# The University of Maine DigitalCommons@UMaine

**Electronic Theses and Dissertations** 

**Fogler Library** 

Spring 5-5-2023

# Influence of Platinum Nanoparticles on Ionic Transport and Hydrogen Reactivity of Yttria-Stabilized Zirconia Thin Films

Firas Mahyob University of Maine, firas.mahyob@maine.edu

Follow this and additional works at: https://digitalcommons.library.umaine.edu/etd

Part of the Ceramic Materials Commons, Condensed Matter Physics Commons, Inorganic Chemistry Commons, Materials Chemistry Commons, and the Physical Chemistry Commons

#### **Recommended Citation**

Mahyob, Firas, "Influence of Platinum Nanoparticles on Ionic Transport and Hydrogen Reactivity of Yttria-Stabilized Zirconia Thin Films" (2023). *Electronic Theses and Dissertations*. 3793. https://digitalcommons.library.umaine.edu/etd/3793

This Open-Access Dissertation is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of DigitalCommons@UMaine. For more information, please contact um.library.technical.services@maine.edu.

# INFLUENCE OF PLATINUM NANOPARTICLES ON IONIC TRANSPORT AND HYDROGEN REACTIVITY OF YTTRIA-STABILIZED

#### ZIRCONIA THIN FILMS

by

Firas M. Mahyob

B.S. University of Basrah, 2002

M.S. University of Basrah, 2007

#### A DISSERTATION

Submitted in Partial Fulfillment of the

Requirements for the degree of

Doctor of Philosophy

(in Physics)

The Graduate School

The University of Maine

May 2023

Advisory Committee:

Robert J. Lad, Professor of Physics and Astronomy & FIRST, Advisor Robert W. Meulenberg, Professor of Physics and Astronomy & FIRST James P. McClymer, Associate Professor of Physics and Astronomy MacKenzie R. Stetzer, Associate Professor of Physics and Astronomy Carl P. Tripp, Professor of Chemistry & FIRST

### DISSERTATION ACCEPTANCE STATEMENT

On behalf of the Graduate Committee for Firas Mahyob I affirm that this manuscript is the final and accepted dissertation. Signatures of all committee members are on file with the Graduate School at the University of Maine, 42 Stodder Hall, Orono, Maine.

Robert J. Lad, Professor of Physics and Astronomy & FIRST

, 2023

© 2023 Firas Mahyob

All Rights Reserved

#### LIBRARY RIGHTS STATEMENT

In presenting this dissertation in partial fulfillment of the requirements for an advanced degree at The University of Maine, I agree that the Library shall make it freely available for inspection. I further agree that permission for "fair use" copying of this dissertation for scholarly purposes may be granted by the Librarian. It is understood that any copying or publication of this dissertation for financial gain shall not be allowed without my written permission.

Signature: \_\_\_\_\_

Date: \_\_\_\_\_

# INFLUENCE OF PLATINUM NANOPARTICLES ON IONIC TRANSPORT

### AND HYDROGEN REACTIVITY OF YTTRIA-STABILIZED

#### ZIRCONIA THIN FILMS

By Firas Mahyob

Dissertation Advisor: Dr. Robert J. Lad

An Abstract of the Dissertation Presented In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy (in Physics) May 2023

Yttria-stabilized zirconia (YSZ) is a widely used ceramic material in solid oxide fuel cells, oxygen sensors, and sensing applications due to its high ionic conductivity, chemical inertness, and thermal stability. YSZ is promising active coating for use in miniaturized harsh environment wireless surface acoustic sensors to monitor gases such as H<sub>2</sub>. Adding catalytic Pt nanoparticles can enhance gas reactivity and lead to associated film conductivity changes.

In this work, thin films with an  $(8\% Y_2O_3 - 92\% ZrO_2)$  composition were deposited onto piezoelectric langasite substrates using RF magnetron sputtering in Ar:O<sub>2</sub> - 95:5 gas mixture. Films were grown using growth temperatures (30 - 700<sup>o</sup>C), deposition rates (0.03 - 0.07 nm/s), and substrate bias (-300 - +300 V). Platinum was deposited in-situ via e-beam evaporation at either 30<sup>o</sup>C or 400<sup>o</sup>C and then subsequently annealed to cause nanoparticle formation. YSZ and Pt/YSZ films ionic conductivities were measured and characterized with electrochemical impedance spectroscopy (EIS) in pure N<sub>2</sub>, or in a 4% H<sub>2</sub> - 96% N<sub>2</sub> mixture. X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM) were also used to analyze the surface composition, crystal structure and nanoparticles morphology, respectively.

By manipulating the deposition parameters, either (111) or mixed (111)/(200) YSZ film crystallographic texture can be achieved. Post-deposition annealing up to 1000°C in air causes grain growth, strain relief and yttria segregation. EIS measurements from YSZ films over the range 400°C - 600°C indicate that ionic conductivities are strongly dependent on yttria segregation and film nanostructure.

For YSZ films decorated with Pt nanoparticles, the surface becomes reactive towards hydrogen. Pt nanoparticles form (111) oriented crystallites, and the amount of yttria segregation is less than that for Pt-free films. Ionic conductivities and sensitivities towards hydrogen depend on the nanoparticle size and film nanostructure. Pt nanoparticles lower the H<sub>2</sub> adsorption energy and facilitate the interaction. The conductivity changes that occur corresponding to pure N<sub>2</sub> versus exposure to 4% H<sub>2</sub> - 96% N<sub>2</sub> were found to be reversible. These results indicate that Pt/YSZ films hold promise as hydrogen sensing films that can be incorporated onto a variety of sensing platforms for H<sub>2</sub> gas detection and management.

### **DEDICATION**

I dedicate this dissertation to my beloved wife Tuqa Al-Asadi. Your love, support, and patience have always been the foundations of my inspiration.

I also dedicate this work to my children Malath, Zulfa, and Mousa. You have taught me how to be happy even in the most imperfect circumstances.

I am truly blessed to have you all in my life.

#### ACKNOWLEDGMENTS

All praise is to God Almighty Who continues to bless my life.

Imam Zayn al-Abidin (p) is reported to have said: "The most thankful among you to God is the one who is most thankful to others."

This work would not have been possible without the effort and collaboration of many people who believed that I would succeed.

First and foremost, I would like to express my sincere gratitude and deepest appreciation to my doctoral advisor Dr. Robert Lad, for giving me the opportunity to join his group and carry out this research project leading to this PhD dissertation. His intelligence, diligence, enthusiasm, leadership, expertise, philosophy, and unwavering patience have had a significant impact on me and added considerably, not only in my graduate research experience but also in my daily life.

Dr. Lad's great passion for addressing industrial challenges by incorporating fundamental theories and scientific methods into engineering research work has inspired me a lot. Dr. Lad provided countless support, valuable guidance, and great insight to me throughout this research project. He always had great ideas to advance the research with consistent trust, tremendous patience, and a kind personality to make my efforts fruitful. Whenever I got stuck with my research, he was always available to provide kind help with lots of encouragement, optimism, and inspiration. This gave me a lot of strength and passion going through some of the difficult days of my PhD life. I also would like to thank him for his technical enlightenment and crucial advice on how to strive for excellence and perform high-standard scientific research. I have learned a lot from his insightful comments and suggestions during each update meeting and scientific discussion. This dissertation would not have been possible without his endless support, continuous motivation, and valuable suggestions. I am fortunate to have had the opportunity to study under his mentorship. I would also like to especially thank Dr. Robert Meulenberg, Dr. James McClymer, Dr. MacKenzie Stetzer, and Dr. Carl Tripp for being part of my PhD dissertation committee. Their constructive comments, valuable suggestions, useful discussions, diverse expertise, and perspectives have greatly enriched my educational and research experience and helped to guide me through this journey.

I specifically acknowledge Dr. George Bernhardt for invaluable discussions, training relating to synthesis and characterization, and extensive assistance with imaging needs throughout my research project. Dr. Bernhardt has always been a great laboratory support and an excellent collaborator in my work and a pleasure to work with. This work could not have been accomplished without his indispensable assistant. I thank Michael Call, who is among the most helpful people I have ever met, for his assistance with building the impedance analyzer experiment.

I sincerely thank David Stewart and Robert Fryer who first brought the theme of this thesis to my attention, and I have had the pleasure of working with them for the first year in my research. They shared their expertise in XRD and XPS in an attempt to shed light on this work. Special thanks to Robert Fryer for all his academic advice and for agreeing to go through the pain of reading my thesis. I am indebted to Roger Feeley for being a good friend and teaching me experimental skills and helping with my research over the years.

I would like to express my thanks to Dr. Mauricio da Cunha (Electrical Engineering Department) and his group Anin Maskay and Armando Ayes for kindly helping me with all the logistics I needed during my project. Dr. Cunha generously supplied the LGS substrate material and the RF cables for our research and kindly let me use their wire bonding facility. Special thanks are extended to my colleague Armando Ayes for his help, technical consultancy, and collaboration during this project.

I owe a great debt to my colleagues John Speirs, Benjamin Schermerhorn, Matthew Valles, and Stuart Lawson in the Physics Department for their friendship and assistance who helped to guide me through the coursework. The friendship created with all of you is impressive and will be my most important treasure. Alex Khammang, thanks for the coffee, jokes, and affability. Additionally, I would like to thank the administrative secretary Pat Byard (Physics Department) and Tracy Richardson (FIRST) for their constant assistance with paperwork and printouts throughout my degree.

There is a list of individuals who I sincerely would like to thank and acknowledge for their financial support and endless assistance along the way to complete my Ph.D. successfully: higher committee for education development in Iraq (HCEDIraq), office of international program (OIP) at the University of Maine, Dr. John Thompson and Dr. MacKenzie Stetzer (Physics Department), and Dr. Scott Delcourt (Graduate School). Without their generous funding, this research would not be possible to conduct.

I am happy to have made wonderful friends in Orono who made me, and my family stay in Orono a memorable experience. I would like to acknowledge and appreciate the Hildebrand family, Hasbrouck family, Quirk family, Stoner family, and Brichacek family for their unconditional love, support, kindness, and generosity. Emily, we really enjoyed the ice candle every year, thank you for all the unforgettable memories.

I would like to specifically express my sincere appreciation to our friend Sally Dobres for being part of our family and providing unconditional support and love for so many years. Sally, your friendship and support during the adventure of moving to a new country were of great value to me and my family. All the sweet memories I share with you are priceless. You are a real friend, a friend that I can always trust and consult with. I would like to sincerely thank Michael Parks, Maged Rizkallah, and all the physical measurements team at Shimadzu Scientific Instruments for their unwavering support, advice, and technical knowledge in my industrial career.

