy when the primary electron beam interacts with the sample. Then the reflection of high-energy electrons by elastic scattering is got by energy exchanging between the
electron beam and the sample. The emission of secondary electrons and electromagnetic radiation can be detected by specialized detectors, which are used to create images. 35

3.4 LCR Meter

An LCR meter is electronic test equipment that measures inductance (L), capacitance (C) and resistance (R) of a material. The LCR meter uses an AC voltage at a specific frequency or frequencies to test the material. The LCR meter measures the voltage across and the current through the device under test. Also the phase angle between the voltage and the current is measured at the same time. So the resistance, capacitance and inductance can be displayed.

In this work we use a Quadtech 7400 precision LCR meter Model B to do electronic characterizations on thin film samples. A picture of the LCR meter is illustrated in Fig(12). 42

Figure 12 7400 Precision LCR meter
3.5 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS), a technique that is similar to dielectric spectroscopy,\(^\text{43}\) EIS is an experimental method to characterize a electrochemical system. It measures the impedance of electrochemical reactions over a range of frequencies. After the frequency response shows up, the electrochemical performance of the system is revealed.\(^\text{44}\)

The EIS technique has been growing faster over the past few years. EIS can reveal information about the reaction mechanisms that govern the electrochemical system. Different phenomena such as ionic migration (conductivity), electron-transfer reactions (kinetics), ionic mass transfer and absorption/desorption will dominate at certain frequencies.

![Electrochemistry Impedance Spectroscopy](image)

**Figure 13** Electrochemistry Impedance Spectroscopy

In this study, we apply the technique of electrochemical impedance spectroscopy to study the electrochemical performance of thin film electrode and electrolyte materials for solid oxide fuel cells.
4 RESULTS AND DISCUSSION

4.1 Nanostructured Ni-YSZ anode for Solid Oxide Fuel Cells by Atomic Layer Deposition

4.1.1 Introduction

Solid Oxide Fuel Cells (SOFCs) are promising next generation electrochemical energy conversion devices that convert chemical energy in fuel directly into electricity. The anodes used in SOFCs are mostly based on porous composite metals such as Ni\textsuperscript{12}, Pt\textsuperscript{13} and Ru\textsuperscript{14} and oxygen-ion conducting ceramics such as yttria-stabilized zirconia (YSZ).\textsuperscript{15} As a commonly used anode for SOFCs, micron Ni-YSZ composite have been prepare by several wet chemical and gas phase techniques, such as slurry coating\textsuperscript{16}, pulsed laser deposition (PLD)\textsuperscript{17} and physical vapor deposition (PVD)\textsuperscript{18}.

A high triple phase boundary (TPB) where the electrode, electrolyte and gas phases meet, is required for high electrochemical performance.\textsuperscript{22} The electrochemical performance of Ni-YSZ anodes can be extensively improved when the size of constituent particles is reduced.\textsuperscript{19} Therefore, by reducing the particle size and improving the electrode’s nanostructure, a better cell performance can be expected. However, under SOFC operating environment, nano-sized Ni particles suffer from sintering\textsuperscript{20}. Ni-YSZ anodes can undergo severe structure changes, so as to yield a cell performance degradation, which constrains the development of nano-scale Ni-YSZ anodes. Therefore, nanostructure stabilized Ni-YSZ is necessary for
nanoscale SOFCs.

To achieve a stable performed nanoscale anode, a carefully engineering and optimization of the TPBs is required. Among various deposition techniques, atomic layer deposition (ALD) stands out as a new fabrication technique for preparing YSZ phase. Research has been successfully done on depositing YSZ electrolyte layer by ALD. ALD is able to meet the needs of conformal deposition using sequential, self-limiting surface reactions. No other thin film technique can approach the conformity achieved by atomic layer deposition on high aspect structures. Therefore ALD is able to achieve the formation and uniform deposition of nanoscale YSZ electrolyte phase on the surface of porous Ni electrode scaffolds. The advantages of ALD nanoscale approach are the flexibility in combination of highly structurally stable and ionic conductive YSZ electrolyte phase with catalytic active and electrical conductive Ni phase, controllability in nanostructure and porosity without the help of template or pore former and the extension of TPBs to three dimensional nanoscale level.

In this work, nanoscale Ni-YSZ anode was prepared by combining ALD and glancing angle deposition (GLAD) techniques. GLAD is a physical vapor deposition (PVD) technique based on deposition at oblique angles. We applied GLAD technique to deposit template free, self-organized, nanoporous nanorod Ni films as electrode. The nanorod structure contributes to a lateral surface area, so the surface area is increased to more than 3 times as large as plane area and orientation of the parallel nanorods reduces the ohmic loss and gas transfer resistance. ALD was applied to
uniformly deposit a nanoscale YSZ layer to stabilize the nano-sized Ni and provide an ionic conductive phase, which resulted in an increased stability under elevated temperatures compared to uncoated nano-sized Ni. The nano-composite anode was also characterized with respect to morphology, wettability, surface chemistry and conductivity.

4.1.2 Experiment

Prior to atomic layer deposition of YSZ layer, the porous Ni electrodes were first prepared by GLAD of Ni (99.9% by wt) on 1.7×1.7cm$^2$ sections of Si (100) substrates using an electron beam evaporator (Varian model no. NRC3117). The electron beam was under a power supply of 1kW, with an operation pressure of $5 \times 10^{-7}$ torr, resulting in a 0.1 nm/sec Ni deposition rate, as determined by quartz crystal monitor. By placing the substrate onto customer-made holders, the Ni vapor flux incidence angle was set to be 87°, and distance between substrate and vapor source was 35cm. A targeted 100 nm thick Ni coating was deposited on the silicon substrates in this manner.

Atomic layer deposition of YSZ was performed in a custom-made hot wall, tubular reactor$^{45}$, using tris (isopropyl-cyclopentadienyl) yttrium [Y (iPrCp)$_3$] as the yttrium precursor (>99%, American Air Liquide), tris (dimethylamino) cyclopentadienyl zirconium [ZrCp(NMe$_2$)$_3$] as the zirconium precursor (99.9%, American Air Liquide), and water as oxygen donor. The co-deposition was carried out at 260°C while the Yttrium precursor reservoir was maintained at 107°C and
Zirconium precursor reservoir was maintained at 55°C. In each ALD process, water vapor was provided to the reactor by passing N\textsubscript{2} through a water bubbler maintained at 0°C. In the case of YSZ deposition, the \([\text{Y } (\text{iPrCp})_3]/\text{H}_2\text{O}\) to \([\text{ZrCp } (\text{NMe}_2)_3]/\text{H}_2\text{O}\) ratios used were 1:5 to deposit 9mol% YSZ film. These cycle ratios were repeated until the desired film thickness was obtained. In this work, Ni-YSZ with YSZ thicknesses of 1.9 nm, 3.8nm and 7.6nm were studied.

**Figure 14** Fabrication process of nanostructured Ni-YSZ anode (1) glancing angle deposition of 100nm Ni on Si (100) substrates with an incidence angle of 87° (2) Atomic layer deposition of YSZ over nickel nanorod with ALD cycle ratio \([\text{Y } (\text{iPrCp})_3]/\text{H}_2\text{O}\)
\[ \text{ZrCp(NMe}_2\text{)}_3]/\text{H}_2\text{O} \text{ of 1:5 at } 260{\degree}\text{C} \text{ (3) post-deposition annealing of Ni-YSZ thin film following a process of introducing oxygen at 500{\degree}\text{C for 60 min and 4\% hydrogen at 300 }{\degree}\text{C for 30 min.} \]

Ni-YSZ thin film samples with YSZ of varied thicknesses were post-deposition annealed in a quartz horizontal furnace (Lindberg Blue three-zone furnace) that followed a process of introducing oxygen at 500{\degree}\text{C for 60 min and 4\% hydrogen at 300 }{\degree}\text{C for 30 min. The parallel sequence of the process during fabrication of the nanostructured Ni-YSZ anode is illustrated in Figure 14.} 

A field emission scanning electron microscope (FE-SEM SU8030, Hitachi Ltd.) was employed for the surface structural and morphological characterization. The film thickness and refractive index was measured with a spectral ellipsometer (model M-44, J.A. Woollam Co. Inc.), equipped with a Xenon arc lamp (UXL-75XE USHIO America Inc.). To evaluate the wettability of Ni-YSZ surfaces, water droplet contact angles were measured with a goniometer (model 100-00, Rame-Hart instrument Co.). The surface chemistry of Ni-YSZ was determined with a high-resolution X-ray photoelectron spectroscopy (XPS) (Kratos AXIS-165, Kratos Analytical Ltd.). The resistance of the Ni-YSZ films were measured by a 7400 Precision LCR Meter (Model B, QuadTech, Inc.), prior to measurement, silver paint (C8829, Heraeus) was applied to paste 4 paralleled silver wires on the top of the film.

4.1.3 Results and discussion

In order to identify the nanostructure of glancing angle deposited Ni film, SEM images were taken. The SEM image of the GLAD Ni is shown in Figure 14(a).
seen in Figure 15(a), the Ni nanorods form a film with a thickness of 100 nm and porosity of 53%; the nanorod density is $25 \times 10^{13}$ /m$^2$ with a tilting angle of 35° (determined from Image J software). In order to characterize reactor process of ALD YSZ film growth, the YSZ film growth and thickness were examined as a function of cycle number on Si substrate prior to studies on Ni. As seen in Figure 16, the ALD YSZ film has a growth rate of 0.08 nm/cycle with a [Y(iPrCp)$_3$/H$_2$O to [ZrCp(NMe$_2$)$_3$/H$_2$O ratio of 1:5. The SEM image of the 3.8 nm ALD YSZ coated Ni electrode is shown in Figure 15(b). Compared to micron scale Ni-YSZ anodes, the constituent particles are reduced to nanoscale and the triple phase boundaries are extended to 3 dimensions. The nanorod structure contributes to a lateral surface area, so the surface area is increased to more than 3 times as large as plane area and orientation of the paralleled nanorods reduces the ohmic loss and gas transfer resistance.

**Figure 15** SEM image of (a) top-view of GLAD Ni nanorod film, (b) top-view of Ni-YSZ with an ALD YSZ coating thickness of 3.8nm over Ni nanorod
Figure 16 Thickness of ALD YSZ as a function of number of ALD cycles at 260 °C on Si substrate with ALD cycle ratio [Y (iPrCp)₃]/H₂O to [ZrCp (NMe₂)₃]/H₂O of 1:5. The linear relationship between film thicknesses and reaction cycles resulted in a 0.08nm/cycle.

Refractive index measurements were carried out on the GLAD Ni bare film, as-deposited Ni-YSZ films, and post-deposition annealed Ni-YSZ films with incidence light from the vertical direction of Ni nanorod tilting direction. The experimentally-determined relationship between the Ni-YSZ refractive index (measured by ellipsometry at λ=488 nm) and YSZ coating thickness is shown in Figure 17. As seen in Figure 17, the refractive index value of as-deposited bare GLAD Ni nanorod film is 1.307, which is much lower than then bulk Ni material (n=1.666) and the corresponding porosity of the GLAD Ni film is calculated to be 53.9%, which is consistent with the data from SEM. The refractive index value of YSZ coated film is found to be 1.379 for the 1.9 nm YSZ coated sample and the refractive index increases gradually with increasing YSZ coating thickness, indicating
a continuous decrease in film porosity. Because with a conformal coated ALD YSZ layer, the nanopores between Ni nanorods become narrower, and thus the refractive index is simultaneously increasing. Upon post-deposition annealing of the samples, nano pores are formed on the YSZ layer, hence the morphology is modified by thermal effects, which lead to a higher porosity. As seen in Figure 17, the refractive index is found to be lower than that of as-deposited films with the same coating thickness. Consequently, ALD coating approach is flexible in combining ionic conductive YSZ electrolyte phase with electrical conductive Ni phase; hence control the porosity of the nano-composite electrode freely. So far, the most common method of modifying anode porosity is through template\textsuperscript{46} or pore formers\textsuperscript{47}, the ALD-GLAD novel technique can effectively modify the Ni-YSZ porosity solely through deposition and post-deposition annealing process.

![Figure 17](image)

**Figure 17** Refractive index of bare GLAD Ni, as-deposited YSZ on Ni and post-deposition annealed YSZ on Ni with different YSZ coating thickness 1.9 nm, 3.8 nm and 7.6 nm measured at $\lambda=488$ nm
The wettability of GLAD Ni bare film, as-deposited Ni-YSZ films and post-deposition annealed Ni-YSZ films was also investigated by using a goniometer at room temperature. As seen in Figure 18(a), the bare GLAD Ni nanorod film is hydrophobic with a water contact angle of 130°. The water contact angle of as-deposited 1.9 nm YSZ on Ni film is found to be 106° (Figure 18 (b)). Moreover, Figure 18 (b), (c) and (d) indicate that the water contact angle is decreasing continuously with increasing the YSZ coating thickness. For the post-deposition annealed films, as seen in Figure 18 (e), (f) and (g), the water contact angles are slightly increased from the as-deposited state.