Last but not least, I lovingly would like to acknowledge my dearest family, in Iraq, my father Mohammed, my mother Amenah, and my sister Huda for their love, understanding, and patience that have helped me along every step of this path. Nothing that I was granted in life was as valuable as having you, and nothing that I have achieved in life made me as delighted as the times I spent with you. Mother and Father, no words are enough to describe what you have done for me and how much you mean to me. No sentence can show my deep appreciation. You are the best. You have supported me financially and spiritually over the years and for that and many other reasons I owe you my eternal gratitude. I would also like to thank my wife's family for their support, love, and understanding.

Finally, and most importantly, I would like to thank my wife and best friend, Tuqa, and my three wonderful children, Malath, Zulfa, and Mousa for endless belief in me, standing beside me throughout the busy days of my PhD years and drafting this dissertation, and making my life much more enjoyable and colorful. Tuqa is the most valuable and supportive teammate in reaching the finish line. Her patience, encouragement, and intelligence have assisted me in writing and proofreading and her immeasurable trust in me was necessary to make it through intense moments of doubt and personal disappointment. Your everlasting love is and always will be the biggest motivation for my entire life. I cannot imagine having done this without you.

# **TABLE OF CONTENTS**

DEDICATION	V
ACKNOWLEDGEMENTSv	'n
LIST OF TABLESxiv	v
LIST OF FIGURES	V

# CHAPTER

1	INTRODUCTION 1
	1.1 Motivation for the Research 1
	1.2 Hydrogen Sensors for Use in High Temperature Harsh Environments
	1.3 Properties of Yttria-Stabilized Zirconia Materials7
	1.4 Strategies for Using Catalyzed YSZ Films to Detect Hydrogen Gas 13
	1.5 Gas Sensing in Metal – Metal Oxide Catalytic Systems 15
	1.6 Thesis Organization
2	EXPERIMENTAL METHODS FOR THIN FILM SYNTHESIS AND
	MATERIALS ANALYSIS

	2.1 Introduction	3
	2.2 Synthesis of YSZ Thin Films with and without Pt Nanoparticles	3
	2.3 Electronic Structure and Chemical Composition	8
	2.4 Crystallography and Morphology	3
	2.5 Electrical and Ionic Conductivity42	2
3	NANOSTRUCTURE AND MORPHOLOGY OF YSZ FILMS DEPOSITED	
	ON LANGASITE SUBSTRATES 54	4
	3.1 Introduction	4
	3.2 Deposition Parameters for YSZ Thin Film Growth	5
	3.3 Characterization of As-Deposited YSZ Films	8
	3.3.1 Film Compositional Analysis	8
	3.3.2 XRD Analysis of Crystal Structure	9
	3.3.3 Analysis of Film Morphology	7
	3.4 Influence of Substrate Bias during YSZ Film Growth72	1
	3.5 Formation of (111) versus (200) Grain Orientations in As-Grown YSZ	
	Films75	5
	3.6 Roughness of As-Grown YSZ Thin Films	9

	3.7 Characterization of YSZ Thin Films Subjected to Post-Deposition	
	Annealing Treatments	80
	3.8 Comparison of the Sample Set of YSZ Thin Films	85
	3.9 Impedance and Ionic Conductivity of YSZ Films	94
	3.10 Ionic Conductivity of As-Grown and Annealed YSZ Thin Films	100
	3.11 Ionic Conductivity and Activation Energy of As-Grown and Annealed	
	YSZ Films	107
	3.12 Chapter Summary	111
4	CHARACTERISTICS OF YSZ FILMS WITH CATALYTIC PT NANOPARTICLES	113
	4.1 Heterogenous Catalysis of Metal Nanoparticles on Oxide Supports	113
	4.2 Deposition of Pt on top of YSZ films	115
	4.3 Thermal treatments of Pt/YSZ films	118
	4.4 Ionic conductivity of Pt/YSZ Films in N2 environment	125
	4.5 Chapter Summary	130
5	INFLUENCE OF HYDROGEN EXPOSURE ON IONIC CONDUCTIVITY	
	OF YSZ AND PT/YSZ FILMS	131

5.1 Hydrogen Interactions with YSZ Films 1	31
5.2 Hydrogen Interactions with Pt/YSZ Films 1	.33
5.3 Reversibility of Pt/YSZ Film Conductivity with Repeated $\rm H_2$ / $\rm N_2$	
Exposures1	.42
5.4 Oxygen Interactions with YSZ and Pt/YSZ Films 1	.44
5.5 Chapter Summary 1	.45
6 CONCLUSIONS AND FUTURE WORK 1	.47
6.1 Conclusions1	.47
6.2 Future Work 1	51
REFERENCES 1	.53
BIOGRAPHY OF THE AUTHOR 1	80

# LIST OF TABLES

Table 3. 1. Atomic concentration and XPS binding energies for YSZ measured values	
from an 8-YSZ single crystal compared to average value determined	
from 16 film depositions at 30°C	60

## LIST OF FIGURES

Figure 1. 1.	The total annual energy consumed in the U.S. over the past 7 decades
	reported by the U.S. Energy Information Administration (EIA) [1].
	Petroleum and natural gas are the main energy sources for the industrial
	and transportation sectors
Figure 1. 2. I	Example of SAW sensor devices (A) Portion of a piezoelectric LGS wafer
	showing photolithographically patterned SAW devices fabricated in the
	UMaine clean room facility (B) Schematic illustration of a SAW
	resonator device (C) Nanocomposite Pt-ZrO2 IDT electrodes that remain
	stable up to 1000°C [28] (D) Hillocks formed on the surface of a YSZ
	film on an LGS substrate due to thermal stresses
Figure 1. 3.	Bulk equilibrium phase diagram for the Zirconia (ZrO <sub>2</sub> ) – Yttria (Y <sub>2</sub> O <sub>3</sub> )
	system
Figure 1.4.S	Schematic representation of the insertion of Yttria (Y2O3) into the zirconia
	(ZrO <sub>2</sub> ) lattice which leads to the creation of oxygen vacancies [45] 10
Figure 1. 5.	The conductivity of YSZ at 1000°C as a function $Y_2O_3$ content for
	unannealed and annealed samples with 5-11 mol % ( $\square$ , $\blacksquare$ ) and a co-
	precipitated 8 mol% YSZ sample ( $\circ$ , $\bullet$ ). The maximum conductivity
	occurs over the range of 7.7 to 8.5 mol% after annealing [41] 11
Figure 1. 6. S	Schematic of oxygen vacancy migration between YSZ unit cells [45]

Figure 1. 7. Gas adsorption on noble metal NPs can be influenced by either a (left) chemical sensitization or (right) electronic sensitization mechanism [80].

- Figure 2. 3. XPS spectra from (red scan) as-grown YSZ thin film deposited on a LGS substrate at 30°C and (green scan) YSZ single crystal obtained from MTI Corporation. These survey scans show O 1s, Zr 3d, Y 3d peak regions for the thin film and the single crystal and C 1s for the single crystal. The scans are charge referenced to O 1s at 529.0 eV and C 1s at 284.5 eV (when present).

Figure 2. 8. (a) XRD scan geometry for pole figure diffraction where $\Delta k$ is set fixed	
while the sample is rotated through a full hemisphere of $\chi$ and $\phi$ angles.	
(b) The continuous intensity distribution along $\varphi$ indicates a (311)	
textured film with nearly random grain orientation within the plane of	
the film	
Figure 2. 9. X-ray reflectivity (XRR) spectrum from a 40 nm thick YSZ film deposited	
on LGS substrate at 700°C. The simulation from X'Pert Reflectivity	
software indicates a film thickness of 38 nm calculated from the distance	
between fringes	
Figure 2. 10. Physical processes involved during SEM analysis of a material using an	
energetic electron beam.	
Figure 2. 11. SEM images from a 200 nm thick YSZ film decorated with 1 nm Pt	
nanoparticles, (a) secondary electron image and (b) backscattered	
electron image.	
Figure 2. 12. Fundamental concepts of electrochemical impedance spectroscopy	
[123]	
Figure 2. 13. Theoretical modeling of the electrochemical impedance spectroscopy	
(Nyquist plot) and equivalent circuit of 8 mol% YSZ, measured at 300	
°C [124]	44

Figure 2. 14. Impedance spectrum of YSZ thin film with a thickness of 200 nm. At
frequencies below 1 Hz is clearly visible the contribution of the
electrode
Figure 2. 15. Ideal circuit elements used to interpret a Nyquist plot
Figure 2. 16. Constant phase element on a Nyquist plot
Figure 2. 17. A Cole element (RQ) forms a depressed semicircle in a Nyquist plot
Figure 2. 18. Hydrogen sensing configuration
Figure 2. 19. Example impedance spectroscopy data acquired from a YSZ film (200
nm) decorated with Pt nanoparticles (10 nm) before and after exposure
to hydrogen gas. Hydrogen adsorption causes an inward shift of the low
frequency arc on the Nyquist plot
Figure 2. 20. (a) Photograph of the experimental setup used for impedance
spectroscopy measurements at elevated temperatures; (b) schematic
cartoon showing a YSZ film with Pt nanoparticles and Pt contact pads;
(c) overall configuration for carrying out $H_2$ gas dosing experiments
Eiren 2 1 XDS martine from XSZ film langitul at 2000 The start

Figure 3. 1. XPS spectrum from a YSZ film deposited at 30°C. The atomic concentrations and binding energies for each element averaged for 16 different YSZ films are shown Table 3.1 in comparison to measurements from a (111) YSZ single crystal standard. Both the measured Y/Zr ratio

and the	observed	Zr3d and	Y3d	binding	energies	were	nominally	the	
same fo	r all the as	s-deposite	d YSZ	films					60

- Figure 3. 4. Characterization of 200 nm thick YSZ films (grown at 30°C and 0.07nm/s) to determine grain size and strain. (A) Gonio (2θ) scan (B) GIXRD scan, sample stage tilted 5° (C) Williamson Hall plot. The negative slope is due to compression stress, while the positive slope reflects a tensile stress (D) 3D plot showing the grain (crystallite) size for different films versus the relevant parameters shown by the colors in the legend: deposition rate and deposition temperature (E) Strain analysis for as-deposited YSZ films grown under different conditions. Negative

- Figure 3. 8. Strain and morphology of YSZ films grown with biases of -300V, -100V,
   +100V, +300V on a LGS substrate. The mean crystallite size and
   microstrain as determined from the Williamson-Hall method are shown.

|--|

Figure 3. 9. XRD gonio scans from films deposited at various deposition rates and bias voltages showing coexistence of (111) and (200) grain orientations.

Figure 3. 10. SEM images from as-deposited YSZ films on LGS substrate. YSZ films	
grown at 0.07 nm/s rate and 30°C deposition temperature. Films show a	
periodic repeatable arrangement of line patterns morphology on the	
surface. Images conducted from three different samples grown with the	
same deposition parameters	79
Figure 3. 11. XPS high resolution spectra from as-deposited and annealed YSZ thin films.	
Figure 3. 12. Ratio of Y/Zr in YSZ films as measured by XPS as function of the	
annealing conditions for films grown at different deposition rates and	
temperatures	
Figure 3. 13. Ratio of Y/Zr in YSZ films as measured by XPS as function of the post-	
deposition annealing conditions for films grown at 30°C under different	
substrate bias conditions. The substrate bias hinders yttrium segregation	
towards the surface	
Figure 3. 14. Ratio of Y/Zr in YSZ films as measured by XPS for films deposited at	
different temperatures (30°C, 400°C, 700°C) and then annealed at 600°C,	
800°C, and 1000°C in air	
Figure 3. 15. XRD gonio scans from as-grown and annealed YSZ films. Peaks shift	
and broadening indicate changes in crystallite size and film strain. Peaks	
shift to lower angles in as-deposited films compared to the position for	
an unstrained powder standard, due to compressive strain. The annealing	
an unstrained powder standard, due to compressive strain. The annearing	

	temperature treatments shift the peaks to higher angle as strain is	
	relieved.	87
Figure 3. 16	6. 3-D plot showing YSZ crystallite size (a) as-deposited (b) annealing up	
	to 1000°C. Crystallite sizes were calculated by the Williamson - Hall	
	method	88
Figure 3. 17	7. YSZ film strain versus annealing temperature as determined from the	
	Williamson – Hall method. It is found that the compressive stress in the	
	as-sputtered YSZ film starts to decrease in magnitude at a temperature	
	higher than 600°C, reaches zero stress at a temperature between 800 and	
	1000°C, and becomes tensile and decrease in magnitude at higher	
	temperatures. The annealing temperature simply becomes too low to	
	completely relieve the compressive residual stress induced by sputtering	
	[28]	88
Figure 3. 18	8. Films grown at low deposition temperature (30°C) and high deposition	
	rate (0.07 nm/s) show that the free surface of YSZ film is not perfectly	
	flat and exhibit hillock formation.	89
Figure 3. 19	9. SEM images for as-grown and annealed YSZ thin films. Films deposited	
	at high deposition temperature (700°C) and low deposition rate (0.03	
	nm/s), and films deposited at low deposition temperature (30°C) and high	
	deposition rate (0.07 nm/s) exhibit hillock formation. However, rest of	

the films have a range of stress process between compression and tensile	
stress. Images are for films annealed at 1000°C in air for one hour	0
Figure 3. 20. XRD gonio scans from as-grown YSZ thin films and the same films	
after annealing at 1000°C in air for 1 hour. The YSZ films were all	
deposited at 30°C, a rate of 0.07 nm/s and with a 95:5 Ar:O <sub>2</sub> ratio but	
with biases of -300V, -100V, +100V and +300V	1
Figure 3. 21. XRD crystallite size of as-deposited YSZ films and after annealing at	
1000°C in air for different substrate biases	2
Figure 3. 22. Film strain in as-grown and annealed YSZ films is determined by the	
XRD Williamson-Hall method9	2
Figure 3. 23. SEM images from as-grown YSZ thin films (upper row) and films	
annealed at 1000°C in air for 1 hour (lower row) for different substrate	
biasing conditions. All films were deposited at a deposition temperature	
of 30°C and deposition rate of 0.07 nm/s	3
Figure 3. 24. Typical impedance spectra (Nyquist plots) from 200 nm thick YSZ film	

deposited on LGS substrate at 400°C. The resistivity of the film decreased (semicircles shrink) as expected for ionic conduction with the increase in temperature from 400 to 750°C. The high stray capacitance value observed in the in-plane configuration of the YSZ film makes it impossible to separate the contribution between grain and grain boundary resistance, which effectively reduces the Nyquist plot to a 

- Figure 3. 25. Impedance pattern (Nyquist plot) for YSZ films as function of thickness.
  Two different thicknesses 15 and 200 nm YSZ films deposited at the same temperature (400°C), same deposition rate (0.07 nm/s) and same substrate (LGS) for each film. Film with less thickness 15 nm (orange plot) show a lower ionic conductivity compared to the thicker film 200nm (red plot) which exhibit higher ionic conductivity. Impedance measurement temperature for both films (500°C). The electrochemical impedance spectra were fitted using EC-Lab software.
- Figure 3. 27. (A) and (B) represent a 3D scatter plot for the conductivities measured at 500°C for as-deposited and annealed YSZ films. Plots (C) and (D)

- Figure 3. 29. (A) and (B) Arrhenius plots for as-grown and annealed YSZ films, respectively, measured in a temperature range of 400 600°C under ambient air. (C) Activation energy values calculated from the Arrhenius plot slope. (D) Legend indicating the deposition parameters employed with each sample as each color represent a unique deposition temperature and deposition rate sputtering condition. The total activation energy of the film's increases/decrease with increase in temperature is attributed to the tensile/compression strain and the grain size effect [216].
- Figure 3. 30. Arrhenius plot of the ionic conductivity measured in a temperature range of  $400 600^{\circ}$ C under ambient air. The lattice tensile / compressive strain and yttria segregation / space charge affect the activation energy that is calculated from the slope of the Arrhenius plot. It was found to be that

	deposited at 30°C then annealed to 1000°C (green plot) and increased	
	from 0.88 to 1.3 eV for a YSZ film deposited at 700°C then annealed to	
	1000°C (black plot)	110
Figure 4. 1.	XPS spectra from YSZ film with and without Pt nanoparticles (NPs), all	
	grown on LGS substrate. The inset shows the enlarged area of the core-	
	level Pt 4f spectra.	116
Figure 4. 2.	XRD patterns from 10 nm Pt on 200 nm YSZ film (i) GIXRD scan -	
	Grown at 30°C; (ii) GIXRD scan - Grown at 400°C; (iii) W-H plot -	
	Grown at 30°C (iv) W-H plot - Grown at 400°C. YSZ film deposit at	
	30°C are highly stressed due to hillock formation. Pt major peak is (111)	
	plus two less intensity peaks at (200) and (220)	117
Figure 4. 3.	XPS analysis of YSZ film composition after annealing for 1 hour in air	
	at each temperature. Pt nanoparticle agglomeration on the surface of	
	YSZ limits yttria segregation	119
Figure 4. 4.	XPS spectra from10 nm Pt on 200 nm YSZ grown at 400°C and then	
	annealed at 600°C and 800°C in air. Pt 4f binding energy shifts occur due	
	to Pt agglomeration	121
Figure 4. 5.	Pt 4f 7/2 binding energy versus Pt coverage and annealing temperature	122

the activation energy reduced from 1.28 to 0.9 eV for a YSZ film

	Figure 4. 7. XRD Gonio patterns from 10 nm Pt / 200 nm YSZ films. The upper XRD
	pattern is for 30°C and the lower XRD pattern is for 400°C. The YSZ
	and Pt films were grown at either 30°C or 400°C. The SEM images show
124	stages of the Pt agglomeration process

Figure 4. 9. Impedance spectra measured at 500°C from 200 nm YSZ films decorated with Pt nanoparticles for different Pt coverages and annealed to 800°C to form the agglomerated Pt NPs. (i) Pt/YSZ deposited at 30°C. (ii) Pt/YSZ deposited at 400°C.

- Figure 4. 11. Impedance spectra (Nyquist plots) from 200 nm YSZ decorated with 10 nm Pt nanoparticles. (i) Pt/YSZ (both) deposited at 30°C then annealed

- Figure 5. 2. Impedance spectroscopy spectra (Nyquist plots) from YSZ films deposited using different bias voltages (Brown) (A) -300V (B) -100V (C) +100V (D) +300V. All films were grown at 30°C and annealed to

1000°C in air for one hour. Exposing to hydrogen (White) at 500°C did	
not change the ionic conductivity of the YSZ films	135
Figure 5. 3. Impedance spectroscopy spectra (Nyquist plots) measured at 500°C from	
Pt/YSZ films. The left column are spectra from Pt/YSZ films deposited	
at 30°C and then annealed at 800°C, while the right column are spectra	
from Pt/YSZ films deposited at 400°C and then annealed to 800°C. The	
open points and solid (colored) points data are from $N_2$ and $H_2$ exposure,	
respectively	137
Figure 5. 4. Pt/YSZ film ionic conductivity at 500°C versus Pt thickness after the	
800°C annealing treatment. These experiments were carried out in pure	
$N_2$ (shaded bars) or in $4\% H_2/96\% N_2$ (unshaded bars)	138
Figure 5. 5. The change in the ionic conductivity for Pt/YSZ films upon exposure to	
$4\% H_2/$ 96%N_2 at 500°C. The 10 nm Pt sample deposited on YSZ at	
400°C followed by annealing at 800°C shows the largest response upon	
H <sub>2</sub> exposure.	
Figure 5. 6. A schematic illustration of the H <sub>2</sub> sensing mechanism, indicating the types	
of reactions happening on the surface of a Pt-decorated YSZ film	140
Figure 5. 7. The reversibility of the impedance spectroscopy spectra (Nyquist plots)	
for 200 nm YSZ film with 5 nm Pt upon repeated change between $4\%$ H <sub>2</sub>	
/ 96%N $_2$ and 100%N $_2$ exposures. The green, blue, and sky-blue scans	
exhibit the location of the Nyquist plot when exposed to hydrogen, while	

the	e orange and red scans represent the Nyquist plot location when
exj	posed to the background gas (nitrogen). Each individual plot is an
ave	erage of 15 scans and the data was acquired at 500°C
Figure 5. 8. The	e change in ionic conductivity of Pt/YSZ films upon switching between
969	$\%N_2/4\%H_2$ and 100% $N_2$ at temperatures between 500°C and 600°C.
Ea	ach sample was exposed to the gas for 315 minutes
Figure 5. 9. Im	npedance spectroscopy spectra from a PT/YSZ film (Pt 10 nm and
dej	position temperature 400°C) exposed to three different gases at 500°C:
hye	drogen (4% $H_2$ / 96% $N_2$ ), oxygen (air),and nitrogen (100% $N_2$ ). The
ord	der for these gas exposures is set as oxygen (air) $\leftrightarrow$ nitrogen (100%N <sub>2</sub> )
$\leftrightarrow$	hydrogen (4%H <sub>2</sub> / 96%N <sub>2</sub> )

#### **CHAPTER 1**

#### **INTRODUCTION**

#### **1.1 Motivation for the Research**

Energy generation, storage, and distribution are critical to every part of our global society. In the United States, the industrial sector is an enormous energy consumer followed by the transportation, residential, and commercial sectors as shown in Figure 1.1 [1]. Industry involves large scale processing and manufacturing facilities including petrochemical refineries, electronics fabrication, ceramic, metal and glass production, and power plants. Similarly, transportation consists of complex machinery, vehicles, and equipment such as turbines and diesel engines. To achieve the highest levels of efficiency, productivity, and functionality, this equipment must be constructed from materials that can stand up and resist extreme harsh conditions including, for example, high temperatures up to 1000°C, erosive particles, corrosive gases, and oxidizing environments. Equipment failure has huge financial consequences in terms of maintenance, work delays, and overall safety. In order to ensure the safety and the reliability of the equipment, scheduled maintenance, inspection, and replacement ideally requires a high level of monitoring [2,3]. "Sensing the future before it occurs" is the desirable way of eliminating equipment problems before they occur [4]. There is a major need to develop and implement reliable high temperature harsh environment sensors that can be easily deployed in a variety of industry environments to achieve the goals of improved process control, higher efficiency, and reduced operational costs. These sensors must be constructed from materials that can function in high temperature environments (typically 400°C – 1000°C) and under a variety of oxidizing and reducing gases conditions that exceed the functional range of conventional silicon microelectronics [5].