Under the experiment conditions, water droplet spreading on the film surface indicates a consumption of energy and free liquid surface spreading is a release of energy. The net energy decrease determines the speed of forming spherical drop. For a rougher surface, there will be more actual surface involved in the process, the water droplet will be more spherical and the water contact angle will be higher. The bare GLAD metal nanorod film has a highly porous nanostructure and is made up of pyramidal tips, which makes a very rough surface; consequently it shows significant hydrophobicity. By applying a conformal ALD YSZ film over the Ni nanorods, the surface is smoother. The thicker the YSZ film, the smoother the surface becomes. Therefore, the water contact angle decreases with thicker ALD YSZ films. After post-annealing deposition treatment, it may be that difference in crystal structure or change in lattice energy of the surface changes the surface wettability. The increase in water contact angle reveals that the amorphous as deposited YSZ films tend to
crystallize upon post-deposition annealing process and results in a nano morphology change. Providing ion conduction mainly occurs along the electrolyte surface or at a near-surface depth of the electrolyte surface, the decrease in surface roughness was found to lower the electrode reaction resistance.\textsuperscript{51} Smoothly coated YSZ layer has exhibited significant effect on lowering electrode ohmic resistance.\textsuperscript{52} It is shown that the surface roughness of Ni-YSZ electrode decreases with thicker ALD YSZ coating layer, which indicates a decrease in SOFC electrode reaction resistance and a better cell electrochemical performance.

\textbf{Figure 18} Water droplet profiles of (a) bare GLAD Ni, (b) 1.9 nm, (c) 3.8 nm and (d) 7.6 nm as-deposited YSZ on Ni, (e) 1.9 nm, (f) 3.8 nm and (g) 7.6 nm annealed YSZ on Ni with 5μL water droplet.

\textbf{Table 1} summary of water contact angle

<table>
<thead>
<tr>
<th></th>
<th>GLAD Ni</th>
<th>1.9 nm YSZ coated</th>
<th>3.8 nm YSZ coated</th>
<th>7.6 nm YSZ coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>130°</td>
<td>106°</td>
<td>94°</td>
<td>83°</td>
</tr>
<tr>
<td>Annealed</td>
<td>109°</td>
<td>98°</td>
<td>91°</td>
<td></td>
</tr>
</tbody>
</table>
Figure 19 (Color online) XPS survey spectra of (a) bare GLAD Ni, (b) 1.9 nm, (c) 3.8 nm and (d) 7.6 nm as-deposited YSZ on Ni, (e) 1.9 nm, (f) 3.8 nm and (g) 7.6 nm annealed YSZ on Ni with ALD cycle ratio [Y(iPrCp)$_3$]/H$_2$O to [ZrCp(NMe$_2$)$_3$]/H$_2$O of 1:5 and post-deposition annealing at 500°C in oxygen for 60min and at 300°C in hydrogen for 30min
The XPS wide energy survey spectra of bare GLAD Ni film, as-deposited Ni-YSZ films and post-deposition annealed Ni-YSZ films are shown in Figure 18. The spectra labeled (a) represents survey scans of bare GLAD Ni film, the spectra labeled (b) through (d) represent survey scans on as-deposited films and the spectra labeled (e) through (g) represent annealed films. Prior to ALD, XPS analysis of the GLAD Ni surface indicates the presence of only Ni, O, and C elements (Figure 19 (a)). Carbon is the result of surface contamination and the oxygen comes from the native oxide and adsorbed moisture on the Ni surface. After ALD of 1.9 nm YSZ over Ni surface (Figure 19 (b)), several XPS peaks appeared on the substrate which correspond to Zr 3d (182-185eV), Zr 3p (333-346eV), Zr 3s (433eV), Zr 4p (29 eV) and Y 3d (157-160eV), Y 3p (300eV). The intensity of these XPS peaks increases with increasing thickness of YSZ films, while at the same time, the Ni 2p peak intensities decrease due to the growth of YSZ on top of the Ni surface (Figure 18 (b)-(d)). After annealing the films, the intensity of Ni 2p peaks increases compared to the as-deposited films (Figure 19(e)-(g)).

A summary of the elements detected on the surfaces and their relative quantities for each of the samples is presented in Table 2. The calculations are based on the core level spectra of the most intense peak for each element. The first three columns give the relative at% of each element on the sample surface without C and O, column 4 provides the ratio of Ni to the total amount of Y and Zr and column 5 represents the mol% of Y₂O₃ to the total mole amount of ZrO₂ and Y₂O₃. It is shown that, the surface concentration of nickel is getting lower with thicker YSZ layer, and in all
cases, the relative amount of Ni at the surface after annealing is enhanced in comparison with the as-deposited samples. This is because the interface oxide growth is enhanced by annealing in oxygen environment.\textsuperscript{54} As a consequence of oxygen consumption through hydrogen treatment, the thickness of ALD film decreases. It is also noted that, in all cases, the mole percentage of Y\textsubscript{2}O\textsubscript{3} in the total mole amount of ZrO\textsubscript{2} and Y\textsubscript{2}O\textsubscript{3} is in the range of 8.5~9.1\%, indicating the atomic composition of YSZ film is precisely controlled by ALD process and not affected by the post-annealing process.

\textbf{Table 2} Summary of elemental concentrations of Ni-YSZ surface, proved using XPS

<table>
<thead>
<tr>
<th>YSZ thickness (nm)</th>
<th>At% of elements</th>
<th>At% of</th>
<th>Mol% of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zr</td>
<td>Y</td>
<td>Ni</td>
</tr>
<tr>
<td>1.9nm (as-deposited)</td>
<td>55</td>
<td>10</td>
<td>35</td>
</tr>
<tr>
<td>3.8nm (as-deposited)</td>
<td>74</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td>7.6nm (as-deposited)</td>
<td>82</td>
<td>16</td>
<td>2</td>
</tr>
<tr>
<td>1.9nm (annealed)</td>
<td>45</td>
<td>9</td>
<td>46</td>
</tr>
<tr>
<td>3.8nm (annealed)</td>
<td>62</td>
<td>12</td>
<td>26</td>
</tr>
<tr>
<td>7.6nm (annealed)</td>
<td>72</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