Figure 1. 1. The total annual energy consumed in the U.S. over the past 7 decades reported by the U.S. Energy Information Administration (EIA) [1]. Petroleum and natural gas are the main energy sources for the industrial and transportation sectors.

The demand for high temperature harsh environment sensors that operate in hostile environments containing corrosive gases has increased rapidly over the past decades, particularly for use in power plants, aerospace, and advanced manufacturing. For example, the sensing of hydrogen gas leaks is very critical under many industrial environments since a 4% hydrogen leak could result in an explosion [6].

Surface acoustic wave (SAW) sensor devices possess attractive and unique characteristics for use as a harsh environment sensor platform to potentially detect  $H_2$  gas, such as piezoelectricity, low cost, small size, free battery (passive) and operation at high temperatures. To perform properly, the functionality of the SAW sensor platform requires three elements: a piezoelectric substrate, stable electrodes, and a stable selective gas sensing layer [7-9].

This thesis discusses the results of measurements aimed to explore the sensitivity, selectivity, and stability of Yttria-Stabilized Zirconia (YSZ) thin film materials for use as a hydrogen gas sensing layer for integration into a SAW sensor or other sensor platform. The thin sensing YSZ film must be stable in a range from room temperature up to 1000°C in air.
The scope of this research project encompasses the following: (i) optimization of synthesis parameters for YSZ thin films deposited onto a langasite (LGS) single crystal piezoelectric substrate for potential use in hydrogen sensing; (ii) characterization of as-grown and annealed YSZ films on LGS; (iii) decoration of the YSZ sensing layer with Pt catalyst nanoparticles; (iv) characterization of the morphology of Pt nanoparticles versus annealing treatments; (v) measurements of the reactivity of YSZ and Pt/YSZ thin films to  $H_2/N_2$  mixtures ( $H_2:N_2 4\%:96\%$ ) at temperatures from 400°C – 600°C; and (vi) extraction of ionic conductivity data for YSZ and Pt/YSZ thin film configurations in a controlled atmosphere furnace from 400°C – 600°C using an impedance/gain-phase analyzer.

## 1.2 Hydrogen Sensors for Use in High Temperature Harsh Environments

High temperature gas sensors are needed to solve gas detection and monitoring problems within high temperature operating environments (up to  $1000^{\circ}$ C), such as those encountered in gas turbine power plants and internal combustion engines. In addition to hydrogen exposure, high temperature gas sensors are also subject to other harsh environment conditions, such as high pressures and potentially severe vibration. The detection as well as the monitoring of gases, such as nitrogen dioxide (NO<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), ammonia (NH<sub>3</sub>), hydrogen (H<sub>2</sub>), etc., are critical in high temperature environments (> 350°C) due to their harmful and dangerous threat to humans and the ecosystem. A smart sensing system ideally controls the combustion strategies and therefore optimizes efficiency and emission reduction. Combustion is a complex process, which involves both physical and chemical reactions with significant heat transfer, energy dissipation, and chemical constituent change.

Therefore, the hydrogen sensing system in need is expected to be integrated with other sensing technologies, such as mechanical sensors [10], pressure sensors [11], temperature sensors [12], UV sensors [13], other gas sensors [14], thermal flow and viscosity sensors [15], and wireless sensors [16].

Hydrogen is widely used in industrial applications such as fossil fuel production, chemical production, power plants, fuel cells, food production, semiconductor manufacturing, aerospace, and automotive industries. As a new clean renewable energy, hydrogen energy is also receiving increasing attention [1,6]. It is highly flammable in concentrations ranging from 4% to 75% by volume, with its lowest explosion limit being 4.1%, making the need for placing hydrogen sensors near high concentration storage facilities essential. Therefore, the development of efficient and reliable sensors for process monitoring and leak detection applications is very much needed in the development of a hydrogen energy economy. Room temperature sensors that detect hydrogen have been fabricated with various active materials including GaN, ZnO, SnO<sub>2</sub>, WO<sub>3</sub>, and TiO<sub>2</sub> [17-20]. In some application fields, the sensors are required to be placed in environments where temperatures may exceed 600 °C [17-20]. Based on an industrial manufacturing and research survey [21], hydrogen gas sensors can be categorized into one of five classes based on different working principles of each technology [21-25]:

*Electrochemical hydrogen sensors* oxidize hydrogen at the surface of a sensing electrode coated with a catalyst, such as platinum, which gives rise to a potential difference. Electrochemical sensors have a high sensitivity to hydrogen and consume very little power during operation, which is particularly useful in some applications, such as in automobiles. The sensitivity of electrochemical sensors decreases with time, mainly due to deterioration of the catalyst [21-25].

*Metal-oxide semiconductor hydrogen sensors* consist of a metal oxide layer with semiconductive properties that change as hydrogen gas diffuses into the sensing layer and reacts with oxygen at the semiconductive metal-oxide surface, thereby changing the electrical conductivity. The stoichiometry of the oxide film and oxygen vacancies play an important role in the detection scheme. Metal oxide sensors are small, low cost, and easily mass produced. Another configuration of hydrogen sensors has a structure consisting of three layers: a metal layer, an insulator oxide layer, and a semiconductor layer. This class of sensors works on the principle of charge build-up and associated work function changes of the active layer, which is usually a noble metal. This type of technology can operate in the absence of atmospheric oxygen [21-25].

*Catalytic hydrogen sensors* consist of four thin platinum wires each embedded into a ceramic pellistor and connected to each other in a Wheatstone bridge configuration. The pellistors are heated and hydrogen is oxidized on the active bead (thin platinum wires embedded in a porous alumina ceramic) surface causing an increase in temperature and an increase in the resistance of the platinum filament. Catalytic sensors employ a well-developed technology but are not very specific to hydrogen and will respond to any combustible gas. The presence of oxygen is essential to their operation [21-25].

*Optical hydrogen sensors* operate based on the change in the properties of a sensitive layer following hydrogen absorption. Hydrogen sensors may operate in two ways, detect a change in light transmittance across an optical fiber due to a change in the absorption coefficient and refractive index, or exploit a special feature known as Surface Plasmon Resonance. Typical metals that support surface plasmons are silver, palladium, platinum, and gold. Optical sensors may operate in the absence of oxygen [21-25].



Figure 1. 2. Example of SAW sensor devices (A) Portion of a piezoelectric LGS wafer showing photolithographically patterned SAW devices fabricated in the UMaine clean room facility (B) Schematic illustration of a SAW resonator device (C) Nanocomposite Pt-ZrO<sub>2</sub> IDT electrodes that remain stable up to 1000°C [28] (D) Hillocks formed on the surface of a YSZ film on an LGS substrate due to thermal stresses.

*Surface acoustic wave (SAW) hydrogen sensors* use a hydrogen sensing film on a piezoelectric substrate covered with two sets of interdigital transducers (IDT) to measure changes in acoustic wave velocity as gas interacts with the surface. Surface acoustic wave (SAW) gas sensors are very attractive due to their advantages including remarkable sensitivity, fast response and recovery speed, minimal power requirement, low price, small size, good reliability, remote wireless operation ability and compatibility with digital system. For surface acoustic wave devices, the great majority of energy is concentrated near the surface of piezoelectric crystal within a few wavelengths [21-25].

SAW sensors are highly sensitive to any change of the physical or chemical properties on the surface of piezoelectric substrate, such as electrical conductance, elastic moduli, mass loading and permittivity of a sensitive film. The velocity and amplitude of surface acoustic wave are modified when the physical and chemical properties of sensitive films change as a target gas adsorbs or desorbs [20,26,27]. Figure 1.2 shows an example of SAW sensor devices that have been fabricated in the UMaine clean room.

A piezoelectric langasite La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub> (LGS) wafer oriented along Euler angles {0°. 138.5°, 26.7°} was used as a substrate for the SAW high temperature sensor. The langasite crystal has a trigonal crystal system and high-quality crystals have been fabricated using a Czochralski crystal growth method. These LGS crystals exhibit no phase change up to their melting point of 1470°C and highly polished wafers are commercially available [28,29]. Using Pt-ceramic electrodes, such as Pt-ZrO<sub>2</sub> [30], the interdigital transducers have been shown to remain stable up to 1000°C. Defect features such thin film hillocks can arise after thermal treatments due to thermal stresses and need to be minimized for long-term reliable sensor operation.

### 1.3 Properties of Yttria-Stabilized Zirconia Materials

Solid electrolytes based on stabilized zirconia have been studied since the discovery of electrolytic oxygen evolution from  $ZrO_2$ - $Y_2O_3$  solid solutions by Nernst in 1899 [31]. This was the first finding which clearly illustrated that ionic conductivity exists in the solid state. The ionic conductivity in these solid solutions occurs via motion of oxide ionic vacancies ( $V_{\ddot{o}}$ ) generated due to entropy and charge compensation. Stabilized zirconia ceramics have been the subject of extensive scientific research during the last 45–50 years owing to their diverse use in fuel cells,

oxygen separators, oxygen pumps, and electrochemical gas sensors, to name a few of the applications. Thus, stabilized zirconia materials have undergone many advances in manufacturing technology over many decades [32]. The number of publications has been constantly growing since 1970, and now the task of developing zirconia-based solid electrolytes is focused heavily on solid oxide fuel cells and oxygen gas sensors for use at high temperatures [33].

The major success of zirconia-based materials is their use as gas sensors for the detection of equilibrium oxygen partial pressure in automotive exhausts [33]. Despite this attention and commercialization of YSZ-based automotive oxygen sensors, several questions remain to be resolved, including the temperature and concentration dependence of the structural disorder and its interrelation with the high ionic conductivity which underlies many of the industrial uses of these electrolytes.

Zirconia-based solid electrolytes can be represented as  $ZrO_2 + R_2O_3$  (R: rare-earth element), have a centered cubic lattice (fluorite-type). More specifically, zirconia-based solid solutions can be expressed as follows:

$$ZrO_2 + xR_2O_3 \tag{1.1}$$

where x is the mole fraction of the substitutive ion or the mole fraction of  $R_2O_3$  solid solution [44,45]. The cubic phase of ZrO<sub>2</sub> can be stabilized by adding another oxide component such as CaO, MgO, Sc<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub>. The addition of Y<sub>2</sub>O<sub>3</sub> is particularly effective in producing high ionic conductivity and is the most widely used zirconia-based system.



Figure 1. 3. Bulk equilibrium phase diagram for the Zirconia (ZrO<sub>2</sub>) – Yttria (Y<sub>2</sub>O<sub>3</sub>) system.

The  $ZrO_2$ - $Y_2O_3$  phase diagram, shown in figure 1.3, illustrates the effect of  $Y_2O_3$  on the stability ranges of the three zirconia polymorphs - monoclinic (m), tetragonal (t), and cubic (c) as well as regions where a stable solid solution with the fluorite structure can be defined [34,35,37,38].

At equilibrium, pure zirconia, ZrO<sub>2</sub>, adopts three different crystalline structures from room temperature up to its melting point. The monoclinic baddeleyite structure (m-ZrO<sub>2</sub>) is stable under ambient conditions, with the Zr<sup>4+</sup> cations located in a distorted seven-fold coordination. At T ~1097°C , the tetragonal distorted fluorite structure (t-ZrO<sub>2</sub>) forms with Zr<sup>4+</sup> cations surrounded by eight oxygen anions, but with two slightly different Zr<sup>4+</sup> - O<sup>2+</sup> distances. Perfect eight-fold coordination is achieved at T ~2371°C, with a transformation to a cubic fluorite structured phase (c-ZrO<sub>2</sub>), followed by melting at T ~2715°C.



Figure 1. 4. Schematic representation of the insertion of Yttria (Y<sub>2</sub>O<sub>3</sub>) into the zirconia (ZrO<sub>2</sub>) lattice which leads to the creation of oxygen vacancies [45].

The ambient cubic form of yttria c- $Y_2O_3$  can also be viewed as being derived from the c-ZrO<sub>2</sub> fluorite structure by replacing Zr<sup>4+</sup> cations with Y<sup>3+</sup> cations and removing <sup>1</sup>/<sub>4</sub> of the oxygen anions. There are two six-fold-coordinated and symmetry-independent Y<sup>3+</sup> cations, which have anion vacancies arranged along either a face diagonal or a body diagonal [39,40].

The zirconia structure with the highest ionic conductivity is the cubic fluorite phase, which is not the equilibrium stable phase at room temperature. Doping zirconia with larger cations and/or introducing oxygen vacancies stabilizes the cubic fluorite structure as shown in figure 1.4. The vacancies tend to increase the effective ionic size, making the fluorite phase more stable, and enhance the ionic conductivity by creating more sites for ion motion [42].

The conductivity of stabilized zirconia depends on the exact dopant level as shown in figure 1.5. Increasing the amount of doping induces more oxygen vacancy formation, thereby increasing conductivity.



Figure 1. 5. The conductivity of YSZ at 1000°C as a function  $Y_2O_3$  content for unannealed and annealed samples with 5-11 mol % ( $\Box$ ,  $\blacksquare$ ) and a co-precipitated 8 mol% YSZ sample ( $\circ$ ,  $\bullet$ ). The maximum conductivity occurs over the range of 7.7 to 8.5 mol% after annealing [41].

At low Y<sub>2</sub>O<sub>3</sub> concentrations (x < 0.15), there are regions of the crystal ~20 angstroms (Å) in size which contain relatively few oxygen vacancies, causing the lattice to undergo a slight tetragonal distortion of the type observed in the tetragonal phase of (ZrO<sub>2</sub>)<sub>1-x</sub> (Y<sub>2</sub>O<sub>3</sub>) <sub>x</sub> at x < 0.09.

The oxygen vacancies are preferentially arranged in pairs on nearest-neighbor anion sites in the  $\langle 111 \rangle$  fluorite directions, with a cation located between them and extensive relaxations of the surrounding nearest-neighbor cations and anions. As the yttria content increases, these  $\langle 111 \rangle$ vacancy pairs pack together in  $\langle 112 \rangle$  directions to form aggregates, whose short-range defect structure resembles the long-range crystal structure of the ordered compound Zr<sub>3</sub>Y<sub>4</sub>O<sub>12</sub>.

The aggregates are typically ~15 Å in diameter, though both their size and density increase slightly with *x*.



Figure 1. 6. Schematic of oxygen vacancy migration between YSZ unit cells [45].

As temperature increases, these aggregates remain stable up to the melting point. There is also an increasing number of single vacancies and  $\langle 111 \rangle$  vacancy pairs (with surrounding relaxation fields) as *x* increases, and these isolated clusters become mobile at T > 500°C resulting in the high ionic conductivity of the material [49].

It may be expected that by increasing dopant content ( $Y_2O_3$ ) will increase the ionic conductivity due to the increased O vacancy concentration [43,44]. However, a higher amount of  $Y_2O_3$  was found to lower the mobility of O vacancies by increasing the diffusion energy across the Y–Y common edge of the lattice as compared to the Zr–Y common edge. Considering these observations, it has been proposed [9,43] that the anomalous decrease in the ionic conductivity with increasing x is a consequence of the decreasing mobility of the isolated defects, possibly due to blockage by an increasing number of the static aggregates as the vacancies start to interact significantly, thereby lowering their mobility and reducing conductivity. The maximum ionic conductivity in YSZ occurs at a composition of 7 – 9 mol%  $Y_2O_3$  between 327 – 1227 °C and the highest conductivities occur at ~8 mol % YSZ (denoted as 8-YSZ) as shown in figure 1.5 [43,44].

To maintain overall charge neutrality as  $Y^{3+}$  cations replace  $Zr^{4+}$  cations in the zirconia unit cell, one oxygen vacancy is created for each two substituting  $Y^{3+}$  cations.

This process can be summarized by using the well-known Kröger-Vink notation [46], which is also schematically illustrated in figure 1.6.

$$Y_2 O_3 \xrightarrow{ZrO_2} 2Y'_{Zr} + 3O_0^X + V_0^{..}$$
(1.2)

In this notation,  $Y'_{Zr}$  represents a Y<sup>3+</sup> cation in a Zr site with an apparent negative charge,  $V_{\ddot{O}}$  is a vacancy in the oxygen site with double positive charge, and  $O_{O}^{X}$  is a lattice oxygen, i.e., oxygen anion in the oxygen site with net charge of zero. This formation of oxygen vacancies allows oxygen ion O<sup>2-</sup> migration, as schematically represented in figure 1.6.

### 1.4 Strategies for Using Catalyzed YSZ Films to Detect Hydrogen Gas

Heterogeneous catalysis is a form of catalysis where the phase of the catalyst differs from that of the reactants. A heterogeneous catalyst is typically comprised of two major components: active metal particles and a supporting substrate. In concept, the reactants diffuse to the catalyst surface and physically absorb to form a chemisorption bond. Heterogeneous catalysis is of massive importance in the chemical industry that aims to use tailored ultra-selective catalysts for sustainable product manufacture, and metal nanoparticles supported on insulator substrates constitutes an important class of these materials [47,48].

The properties of supported metal particles can be tuned by (i) the control of particle size and (ii) manipulation of metal-support interactions [77]. Nanometer sized metal particles deposited on high surface area supports yield specific electronic properties and/or geometrical features in what is known as the phenomenon of strong metal-support interaction (SMSI) [76-79]. It has been found that the back-spillover charge of the ionic species from the support to the gas-exposed metal catalyst surface can be thermally induced without any electrical polarization by using nanoparticles supported on ionic or mixed ionic conductive ceramics such as yttria-stabilized zirconia (YSZ) [47-51]. Heterogeneous catalysis using supported nanoparticles of noble metals (Ag, Au, Pd, Pt, Rh, or Ru) typically uses particle sizes ranging from 1 – 100 nm diameter. For example, SnO<sub>2</sub> gas sensing materials that are doped with noble metals (Pt, Pd, Ag, Au, Ru, etc.) or metal oxides (CuO, ZnO, WO<sub>3</sub>, TiO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, etc.) are well known to improve their sensitivity, low-temperature operation performance, and selectivity to specific target gas [53-57,84].

By adjusting the fabrication processes, sensors made with Pd surface modified SnO<sub>2</sub> films exhibit very high response towards H<sub>2</sub> compared to other material combinations [20]. Several recent reviews have been published on nano-catalysis citing the tremendous development of these materials and their impact over the past few decades [47,52,58,59]. Many of the experimental studies have focused on correlating nanocatalyst activity with particle size, geometry, composition, oxidation state and chemical/physical environment, which all play a role in determining nanoparticle reactivity [52]. The investigation of heterocatalytic activity of Pt nanoparticles (NPs) deposited on YSZ films towards H<sub>2</sub> in this thesis work was motivated by the fact that Pt NPs have been adapted in widespread applications such as electro-catalytic systems, hydrogen storage, light emitting diodes (LEDs), solar cells, and photocatalytic applications.

As a catalyst of high activity and selectivity, Pt NPs utilized in the electro-chemical applications such as fuel cells can significantly improve the reaction efficiency for the oxidation and oxygen reduction benefitted by the enlarged surface area to volume ratio.

Pt NPs can also be utilized to improve the hydrogen storage capacity in carbon- and metalorganic based spillover hydrogen storage processes by dissociating hydrogen molecules onto receptors [60,61]. Platinum nanoparticles are chosen as the catalyst for nanomaterials-based hydrogen sensors, due to their well-established catalytic properties and high surface area. As an example, embedding platinum nanoparticles into a graphene aerogel provides a highly catalytically active material, which can transfer heat with minimal additional mass and is stable at elevated temperatures [62,63].

### 1.5 Gas Sensing in Metal – Metal Oxide Catalytic Systems

The concept of strong metal-support interactions (SMSI) introduced by Tauster [49] and others to understand catalytic activity is realized even on different supports when the active catalytic phase has the same nanoparticle dispersion. The factors that affect the form and degree of SMSI include the amount and configuration of precious metal [65,66], the nature of support [64,67] and catalyst preparation methods [68]. Many reports in this field focus on the metal-support interactions on a single support for different catalysis configurations, such as Rh/-, Pt/- and Au/TiO<sub>2</sub> [69,70], Pt/C with different carbon materials [71,72], Pt/SnO<sub>2</sub> [73] and Pt/Al<sub>2</sub>O<sub>3</sub> [65]. However, very few studies have investigated metal-support phenomena in catalytic systems that have supporting substrates with appreciable ionic conductivity [74]. Ionic conductivity can modify the catalytic activity of metal nanoparticles. Electron transfer between the oxygen anions in the support and the nearby metal nanoparticles is thought to increase the local electron density and hence reactivity [75]. The charge is transferred from the solid with the lower work function to the solid with the higher work function, hence modifying the catalyst activity.

The dominant interaction, however, is believed to be an ionic attraction as the result of a charge transfer from the reduced cation to the adjacent metal atom which has higher work function [76]. The support is not only a carrier for active catalyst compounds but also can improve the dispersion of the noble metals and suppress the sintering at high temperatures [58]. Typical supports used in catalysis can be classified as either high ionic conductivity, such as YSZ, or non-ionic conductive supports, such as alumina or sapphire (Al<sub>2</sub>O<sub>3</sub>) [77].