The Zr 3d core level XPS spectra are shown in Figure 20. The Ni-YSZ films with different ALD YSZ thickness generally have similar peak shapes and locations of XPS spectrum features. The spectra in Figure 20(a)-(f) only consist of two peaks at
182.3 and 184.7 eV for Zr 3d\(^{5/2}\) and 3d\(^{3/2}\) respectively. A doublet peak with a spin-orbital splitting of 2.4 eV can be observed after deconvolution, which is the signature peak of ZrO\(_2\), indicating the oxidization state of Zr\(^{4+}\) in all YSZ films without any other Zr compound.\(^{55}\) Figure 21 shows the XPS core level spectra of Y 3d obtained from Ni-YSZ films. As seen in the Y 3d core level spectrum Figure 21 (a)-(f), the spectra consist of two peaks at 157.3 and 159.4 eV for Y 3d\(^{5/2}\) and 3d\(^{3/2}\) respectively, which has a doublet peak with a spin-orbital splitting of 2.1 eV, indicating the presence of Y\(_2\)O\(_3\).\(^{55}\) At the same time, Y 3d\(^{5/2}\) and Y 3d\(^{3/2}\) peak deconvoluted at 160.2 eV and 158.1 eV apparently demonstrate the formation of Y hydroxide on the film surface. That confirms earlier reports that water molecules interact strongly with the surface of Y\(_2\)O\(_3\) and forms hydroxide progressively.\(^{56}\) After high temperature treatment, the intensity of Y (OH)\(_3\) peaks is found to decrease. This is because the O-H bonding from the reactivity of Y\(_2\)O\(_3\) and water is partially removed by the high temperature treatment with hydrogen.\(^{57}\) In order to further understand the thickness and thermal effect on the composition and chemical state of elements, O 1s XP spectra of the as-deposited and post-deposition annealed films were analyzed in Figure 22. For the as-deposited GLAD Ni film, only three peaks were observed, peaks at 529.8 eV and 531.5 eV are assigned to NiO and Ni\(_2\)O\(_3\), while a small shoulder peak at 532.9 eV appears after spectral peak deconvolution is likely due to O–H from absorbed moisture on the surface. Peaks 532.0 eV and 530.0 eV appears after deposition of YSZ on Ni, which indicate the formation of M–O–M (M represents Y and Zr) (532.0 eV) and M-OH (530.0 eV) bonding, with the YSZ
thickness increases the intensity of O 1s peak at 532.0eV increases continuously, while the intensity of peaks at 529.8eV and 531.5eV decrease. The O 1s peak at 530.0 eV is presumably from the Y-OH bonding and after hydrogen treatment the peaks decrease rapidly, which are in agreement with the Y 3d spectrum (Figure 21).

**Figure 20** Zr 3d core level XP spectra of (a) 1.9 nm, (b) 3.8 nm and (c) 7.6 nm as-deposited YSZ on Ni, (d) 1.9 nm, (e) 3.8 nm and (f) 7.6 nm annealed YSZ on Ni with ALD cycle ratio [Y (iPrCp)$_3$/H$_2$O to [ZrCp(NMe$_2$)$_3$/H$_2$O of 1:5 and post-deposition annealing at 500°C in oxygen for 60min and at 300°C in hydrogen for 30min.
Figure 21 Y 3d core level XP spectra of (a) 1.9 nm, (b) 3.8 nm and (c) 7.6 nm as-deposited YSZ on Ni, (d) 1.9 nm,(e) 3.8 nm and (f) 7.6 nm annealed YSZ on Ni with ALD cycle ratio [Y (iPrCp)₃]/H₂O to [ZrCp(NMe₂)₃]/H₂O of 1:5 and post-deposition annealing at 500°C in oxygen for 60 min and at 300°C in hydrogen for 30 min
Figure 22 O 1s core level XP spectra of (a)bard GLAD Ni, (b) 1.9 nm, (c) 3.8 nm and (d) 7.6 nm as-deposited YSZ on Ni, (e) 1.9 nm, (f) 3.8 nm and (g) 7.6 nm annealed YSZ on Ni with ALD cycle ratio \([\text{Y (iPrCp)\textsubscript{3}}]/\text{H}_2\text{O} \to [\text{ZrCp(NMe\textsubscript{2})\textsubscript{3}}]/\text{H}_2\text{O}\) of 1:5 and post-deposition annealing at 500°C in oxygen for 60min and at 300°C in hydrogen for 30min.

The electrical resistivity of the bare GLAD Ni and Ni-YSZ films is investigated by using LCR meter with 4 wire set up measurement at room temperature (Figure 23). The resistivity was firstly measured on samples at as-deposited state, and then the Ni-YSZ samples were subject to post-deposition annealing process as stated in the experimental section. To study the stability of the Ni-YSZ material under SOFC anode operation condition, the samples were sequentially annealed in H\textsubscript{2} at 500 °C. The resistivity after being operated for 1h and 5h were measured. Since the resistivity
of silicon is orders of magnitude higher than Ni at room temperature, contributions of the underlying silicon layer to resistivity are negligible. The as-deposited GLAD Ni film is conductive with a resistivity of $5.14 \times 10^{-4}$ cm·S$^{-1}$, due to its pure interconnected metallic Ni phase. For the as-deposited 1.9 nm Ni-YSZ, the resistivity increases to $8.01 \times 10^{-4}$ cm·S$^{-1}$, and with increasing the coating thickness, the resistivity increases continuously. This is explained by the introduction of YSZ to Ni nanorod film, leading to decrease in the concentration of the electrical conductive metallic Ni phase and increase in electrically insulating electrolyte phase. After post-deposition annealing, the resistivity of Ni-YSZ films decreases slightly, which are sufficiently conductive as SOFC anodes$^2$. Film thickness shrinking and slight nanostructure change under thermal effect are possible reasons for the slight resistivity increase after annealing process. After being operated in H$_2$ at 500 °C for 1 h, bare GLAD Ni film shows a significant resistivity change (from $5.14 \times 10^{-4}$ cm·S$^{-1}$ to $2.13 \times 10^{-4}$ cm·S$^{-1}$), which is more than 50%. It indicates a severe nanostructure change, the interconnected Ni nanorods are heavily sintered and Ni film with much larger nickel particles is forming. This result confirms that Ni nanorod arrays suffers severe sintering effect under 500°C.$^{58}$ So it yields a diminishing electrode nanorod structure and disappearing TPBs. At the same time, the resistivity of YSZ coated electrode maintains almost the same after 1h treatment. When the operating time extending to 5h, the resistivity of bare GLAD Ni film further decreases to $1.01 \times 10^{-4}$ cm·S$^{-1}$ but remains for the 1.9 nm, 3.8nm and 7.6nm YSZ coated films. The resistivity change for bare GLAD Ni, 1.9, 3.8 and 7.6nm YSZ coated films after 5h operation are 80%,
2%, 0.9%, 0.9%. The result reveals ALD YSZ coating layer shows distinguished sintering-resistant effect on nanoscale nanostructured electrode with an as thin as 1.9nm coating layer and excellent effect in maintaining the anode performance under SOFC operating conditions.