In YSZ, for example, oxygen anions (O<sup>2-</sup>) are highly mobile and contribute to charge transport over the temperature range of 400 - 1200°C. Wagner [78] was the first to propose in 1970 the use of ion transport in heterogeneous catalysis for the measurement of oxygen activity in metal and metal oxide catalysts. In these oxygen ion conductive solid electrolyte systems, the ionic conductivity is enhanced by the addition of a lower-valent cation which is charge-compensated by the formation of additional oxygen vacancies that are highly mobile at elevated temperatures.

The effect of spillover-backspillover mechanisms play an important role in the overall catalytic activity. Spillover is the migration of one or more adsorbate species from the dispersed catalyst (Pt) to the support (YSZ), while backspillover is the migration of ( $O^{2-}$ ) ions from the support to the metal catalyst. In the case of  $O^{2-}$  conductor supports, a general reaction scheme of oxygen spillover proposed in catalytic systems is functionalized without (equations 1.3 and 1.4) and with metal support interaction (equations 1.5, 1.6 and 1.7) [79].

To clarify the catalytic effect promoted by Pt NPs on a YSZ surface, it is important to investigate the nature of the H<sub>2</sub> interaction with the surfaces of YSZ-based sensors.

The YSZ surface can be prepared to be covered with either atomic (O–, at high temperatures) or molecular ( $O^{2-}$ , at low temperatures) species, interacting with lone pair electrons in oxygen rich atmospheres at temperatures above 400°C [79].

When H<sub>2</sub> is introduced, it reacts with the oxygen species, with the release of electrons responsible for increasing the YSZ conductivity. Based on the preceding reactions, the proposed model for H<sub>2</sub> interaction with O species over a YSZ surface is [79]:

$$2H_2 + O_{2(YSZ)} \rightarrow 2H_2O_{(g)} + e_{YSZ}$$
 (1.3)

$$H_2 + O_{YSZ}^- \to H_2O + e_{YSZ}^- \tag{1.4}$$

When Pt NPs are present at the surface, an additional catalytic step is introduced, as Pt can react with H<sub>2</sub>, by breaking the H-H bond and bind directly with atomic H, in a process known as splitover [79]. Following that step, Pt-bound H can migrate to the surface of YSZ to react with the adsorbed oxygen species (spillover) to further promote a free electron.

The proposed model [79] for Pt sensitization of the  $H_2$  interaction with O species over Ptdecorated YSZ surface can be described by the following equations :

$$H_2 \xrightarrow{Pt} 2H_{Pt} \tag{1.5}$$

$$4H_{Pt} + O_{2(YSZ)} \rightarrow 2H_2O + e_{YSZ} \text{ (Spillover)}$$
(1.6)

$$2H_{Pt} + O_{(YSZ)} \rightarrow H_2O + e_{YSZ} \quad \text{(Spillover)} \tag{1.7}$$

As adsorption is facilitated by the introduction of this step to the kinetic process, a chemical sensitization phenomenon is present, increasing the material's (Pt/YSZ) sensing response to H<sub>2</sub>, as has been reported for other metal oxide-based sensors [79].

Thus, an increase in sensor response is expected, as observed for the Pt/YSZ when exposed to hydrogen. The term backspillover of the species migration from the support to the catalyst is used to distinguish it from the common spillover term used in catalytic systems to depict the migration of species in the opposite direction. In this thesis, impedance spectroscopy measurements were acquired over the temperature range 400-600°C to further investigate the mechanism behind the observed catalytic effects, performed to deconvolute of different contribution to  $H_2$  sensing response. Yamazoe [80] has proposed two types of sensitization mechanisms for enhancing the sensing response of gas sensors due to the presence of noble metal NPs: (i) chemical sensitization and (ii) electronic sensitization, as shown in figure 1.7.

In chemical sensitization, metal NP additives promote the chemical reaction between the sensing material and the target gas by a spillover effect, whereas in electronic sensitization, the change in the oxidation state of noble metal NPs occurs primarily because of the electronic interaction, i.e., the noble metal acts as an electron donor or acceptor on the surface of the sensing material. Noble metals possess high electrical conductivity that facilitate rapid electron transfer and catalyze the oxidation of reducing gas molecules. Because metal oxides generally have a lower work function than metals, upon intimate contact of the metal oxide with noble metals, electrons will transfer from the metal oxide to the noble metal, resulting in contraction of conduction channels inside the metal oxide.



Figure 1. 7. Gas adsorption on noble metal NPs can be influenced by either a (left) chemical sensitization or (right) electronic sensitization mechanism [80].

Accordingly, upon exposure to target gases a larger change in the diameter of conduction channel will result in a higher response in noble metal decorated metal oxide relative to pristine metal oxide [80].

The work in this thesis focuses on the material system consisting of Pt NPs on YSZ films grown on langasite substrates. This configuration is very relevant for the design and operation of Surface Acoustic Wave Resonator (SAWR) sensor devices patterned on a piezoelectric langasite (LGS) substrate as schematically shown in figure 1.8. that are routinely fabricated using FIRST's clean room device fabrication facilities. The Pt/YSZ overlay films investigated in this thesis work can be deposited over an entire patterned wafer of SAWR devices. However, many of the experiments performed in this thesis work focused on Pt nanoparticle – YSZ interactions using blanket films deposited on LGS single crystal substrates, especially for the impedance spectroscopy measurements. This procedure enabled advances in Pt/YSZ film development to be efficiently carried out without adding the complication of lithographic patterning of actual SAWR devices.



Figure 1. 8. Schematic cross-sectional diagram of a Surface Acoustic Wave Resonator (SAWR) device containing thin film Pt/Al<sub>2</sub>O<sub>3</sub> interdigital electrodes and a Pt/YSZ sensing layer on a piezoelectric langasite (LGS) substrate. A Zr adhesion layer is used under the Pt/Al<sub>2</sub>O<sub>3</sub> electrodes, and a capacitive coupling technique is used for sensor interrogation [81-83].

## **1.6 Thesis Organization**

The principal objectives of this research were to (i) investigate the growth of YSZ thin films on piezoelectric langasite substrates using an RF-magnetron sputtering process and study YSZ film stability in high temperature harsh environments (up to  $1000^{\circ}$ C); (ii) fabricate Pt nanoparticles on YSZ films and characterize their dispersion; and (iii) measure the reactivity of Pt/YSZ films to 4%H<sub>2</sub>/96N<sub>2</sub> exposure using impedance spectroscopy methods within the context of metal-support interactions in heterogeneous catalysis over the temperature range  $400 - 600^{\circ}$ C.

Figure 1.9 shows a diagram that maps out the parameter space used for all the YSZ and Pt/YSZ thin film samples that were synthesized, annealed, and exposed to hydrogen gas throughout the research project timeline.

The thesis is organized in the following manner. Chapter 2 reviews the main aspects of the experimental techniques used in the work including film deposition, materials characterization, surface analysis, crystallographic structure, and impedance spectroscopy. Chapter 3 focuses on YSZ film synthesis including the influence of deposition and thermal annealing parameters on the resulting YSZ film properties. The stability of YSZ films for harsh environment sensing applications up to at least 600°C is extremely important since the thin film ionic conductivity must be reproducible in order to make a stable sensor. Chapter 4 discusses the deposition of Pt nanoparticles on YSZ films on langasite including synthesis to different Pt thicknesses under various deposition conditions. Annealing treatments up to 800°C were developed to stabilize the Pt/YSZ nanostructure within the thin films, and these samples were exposed to 4% hydrogen at range from 400-600°C during impedance spectroscopy measurements as documented in Chapter 5. Chapter 6 discusses major conclusions and concludes with possible directions for future work.



Figure 1. 9. Diagram showing all YSZ and Pt/YSZ thin film samples that were synthesized, annealed, and exposed to hydrogen gas throughout the research project timeline. The main parameters include deposition temperature, deposition rate, substrate bias, and Pt thickness.

### **CHAPTER 2**

# EXPERIMENTAL METHODS FOR THIN FILM SYNTHESIS AND MATERIALS ANALYSIS

### **2.1 Introduction**

The experimental work carried out in this thesis involved the methodology of synthesis, processing, and characterization of 8mol% Yttria Stabilized-Zirconia (YSZ) thin films on langasite substrates with and without added platinum (Pt) nanoparticle layers at the surface. Instrumentation present within UMaine's Frontier Institute for Research in Sensor Technologies (FIRST) was used to synthesize and investigate the properties of the Pt/YSZ films at the nanometer scale and up to macroscopic dimensions. In addition to thin film synthesis deposition and thermal annealing, X-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), scanning electron microscopy (SEM), and impedance spectroscopy were the principal techniques that were used throughout this research, and an overview of each technique is discussed in this chapter.

# 2.2 Synthesis of YSZ Thin Films with and without Pt Nanoparticles

YSZ thin films used in this work were synthesized using RF magnetron sputtering of an 8mol% YSZ target in an Argon : Oxygen plasma [85]. The technique of film deposition by sputtering has been widely developed since the discovery of the method in 1852 by Sir W. R. Grove. A major advantage of sputtering is that stoichiometric binary and ternary compounds, such as metal-oxides or metal-nitrides, can be deposited with high precision. Furthermore, the choice of sputtering has conceptual simplicity as well as easy scalability to manufacturing.



Figure 2. 1. Schematic cross-section of an RF-magnetron sputter deposition system used to grow YSZ films in the ultrahigh vacuum Thin Film Deposition and Processing System within UMaine's Frontier Institute for Research in Sensor Technologies (FIRST).

The mechanisms of momentum transfer from plasma ions during the sputtering process causes target material to be ejected into the gas phase and deposited on a nearby substrate using the configuration shown in figure 2.1. Based on this concept, much has been accomplished in the science of sputter-deposition of various thin film materials, ranging from metals to oxides, onto numerous substrates [86]. Magnetron sputtering utilizes a magnetic field parallel to the target surface, which in combination with the electrical field causes the secondary electrons to orbit in a closed circuit in front of the target surface, due to the Lorentz force.

This results in significantly increased ionization efficiency, compared with other sputtering configurations, since each electron is able to ionize more working gas atoms close to the target surface. This in turn means an increased ion bombardment of the target and, therefore, higher evaporation rate. Due to the increased ionization achieved using magnetron sputtering, the glow discharge can be maintained at lower operating pressure ( $\sim 10^{-3}$  Torr) that increases the deposition

rate due to reduced scattering of the evaporated atoms. During the sputtering process, it is also possible to use a reactive gas (oxygen) to impact film stoichiometry and this process is referred to as reactive sputtering [86-89]. During reactive sputtering, the partial pressure of the reactive gas (and the inert gas) is carefully regulated to obtain the correct film stoichiometry [87]. The RF-magnetron sputtering technique avoids charge built up on the target surface by switching the polarity of target. By doing this, are discharges at the target surface that may occur when sputtering low conducting materials are minimized [86-89]. The magnetic field increases the plasma density in the RF sputtering process which leads to an increase of the current density at the cathode target, effectively increasing the sputtering rate at the target. Also, because of the lower gas pressure, the sputtered particles have a lower probability to be scattered by the gas, which results in a stable deposition rate [86-89].

The YSZ films were deposited using a reactive Ar/O2 plasma sputtering gas. Reactive gas consumption by reaction with the sputtered material from the target is effective in lowering the overall gas density in the deposition chamber. When the gas flow reaches a certain level, there is an oxygen oversaturation at the YSZ target surface, and the sputtering rate drops rapidly, as a result, less reactive gas is consumed, and its partial pressure increases.

This threshold is monitored, and the gas flow is continually adjusted using a partial pressure feedback control so that stable depositions can be carried out at any working point [86-89].

The nanostructure and materials properties of YSZ thin films are highly influenced by several growth parameters that impact the growth kinetics including substrate temperature, gas composition, gas pressure, magnetron RF power, substrate bias, and type of substrate.

Structural zone models that were first devised by Thornton [90] have been proposed to categorize the structures of sputter-deposited thin films, in which the various structural zones can be represented as a function of the inert sputtering gas pressure (P) – i.e., deposition rate, and the relative temperature ( $T_s/T_m$ ), where  $T_s$  is the substrate temperature and  $T_m$  is the melting point of the material. Generally, four different zones are identified from these structural zone models:

- Zone 1 is proportional to very low deposition temperatures at which adatom diffusion is minimal. During film growth in Zone 1, columnar structure develops due to atomic shadowing that is imposed by the surface roughness. The columns are generally not single grains but are composed of smaller equiaxed grains or can even be amorphous. The orientation of the grains follows the random orientation of the film nuclei.
- Zone T corresponds to the transition at higher growth temperatures where grain coarsening occurs during coalescence of small islands with large surface-to-volume ratios, resulting in columnar grains with dense grain boundaries. However, orientation selective growth is incomplete, thus giving nearly random oriented crystallites and weak film texture in addition to a wide range of grain-sizes.
- Zone 2 occurs when the growth temperature is higher than in zone T where surface diffusioncontrolled growth becomes dominant, giving rise to a homogeneous structure along the film thickness composed of aligned columns with grain boundaries nearly perpendicular to the film plane.
- Zone 3 is manifested at the highest substrate temperatures where bulk diffusion processes such as grain growth and recrystallization become significant, resulting in a dense film structure with large textured columnar grains.

The main parameters used in our YSZ film work to probe aspects of the Thornton diagram for the YSZ/langasite system were substrate temperature and deposition rate (RF power). Note that both Zone 2 and Zone 3 are uninfluenced by the gas-pressure parameter since the substrate temperatures are high enough to ensure sufficient thermally activated surface and bulk diffusion and so the total gas pressure parameter was not changed. In addition, the substrate bias was chosen as another parameter to include in the structural zone model diagrams as discussed in Chapter 3.

The Ar:O<sub>2</sub> gas ratio was fixed to 95:5 for all YSZ film growths, corresponding to gas flows of 19.95 sccm for Ar and 1.05 sccm for O<sub>2</sub>, at a fixed total pressure of 6mTorr. The varied parameters that were used to influence the film nanostructure were deposition rate (RF power), substrate temperature, and substrate bias. Three substrate temperatures were used: 30°C, 400°C and 700°C; three YSZ deposition rates were used: 0.03 nm/s, 0.05 nm/s and 0.07 nm/s; and four different substrate biases were utilized: -300V, -100V, +100V and +300V. The influence of substrate bias will be discussed further in Chapter 3.

The thickness of the as-grown films was controlled *in situ* to be either 40 nm or 200nm using a substrate QCO calibrated against a profilometry thickness and XRR measurements.

The thicker films were used for XRD and impedance spectroscopy, and the thinner films were used for XRR analysis. Pt nanoparticles were synthesized on the YSZ film surfaces by *in situ* deposition of a Pt evaporant flux immediately following YSZ film growth using the method schematically shown in figure 2.2.

The Pt flux was generated by a 6 kW Telemark e-beam gun equipped with four 7 cc pockets. High-purity Pt (99.99995%) was evaporated with a rate calibrated and monitored in real-time by quartz crystal oscillators (QCOs).



Figure 2. 2. Schematic of the electron beam evaporation deposition process to create Pt nanoparticles on the YSZ film surface. The evaporation rate is controlled by temperature of the Pt source and is monitored by a quartz crystal oscillator (QCO).

The Pt source was sufficiently outgassed to minimize  $H_2O$ ,  $CO_2$  and  $H_xC_y$  contaminants in the film deposition chamber as measured by a Residual Gas Analyzer (RGA). After deposition of Pt onto the YSZ film surfaces, they were transferred via ultra-high vacuum to the XPS chamber for immediate chemical analysis.

## **2.3 Electronic Structure and Chemical Composition**

Chemical bonding and the chemical composition of the near-surface region of the Pt/YSZ thin films was characterized using X-ray Photoemission Spectroscopy (XPS). XPS measures the emission of photoelectrons and Auger electrons from a material under excitation by incident x-rays, and a precise analysis of observed binding energies of electron core levels assist in analyzing the chemical composition and local chemical bonding [91-93].

XPS is a surface-sensitive technique, with a sampling depth that depends on the energydependent inelastic mean free path of photoelectrons [92], and which is typically ~ 1-10 nanometers. The specific XPS apparatus used in this thesis consisted of an Al K $\alpha$  x-ray source (1486.6 eV) and SPECS hemispherical analyzer. The XPS chamber is linked to the deposition chamber through a transportation trolley line that allows for storage of up to 28 sample holders. All chambers are connected with a system-wide base pressure of ~2x10<sup>-9</sup> Torr. The trolley line is isolated from each chamber using gate valves so that the system can be used simultaneously by multiple users. Samples are brought from atmospheric pressure into the trolley via the introduction chamber. The use of the trolley system enabled direct chemical analysis of YSZ and Pt/YSZ thin films, identifying elements present and quantifying film composition, without the sample leaving UHV conditions.

The measured kinetic energy of a photoemitted core electron in XPS,  $E_{kin}$ , is governed by the well-known Einstein photoelectron effect:

$$E_{kin} = h\nu - [E(A^* - E(A)] - \Phi = h\nu - E_B - \Phi$$
(2.1)

where hv is the incident photon energy,  $E_B$  is the binding energy relative to the Fermi level that is determined by the electron energy difference between the ground state E(A) and the photoionized state E(A\*), and  $\Phi$  is the work function of the solid [92,93]. The probability for photoemission decreases exponentially as a function of depth below the surface and is dictated by the electron inelastic mean free path ( $\lambda$ ) which depends on the kinetic energy. About 95% of the XPS photoelectron signal arises within a sampling depth of  $3\lambda$  [92,93].

The photoelectrons emitted from the sample surface without any inelastic energy loss exhibit spectral lines or peaks, while electrons that undergo energy loss contribute to the background in the XPS spectrum. Figure 2.3 shows an example of XPS spectra acquired from a YSZ film (200 nm) deposited on a LGS substrate at 30°C. with the photoelectron peaks labeled by their atomic orbital. One intrinsic effect that is evident in the spectra is spin-orbit splitting, which occurs for orbital states with angular momentum  $1 \neq 0$ , as observed in the Zr and Y 3d doublet. In the final state, after the electron has been ejected, the atom can be in one of two excited states, depending on the spin of the remaining electron in the orbital and whether the spin of the remaining electron and the orbital angular momentum are parallel or antiparallel, the state will have different energies, and so the ejected electron can have two different energies as well. Then, p, d, and f orbitals are all split into two peaks labeled with the multiplicity of the final orbital state and separated by an energy that is characteristic of the mass of the atom [92]. Charging and charging shift reference are two XPS electrostatic phenomena that depend on the properties of the material being analyzed which should be considered while collecting data. Charging is a common problem affecting samples with a low conductivity connection to ground, which occurs with insulating/ oxidized substrates such as LGS. If the sample surface is not well grounded, the ejected electrons cause the surface to charge positively to a higher potential relative to the detector, which reduces the kinetic energy of the electrons into to the detector [94].

It is a common practice to use a charge reference to correct for steady-state surface charging by adding a constant offset to the entire spectrum. The oxygen 1s peak at 529.0 eV is a reliable charge reference or the carbon 1s peak at 284.5 eV can also be used if it is present (along with oxygen) for charge correction applied to annealed and exposed to air samples [95, 100-102].



Figure 2. 3. XPS spectra from (red scan) as-grown YSZ thin film deposited on a LGS substrate at 30°C and (green scan) YSZ single crystal obtained from MTI Corporation. These survey scans show O 1s, Zr 3d, Y 3d peak regions for the thin film and the single crystal and C 1s for the single crystal. The scans are charge referenced to O 1s at 529.0 eV and C 1s at 284.5 eV (when present).

The XPS spectra in figure 2.3 have several resonance peaks corresponding to plasmon excitations, which are collective oscillations of the conduction band electrons with plasmon energy losses appearing at regular intervals. When the background parameters are fitted to an electron energy loss spectrum (as explained in detail in chapter 3), plasmon losses can be accurately accounted for based on the background subtraction, line shape and quantification [92,96,97].

XPS data were collected in two different modes: survey scans and high-resolution mode. In the survey scans, data were collected over a wide range of binding energies (0 - 1400 eV), which was used for the identification and quantification of elemental constituents. The survey scans are also useful to identify any contaminants on the sample surface. The high-resolution scans, figure 2.4, were obtained using a smaller energy window, with a higher density of data points and with a lower pass energy (15 eV) on the hemispherical energy analyzer [92,93,98,99].



Figure 2. 4. XPS spectra of O 1s, Zr 3d, Y 3d and Pt 4f acquired from a 200 nm thick YSZ film deposited on a LGS substrate at 30°C that was subsequently annealed in the air at 800°C for one hour. Peaks are all fitted according to a LF lineshape and include a Tougaard background.

The chemical composition within the surface region of the Pt/YSZ samples are reported in terms of atomic percent and they were derived from the integrated XPS peak intensities corrected by relative sensitivity factors (RSFs) to account for different photoionization cross sections for each element. Using the standard XPS quantification method, peak areas characteristic of an element in a compound,  $I_i$ , are compared to peak areas of all other elements within the same compound. Scofield has published a list of theoretically determined cross section values that are included with the CasaXPS software used for spectrum analysis [92,93]. To determine an atomic concentration within a sample,  $C_i$ , the following formula was used [103,104]:

$$C_{i(Y)} = \frac{n_i}{\sum_{j=1}^m n_j} = \frac{\frac{I_{i/_{RSF_i}}}{\sum_{j=1}^m I_{j/_{RSF_i}}}}{\frac{I_{Z'/_{RSF_2r}} + I_{O/_{RSF_0}} + I_{Y/_{RSF_Y}}}$$
(2.2)

To get accurate values, the quantification method must involve correction for transmission function of the electron analyzer [92,105] and background subtraction of the inelastically scattered electrons [92,105]. The most correct way to perform background subtraction is by using the Tougaard formulism [92,105] that poses a realistic model for the energy loss process [92,105].