**Figure 23** Resistivity of bare GLAD Ni and Ni-YSZ with YSZ coating thickness of 1.9, 3.8 and 7.6nm under different conditions (a)as-deposited (b)post-deposition annealed (c) in 4% H₂ at 500°C for 1h (d) in 4% H₂ at 500°C for 5h
The sintering-resistant effect of ALD YSZ layer was further studied by SEM images in Figure 24. Figure 24 (a) (b) shows the SEM image of as-deposited GLAD Ni and 3.8 nm YSZ coated Ni. Figure 24 (c) shows the bare GLAD Ni after treatment in 4 % H$_2$ at 500°C for 1h. It is shown that the nanorod structure of the bare Ni is changed severely, the interconnected Ni nanorods are heavily sintered, and the diameter of nickel rod changes to 200nm from 40 nm. A Ni film with much larger particle size is formed, which results in the 50% resistivity decrease. So it yields a diminishing electrode porosity and disappearing TPBs. This result confirms that Ni nanorod arrays suffer severe sintering effect under 500°C, which constrains the development of nano-scale anodes. At the same time, the nanorod structure of 3.8 nm YSZ coated Ni electrode maintains (figure 24 (d)) after treating in 4 % H$_2$ at 500°C for 1 h. And the diameter of nickel nanorod doesn’t show any significant change or TPB decrease. When the operating time extending to 5h, the nanorod structure of bare GLAD Ni film is mostly destroyed by thermal effect and the Ni film is sintered to a film of rod structure with diameter higher than 300 nm, which indicates the disappearance of TPBs (figure 24(e)). The nanostructure and porosity of 3.8 nm YSZ coated electrode maintains almost unchanged after 5h (figure 24(f)). The SEM further confirms that ALD YSZ coating layer shows very good sintering-resistant effect on maintaining the nanostructure of the electrodes under SOFC operating conditions.
Figure 24 SEM image of (a) as-deposited GLAD Ni nanorod film, (b) as-deposited Ni-YSZ with an ALD YSZ coating thickness of 3.8nm over Ni nanorod, (c) GLAD Ni nanorod film after treatment in 4% H$_2$ at 500°C for 1h, (d) Ni-YSZ with an ALD YSZ coating thickness of 3.8nm over Ni nanorod after treatment in 4% H$_2$ at 500°C for 1h, (e) GLAD Ni nanorod film after treatment in 4% H$_2$ at 500°C for 5h, (f) Ni-YSZ with an ALD YSZ coating thickness of 3.8nm over Ni nanorod after treatment in 4% H$_2$ at 500°C for 5h.
4.1.4 Summary

Nanoscale nanostructured Ni-YSZ anode was successfully fabricated by combining ALD and GLAD techniques. The GLAD Ni nanorod film has a porosity of 53%; with an ALD growth rate of 0.08 nm/cycle, 1.9, 3.8 and 7.6 nm 9% YSZ coated Ni-YSZ anode was prepared. The surface area is increased to more than 3 times as large as plane area. ALD coating approach is flexible in combining ionic conductive YSZ electrolyte phase with electrical conductive Ni phase and control the porosity of the nano-composite electrode just through deposition and post-deposition annealing process. It is shown that the surface roughness of Ni-YSZ electrode decreases with thicker ALD YSZ coating layer, which indicates a decrease in SOFC electrode reaction resistance. The surface concentration of nickel is getting lower with thicker YSZ layer and the relative amount of Ni at the surface after annealing is enhanced, while the atomic composition of YSZ film is precisely controlled by ALD process and not affected by the post-annealing process. The Ni-YSZ anodes show resistivity in the 10-4 cm-S-1 magnitude. The ALD YSZ coating layer shows distinguished sintering-resistant effect on nanoscale nanostructured electrode with an as thin as 1.9nm coating layer and excellent effect in maintaining the anode performance under SOFC operating conditions. Such nanoscale nanostructured Ni-YSZ anode offers a new avenue in exploring nanoscale SOFCs in the future.
4.2 Electrical and Electrochemical Characterization Methods for Thin Film Materials for Solid Oxide Fuel Cells

4.2.1 Electrical characterization

4.2.1.1 Electrical characterization setup

The anode is the electrode where hydrogen is oxidized and water is formed. The anode should maintain high electronic conductivity under the SOFC operation conditions. To measure the thin film anode conductivity, we deposited anode materials on low conductivity quartz substrates to avoid any substrate effect on the conductivity test. We also designed and constructed a thin-film high-temperature conductivity testing system to conduct in-situ conductivity measurements on the anode material. The setup of the system is shown in figure 25. The system has a wide temperature testing range from room temperature to 800°C. Also it allows multiple gas phase environments.

The LCR-furnace thin film electrical conductivity measurement system is shown in Fig (25). The three-zone furnace was used to provide different gas environments under elevated temperatures. A three-way connection was used to connect the gas output from the furnace to the fume hood and also allows an alumina tube, which sheaths the silver wires going out to the LCR meter to make a gas-tight connection in to the furnace. The silver wires make the connections to the sample inside the furnace.
Figure 25 setup of the in-situ thin film electrical conductivity test system with three-zone furnace providing SOFC operating condition and LCR meter for data collecting.

Silver paste was applied as the current collector. The electric signals were transferred from the film to the LCR meter through the silver wires. High temperature tape was used during the silver paste drying process to stabilize the wires on the sample surface, and silicon wafer was used as the holder in this step and to provide a more rigid support.

4.1.1.1 Result and Discussion

To test the electrical conductivity of Ni-YSZ anode materials, the substrate under the Ni-YSZ films must be a good electrical insulator in the range of room temperature to 800°C so that it will not affect the conductivity of thin film materials. Also the
substrate needs to be a well-polished surface with a minimized surface roughness, to avoid thin film surface defects introduced by rough substrates. Under these requirements, we conducted research on four types of substrates; silicon (100) wafer, thermal oxidized SiO$_2$ on Silicon wafer, glass and fused silica quartz.

![30 nm nickel on silicon](image1)

**Figure 26** resistance of nickel film on silicon and glass substrate glass with 4 point probe system (1) on doped silicon from 300°C to 800°C (2) on glass from room temperature to 350°C

We first compared the Nickel film electrical conductivity in a hydrogen environment on silicon and glass substrate Fig (26). 30 nm Nickel films were deposited on silicon and glass substrate under the same condition. Then the conductivity of each film was measured with the four-wire probe process shown above. It can be seen from the graphs above, that the resistance on the silicon substrate decreased continuously with increasing the temperature, which contradicted a metal conductor conductivity profile. However, the trend is very similar to what would be expected with the silicon material without the thin-film in these experiments, the resistance of silicon contributed a larger portion of the overall conductivity, and
hence the resistivity of the nickel film cannot be observed when measuring on the silicon substrate. Consequently it was concluded that silicon is not a good substrate when measuring thin film conductivity under elevated temperatures. The same experiment was done on a nickel film deposited on glass substrate. The conductivity of the film increases continuously with increasing temperature, which is consistent with the resistivity vs temperature profile of a metal. This occurs because glass can

![200 nm SiO2 on Silicon vs Quartz](image)

**Figure 27** resistance of thermal oxidized silicon dioxide on silicon and quartz with 4 point probe system (1) 200 nm silicon dioxide on silicon from 500°C to 800°C (2) quartz from 500°C to 800°C

maintain a high resistivity under elevated temperatures, and hence the overall resistance is entirely from the upper layer nickel film. It is concluded that glass is a good substrate candidate for measuring thin film conductivity under elevated temperatures.

According to bulk-nickel resistivity data, when temperature is increasing, the resistivity should also be increasing at the same time. This trend corresponds to the
conductivity data on the glass substrate, but a reverse trend on silicon wafer. That is because, as a crystalized semiconductor material, the resistivity of silicon decreases significantly with increasing temperature. The thickness of silicon is 0.5cm and the thickness of the nickel film is less than 100nm. So the silicon dominates the resistivity under high temperature. Although, glass seems to be a good candidate as the substrate material, we did observe in further experiments that, it starts chemically decompose at 300°C, which is much less than SOFC operation temperature.

We further studied thermal oxidized SiO$_2$ on Si wafer substrates and fused silica quartz as the substrate for the thin film conductivity measurements. We prepared silicon dioxide layer by thermal oxidize silicon (100) wafer in oxygen under 1000°C for 4 hours to achieve a 200nm SiO$_2$ layer over silicon. The quartz was cut by a glass wheeler cutter to 1.7×1.7cm which can fit the ALD reactor. The in-situ resistance test result is shown in figure 27.

The resistance of quartz is five orders higher than nickel at 800°C, but thermal oxidized SiO$_2$ on Si is in the same other with nickel thin film. Thermal oxidized SiO$_2$ on Si substrates will make a large portion to the overall signal under elevated temperatures. But the quartz substrate will maintain a high resistivity and a very stable chemical property over the temperature range studied. It was concluded from these experiments of all the above materials, that only quartz can serve as the best substrate for in-situ conductivity measurement of thin film electrode materials in the temperature range over 300 °C.
4.2.2 Electrochemical characterization

4.2.2.1 Electrochemical characterization on thin film electrolyte materials

To study the electrochemical performance of thin film materials with electrochemical impedance spectroscopy, we developed two methods.

Characterization Setup

**Method 1** Quartz substrate with Pt serving as bottom and top electrodes

![Diagram of Method 1](image)

**Figure 28** illustration of method 1 quartz as the substrate with Pt film serving as bottom and top electrodes (the thickness of quartz substrate is 1mm)
In this configuration, quartz serves as the substrate. A layer of 30 nm Pt was uniformly sputtered to the substrate with E-beam evaporation, as figure 29 shows. Then half of the substrate was masked with well-polished silicon wafer, and allow the deposition on the unmasked side selectively (figure 30). Then photolithography process was applied to prepare a top electrode (figure 31). The detailed process is shown in figure 29-31.

**Sample preparation process**

Substrate: Quartz

**Step 1** Sputtering 30 nm Pt on Quartz with E-beam evaporation

![Figure 29 Sputtering 30 nm Pt on quartz with e-beam evaporation](image)

Since the surface of silicon wafer is well polished, the distance between silicon wafer mask to Pt substrate is in the range or 10 nm. The ALD precursor vapors will not diffuse to the masked area. To prove this, an experiment was done on a masked and unmasked substrate. A part of the substrate was covered with a silicon wafer and the other half was left exposed. The thickness of the two sections was measured. When a deposition of 200 cycle of CeO$_2$ was performed, 300 Å thickness was measured on the unmasked substrate and 0 Å on the masked substrate. It was concluded from this experiment that silicon wafer can be used as a mask for the ALD process.
Step 2 YDC depositions on half of the substrate with Si wafer mask

1. Substrate

| Pt | Quartz |

2. Mask half substrate with silicon wafer

| Pt | Quartz |

3. Deposit YDC

| ALD-YDC | Silicon wafer |
| Pt | Quartz |

4. Remove Si wafer

| ALD-YDC |
| Pt |
| Quartz |

Figure 30  Atomic layer deposition of YDC films on half of the substrate with well-polished Si wafer mask to block deposition on the other half
Step 3 Photolithography of top Pt electrode deposition

By processing the above three steps, the sample with a Pt electrode on the top and the bottom can be prepared. The reason is when performing the electrical or electrochemical measurements; the current will go through the ALD thin film electrolyte material perpendicularly, as opposed to the planar measurements in
Section 4.2. Using this test design, the electrochemical properties of various films will be studied.

**Method 2** Doped silicon substrate with silver paste serving as current collectors

![Diagram](image)

**Figure 32** Illustration of method 2: doped silicon as the substrate with silver paste serving as top and bottom current collectors and silver wire to conduct current. (a) Cross-section view (b) top view

In method 2, conductive silicon wafers were used as the substrate, and YDC films were uniformly deposited by atomic layer deposition on the silicon substrate. A layer of silver paste was applied uniformly on the backside of the silicon wafer as the
current collector and a silver dot with dimensions of 1 mm*1mm serving as the top electrode (as shown in figure 32).

• Signals are a series circuit combination of silicon and ALD film

![Equivalent Circuit](image)

**Figure 33** Equivalent circuit of method 2 with Si, SiO₂ and YDC as main parts for data analysis

Equivalent circuit as figure 33 shows was applied to analyze the impedance signals. The silicon wafer was fitted as a pure resistance and native silicon dioxide layer was fitted as a resistance/capacitor paralleled and the yttria-doped ceria layer was fitted as resistance/capacitor paralleled. Experiments on new silicon wafer (figure 34), 40 nm 20% YDC (figure 35) were done with this method.

**Result and discussion**

Electrochemical impedance spectra on new silicon wafers with, 40 nm 20% YDC and new silicon wafers with cerium oxide were done with method 2. Silicon wafers were used as the substrate for atomic layer deposited YDC and cerium oxide films uniformly. A layer of silver paste was applied on the backside of the silicon
wafer as the current collector and a silver dot with dimensions of 1 mm*1 mm serving as the top electrode.

![Image](image.png)

**Figure 34** Impedance spectra of new doped silicon wafer from 25 - 500°C

As shown in Fig 34, the electrochemical impedance of silicon wafer was characterized from 25 to 500°C in air. The total resistance of the layer is $7.10 \times 10^4 \Omega$ at 25°C, which is mostly the contribution from the native silicon dioxide layer. When the operating temperature is increased, the total resistivity decreases as indicated by the decrease in the size of the semi-circle on the Nyquist plot. The impedance spectra were taken under the voltage of -2.5-2.5 V and frequency 1 Hz to 5 MHz.
Figure 35  Impedance spectra of 40nm 20% YDC on silicon substrate from 25 -500°C

As shown in Fig (35), the electrochemical impedance of 40nm 20% YDC on silicon wafer was characterized from 25 to 500°C in air. The total resistance of the layer is over $1.20 \times 10^7 \Omega$ at 25°C, which is more than 100 times higher than the resistance of native silicon dioxide layer. In the spectra, the first arc represents the signal of silicon dioxide layer, and the second arc represents the signal of YDC layer. We can filter out the signal of the YDC film up to 500 °C with this method.

To compare the signals of Si and YDC film, the resistance of silicon wafer and YDC films on silicon wafer are listed in table 3.
Table 3  Resistance of Si and 40nm 20% YDC

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>R_Si</th>
<th>R_SiO₂</th>
<th>R_YDC</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>4</td>
<td>7.10E+04</td>
<td>1.19E+07</td>
</tr>
<tr>
<td>200</td>
<td>2.7</td>
<td>1.30E+04</td>
<td>3.07E+05</td>
</tr>
<tr>
<td>300</td>
<td>2.1</td>
<td>2.80E+03</td>
<td>2.92E+04</td>
</tr>
<tr>
<td>400</td>
<td>1.9</td>
<td>4.80E+02</td>
<td>3.22E+03</td>
</tr>
<tr>
<td>500</td>
<td>1.8</td>
<td>7.80E+01</td>
<td>1.92E+03</td>
</tr>
</tbody>
</table>

Form the table 3, we can see, the resistance of 40nm 20% YDC film is about 1000 times higher than the resistance of silicon wafer at room temperature and maintains more than 100 times higher than Si at 500°C. So method 2 is able to evaluate the electrochemical property of YDC film up to 500 °C. With the effort of exploring this method characterizing the thin film materials, it opens a new way to researching the thin film electrochemical properties.

Ionic conductivity of CeO₂ by atomic layer deposition

To study the ionic conductivity of CeO₂ thin film prepared by atomic layer deposition, we applied method 2. The working electrode was 1mm×1mm silver dot applied on the top of CeO₂ film and the counter was 1.5cm×1cm silver paste applied
uniformly on the backside of silicon wafer. The impedance Spectra was taken from 95 to 305°C (figure 36). The impedance spectra were taken under the voltage of -2.5-2.5V and frequency 1Hz to 5MHz.

![Impedance Spectra](image)

**Figure 36** impedance Spectra of 45 nm CeO$_2$ by ALD from 95 to 305°C

To analyze the impedance spectra, the data was fitted as the following equivalent circuit.

![Equivalent Circuit](image)

**Figure 37** Equivalent circuit of 45 nm CeO$_2$ on silicon substrate with silver electrode, with Si, SiO$_2$ and CeO$_2$ as main parts for data analysis
Figure 38 Fitting result of electrochemistry spectra of 45 nm CeO2 on silicon substrate with silver electrode, with Si, SiO2 and CeO2 as main parts for data analysis at 25°C using the equivalent circuit showed in Figure 36 (1)Blue Line Z data (2) Red Line Z fitting

Table 4 Resistance of Si substrate and Ceria Prepared by Atomic Layer Deposition

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>R_Si</th>
<th>R_SiO2</th>
<th>R_Ceria</th>
</tr>
</thead>
<tbody>
<tr>
<td>95</td>
<td>3.1</td>
<td>451</td>
<td>816</td>
</tr>
<tr>
<td>135</td>
<td>2.4</td>
<td>411</td>
<td>320</td>
</tr>
<tr>
<td>205</td>
<td>2.1</td>
<td>298</td>
<td>103</td>
</tr>
<tr>
<td>230</td>
<td>1.9</td>
<td>296</td>
<td>60</td>
</tr>
<tr>
<td>280</td>
<td>1.7</td>
<td>266</td>
<td>35</td>
</tr>
<tr>
<td>305</td>
<td>1.7</td>
<td>231</td>
<td>11</td>
</tr>
</tbody>
</table>
Table 4 summarizes the resistivity of each component in the equivalent circuit. Equivalent circuit in Figure 37 was applied as the model to analyze the impedance spectra. At 95°C the ceria layer shows an resistance of 816 Ω. It shows that with increasing the temperature from 95 to 305°C, the resistivity of ceria layer is increasing much faster than the silicon dioxide layer due to the high activation energy of ceria. When temperature goes to higher than 305°C, the arc of ceria becomes very small compared to the arc of silicon dioxide. Figure 39 shows the ionic conductivity of the ceria prepared by atomic layer deposition.

![Graph](image)

**Figure 39** Ionic conductivity of ceria prepared by atomic layer deposition on silicon substrate (1) experiment data (2) literature data⁵⁹
The ionic conductivity of ceria was measured by electrochemical impedance spectroscopy. Compared with literature data, the ceria deposited by atomic layer deposition achieved a higher ionic conductivity under 300 °C. The activation energy of ALD ceria in the temperature range 95~305°C is 0.31eV. The ALD ceria may be a good candidate as electrolyte materials for low temperature SOFCs.

4.2.2.2 Electrochemical measurements on thin film anode half-cells

Figure 40 Setup of anode half-cell with nickel gasket as support, physical vapor deposited Pt as electrode, ALD YSZ as electrolyte and nanostructured Ni-YSZ as anode

Electrochemical characterization of the thin-film anode materials will follow electrochemical measurements on anode half-cells. The setup of anode half-cells is shown in figure 40. A nickel VCR face seal fitting, silver-plated snubber gasket
Figure 41 setup of the electrochemical test system of SOFC with thin film components

(Ni-8VCR-2..5M) is selected as the substrate for the cathode supported thin film anode half-cell. We use physical vapor deposition (PVD) to deposit a layer of platinum to seal the micron pores of the gasket to leave nanoporous structure. Then
we deposit an ALD-YSZ layer as the electrode for the cell and add the nanostructured Ni–YSZ as the anode.

Measurements using a half-cell setup allow the individual properties of the anode to be measured separately and to quantitatively determine catalytic activity, mass transfer limitations, capacitances, and ionic/electronic conductivity. The half-cell assembly will be attached to silver wires coated by multi bore alumina tube using silver paste and placed in an electric furnace. Hydrogen and air will flow into the furnace from two sides to provide the fuel and oxidant. The setup of the electrochemical test of the SOFC is shown in figure 41. Electrochemical methods such as cyclic voltammetry, I-V scans and ac techniques such as electrochemical impedance spectroscopy can be used to study the performance of the SOFCs and to characterize the underlying electrochemical processes.

4.3 Summary

The anode is the electrode where hydrogen is oxidized and water is formed. The anode should maintain high electronic conductivity under the SOFC operation conditions. To measure the thin film anode conductivity, we deposited Ni anode materials on quartz substrate to avoid any substrate effect on the conductivity test. In this work, we developed the characterization technique to study the thin film electrical properties. A new four point probe method was applied to study the electrical conductivity of the Ni-YSZ thin film electrode materials prepared by atomic layer deposition and glancing angle deposition. In this method, it becomes possible to study
the in-situ electrical conductivity of thin film materials on different substrate under different environment. The system has a wide temperature testing range which is from room temperature to 800°C. Also it allows multiple gas phase environments. This development will be a good supplemental method for studying electrical properties of thin film materials.

In the study of electrochemical properties of atomic layer deposition prepared thin film electrolyte materials, we developed a new method of characterizing the ionic conductivity. Silicon wafer was used as a substrate and silver paste was applied as current collectors. In this method, the impedance spectra was successfully taken and the ionic conductivity was evaluated to up to 500°C. The ionic conductivity of ceria prepared by atomic layer deposition was also measured using electrochemical impedance spectroscopy with the characterization method. Compared with literature data, the ceria deposited by atomic layer deposition achieved a higher ionic conductivity under 300 °C. However, the activation energy is lower than reported data. With the effort of exploring a new method characterizing thin film materials’ electrochemical performance, it opens a new way to researching the electrochemical thin film material.

A new half-cell/full cell electrochemistry characterization system was designed. This design makes the further electrochemical characterization of thin film SOFC components and half/full cell possible.
5 Conclusion

Nanoscale nanostructured Ni-YSZ anode was successfully fabricated by combining ALD and GLAD techniques. The GLAD Ni nanorod film has a porosity of 53%; with an ALD growth rate of 0.08 nm/cycle, 1.9, 3.8 and 7.6 nm 9% YSZ coated Ni-YSZ anode was prepared. The surface area is increased to more than 3 times as large as plane area. ALD coating approach is flexible in combining ionic conductive YSZ electrolyte phase with electrical conductive Ni phase and control the porosity of the nano-composite electrode just through deposition and post-deposition annealing process. It is shown that the surface roughness of Ni-YSZ electrode decreases with thicker ALD YSZ coating layer, which indicates a decrease in SOFC electrode reaction resistance. The surface concentration of nickel is getting lower with thicker YSZ layer and the relative amount of Ni at the surface after annealing is enhanced, while the atomic composition of YSZ film is precisely controlled by ALD process and not affected by the post-annealing process. The Ni-YSZ anodes show resistivity in the $10^{-4}$ cm·S$^{-1}$ magnitude. The ALD YSZ coating layer shows distinguished sintering-resistant effect on nanoscale nanostructured electrode with an as thin as 1.9 nm coating layer and excellent effect in maintaining the anode performance under SOFC operating conditions. Such nanoscale nanostructured Ni-YSZ anode offers a new avenue in exploring nanoscale SOFCs in the future.

The anode is the electrode where hydrogen is oxidized and water is formed. The anode should maintain high electronic conductivity under the SOFC operation
conditions. To measure the thin film anode conductivity, we deposit anode materials on quartz substrate to avoid substrate effect of the conductivity test. In this work, we developed the characterization technique to study the thin film electrical properties. A new four point probe method was applied to study the electrical conductivity of the Ni-YSZ thin film electrode materials prepared by atomic layer deposition and glancing angle deposition. In this method, it becomes possible to study the in-situ electrical conductivity of thin film materials on different substrate under different environment. The system has a wide temperature testing range which is from room temperature to 800°C. Also it allows multiple gas phase environments. This development will be a good supplemental method for studying electrical properties of thin film materials.

In the study of electrochemical properties of atomic layer deposition prepared thin film electrolyte materials, we developed a new method of characterizing the ionic conductivity. Silicon wafer was used as a substrate and silver paste was applied as current collectors. In this method, the impedance spectra was successfully taken and the ionic conductivity was evaluated to up to 500°C. The ionic conductivity of ceria prepared by atomic layer deposition was also measured electrochemical impedance spectroscopy with the new characterization method. Compared with literature data, the ceria deposited by atomic layer deposition achieved a higher ionic conductivity under 300 °C. However, the activation energy is lower than reported data. With the effort of exploring a new method characterizing thin film materials’ electrochemical performance, it opens a new way to researching the electrochemical thin film material.
A new half-cell/full cell electrochemistry characterization system was designed. This design makes the further electrochemical characterization of thin film SOFC components and half/full cell possible.
6 Future Work

During this research work, nanostructured Ni-YSZ anode for solid oxide fuel cells has been successfully deposited by atomic layer deposition. Several materials of different composition, morphology and electronic performance have been studied. It is recommended that the electrochemical performance of these materials be studied under different SOFC operating conditions. Also, a novel single cell or half-cell design was developed that has the potential of providing electrochemical performance data on thin-film SOFC’s. The novel test cell can be assembled with electrolyte and cathode material fabricated by atomic layer deposition or other deposition techniques, so that to characterize the nanostructured atomic layer deposited Ni-YSZ material’s performance under real SOFC operation condition.
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