Experimentally, I measured the atomic percentage of YSZ single crystals elemental components to check that my film compositions numbers close to the one used by CasaXPS. The YSZ single crystal thermally annealed up to 200°C for one hour in vacuum to clean the surface from the carbon and hydroxide.

### 2.4 Crystallography and Morphology

A Panalytical (Malvern) MRD Pro X-ray diffraction (XRD) system (see Fig. 2.7) was used in this work to identify crystalline phases present in thin films and to characterize their structural properties including the presence of defects, grain size, phase composition, stress, etc. [106]. The system has a fixed Cu target excited by electrons from a hot filament, which produces nonmonochromated Cu K $\alpha$  radiation with a wavelength of 1.54059A°, and the sample is rotated along  $\omega$  to adjust the incident angle  $\theta$  [107]. According to Bragg's law, constructive interference of xrays from crystalline planes occurs when the path difference between scattered x-rays (2d.sin  $\theta$ ) is an integral number of wavelengths (n. $\lambda$ ), where, d is the lattice spacing,  $\theta$  is the scattering angle,  $\lambda$  is the wavelength of x-rays and n is an integer. Several different XRD configurations can be used including  $\theta$ -2 $\theta$  gonio scans, grazing incidence XRD, pole figures, and x-ray reflectivity measurements.



Figure 2. 5. Photograph of PANalytical MRD Pro X-ray diffraction system used for this work that is based on a 6-axis goniometer stage. A setup configuration of different incident x-ray optics and detectors were used depending on the specific measurement that was performed.

The XRD spectra from YSZ films were compared to ICDD PDF cards [108-110] representing patterns of three polymorphs of cubic-YSZ (PDF# 00-030-1468), cubic-Pt (PDF# 00-004-0802) and hexagonal langasite - LGS (PDF# 04-011-7881). PANalytical *Data Collector* software was used to run the XRD scans and Data Viewer software was used to analyze the spectra including areas and full-width-half-maximum (FWHM) of the peaks. The rest of this section discusses aspects of each of these types of XRD measurements. Figure 2.8 shows a diagram of a typical x-ray diffractometer configuration in which a sample is mounted on a stage between an x-ray source and a detector. The arms of the goniometer move the source and detector in a circle, adjusting  $\theta$  and 2 $\theta$ , while the sample stage moves and rotates the sample about three cartesian axes.

This allows the full range of motion for different types of XRD scans. Although Braggs's law is always true, the incident angle  $\omega$  is not necessarily equal to  $\theta$ .

The distinction between the angle of incidence on the crystal plane  $\theta$  and the angle of incidence on the sample surface  $\omega$  becomes important when the crystal planes are not aligned with the surface normal, or in certain measurements where the direction of a crystal is less important than the direction of the surface normal, figure 2.6. This scan is called a gonio scan, figure 2.6 in which  $\omega$  and 2 $\theta$  are adjusted in a reflection geometry, such that  $2\theta = 2\omega$ . During this scan, the magnitude of the x-ray scattering vector  $\Delta \vec{k}$  is variable with a constant direction and only surface aligned crystallographic planes can be detected [111-114].

However, there are two issues to consider when acquiring a gonio scan from thin film samples. The first is that there is usually crystallographic texture in thin films, and so a gonio scan will not show the peaks from planes that are not aligned to the surface of the film, which could affect phase identification. The other is that the piezoelectric LGS substrates are usually single crystals cut with a certain orientation not necessarily normal to the surface. LGS peaks are usually very sharp, but an angular offset  $\omega_0$  must be applied to  $\omega$  to detect a non-normal Miller plane at  $2\theta$ =  $2\omega + \omega_0$ .

Another measurement approach is to use a grazing incidence scan geometry as shown in figures 2.6. Typically,  $\omega$  is set at a small angle (less than 5°) and 2 $\theta$  is swept as usual [115-117]. In this case,  $\Delta \vec{k}$  is variable in both magnitude and direction. The grazing incidence allows the analysis of planes other than the surface-oriented ones. The diffracted intensity varies considerably depending on 2 $\theta$ .



Figure 2. 6. XRD scan geometry for gonio and grazing incidence scans. (a) Gonio scan  $\theta$ -2 $\theta$  geometry in which the direction of  $\Delta \vec{k}$  is not changed as 2 $\theta$  is scanned. (b) Grazing incidence scan in which both the direction and magnitude of  $\Delta \vec{k}$  changes during the scan.



Figure 2. 7. Comparison of XRD spectra from a cubic YSZ film on LGS substrate measured using different scan geometries (a)  $\theta$ -2 $\theta$  gonio scan method and (b) GIXRD method.



Figure 2. 8. (a) XRD scan geometry for pole figure diffraction where  $\Delta \vec{k}$  is set fixed while the sample is rotated through a full hemisphere of  $\chi$  and  $\varphi$  angles. (b) The continuous intensity distribution along  $\varphi$  indicates a (311) textured film with nearly random grain orientation within the plane of the film.

Thin film crystallographic texture and grain orientation can be investigated using XRD pole figure analysis. Pole figures can determine texture more completely than standard  $\theta$ -2 $\theta$  scans as it is possible to distinguish differences between (i) random orientation - no texture, (ii) fiber texture - where the in-plane orientation is random but with a preferred out-of-plane orientation, (iii) biaxial texture - with an inherent in-plane mirror symmetry, and (iv) epitaxy - where all inplane and out of-plane orientations are in registry [118]. Pole figures of specific hkl reflections (originating from a specific set of lattice planes) can be measured by keeping the respective  $\theta$  and 2 $\theta$  angles fixed. Then, to detect the reflection from a certain plane the azimuth angle  $\varphi$  range (0 – 360°) and the tilt angle  $\chi$  (range 0 – 90°) are scanned, measuring the intensity of the reflections from these lattice sites in all possible directions. The tilt axis lies at the intersection of the scattering plane and the sample surface. When the full  $\varphi$  scanning range is completed, the scattering plane is tilted by angle  $\chi$ , and a new scan is performed. After repeating the scan cycles for several tilt angles, a stereographic projection of the reflections present can be presented as a pole figure.



Figure 2. 9. X-ray reflectivity (XRR) spectrum from a 40 nm thick YSZ film deposited on LGS substrate at 700°C. The simulation from X'Pert Reflectivity software indicates a film thickness of 38 nm calculated from the distance between fringes.

An example can be seen in figure 2.8, which is a (311) pole-figure plot from a YSZ film deposited on a langasite substrate. A diffraction ring is observed at a tilt angle  $\chi = 60.5^{\circ}$  corresponding to the angle between the (111) and (311) planes. A pole figure for a polycrystalline aggregate, which shows completely random orientation, does not necessarily appear as might naively be expected. Angular distortions inherent in the stereographic projection result in the accumulation of points measured in distance from center of the pole figure, figure 2.8.

X-ray reflectivity is a grazing incidence x-ray diffraction technique that uses incidence and exit angles  $\theta$  in the range 0.1 - 5°. XRR provides information on film thickness, bilayer thickness in multilayers, electron densities of layers, and interface roughness. In this thesis work, X-ray reflectivity has mainly been used to measure film thicknesses (less than 100 nm) and to reveal the interface roughness [119].
In the case of X-rays reflected at an interface between air and a solid material, the application of Snell's law shows that total external reflection occurs for incident angles below the critical angle  $\theta_c$ , which in a small-angle approximation can be written as,

$$\theta_c = \sqrt{\frac{\rho r_0}{\pi}} \,\lambda \tag{2.3}$$

where  $\rho$  is the electron density, and  $r_0 = 2.82 \times 10^{-6}$  nm is the Thomson scattering length describing the ability of an electron to scatter an X-ray [120]. In figure 2.9, an x-ray reflectivity curve measured from a 40-nm-thick YSZ film deposited on a langasite single crystal is shown. A plateau of nearly constant reflectivity is observed below  $\theta_c$ .

For incident angles greater than the critical angle, the X-rays penetrate the film and exhibit oscillations due to interference between the scattered beams at the air/film - and film/substrate interface. The length scales probed in X-ray reflectivity measurements are typically greater than the crystalline lattice spacing that comes across in the individual layers. Hence, only the periodicity of the interfaces causes peaks in the reflectivity curve, with scattering factors associated with each interface. In the case of reflectivity from a uniform thin film, the scattering factors, and hence the measured intensity of the reflected X-rays, are highly dependent on the actual composition profile, which is related to the electron density profile. This makes it possible to quantify the surface and interface roughness by means of X-ray reflectivity. In an often-applied formalism, roughness is considered by assuming a Gaussian distribution around the average layer thickness. The recorded X-ray reflectivity scans were analyzed with the software package X'Pert Reflectivity [118-120].

To complement measurements of film crystallography by XRD, Scanning Electron Microscopy was used to characterize the morphology of YSZ films.

A Zeiss NVision 40 focused ion beam / scanning electron microscope (FIB/SEM) with a magnification range of 20X – 600,000X and an accelerating voltage range of 100V - 30KV was used to visualize and study the nanostructure of as-deposited and annealed films. It has a six axis eucentric goniometer stage, and multiple detectors including secondary electron and backscatter electron detectors.

Image contrast in a SEM arises from various electron interactions within the sample. The most common imaging mode relies on the detection of low energy secondary electrons emitted from a subsurface depth of no more than a few nanometers. This provides a topographical image of the surface, where sloped surfaces and edges appear brighter, since the portion of the interaction volume projected onto the sloped surface is larger than on a horizontal surface, thereby producing a greater secondary-electron yield.

Alternatively, backscattered electrons can be detected to obtain compositional contrast between specimen regions which differ widely in the atomic number *Z*, since the backscattering cross-section increases with *Z*. Since the escape depth for high-energy backscattered electrons is much greater than for low-energy secondary electrons, there is much less topographical contrast in backscattered images [121].

Figure 2.11 shows the SEM images from a 200 nm thick YSZ film decorated with 1 nm Pt nanoparticles. In backscattering images, regions comprised of higher-Z (at. no.) materials (Pt NPs) show up brighter, lower-Z materials (YSZ) show up darker.



Figure 2. 10. Physical processes involved during SEM analysis of a material using an energetic electron beam.



Figure 2. 11. SEM images from a 200 nm thick YSZ film decorated with 1 nm Pt nanoparticles, (a) secondary electron image and (b) backscattered electron image.

#### 2.5 Electrical and Ionic Conductivity

The mechanism for bulk ionic diffusion in YSZ at high temperatures occurs via oxygen vacancy motion in the crystal lattice under the influence of an external electric field which produces a net ionic current. Simple DC experiments with two inert metal electrodes are unsuitable for the measurement of ionic conductivity in electrolytes because of the blocking of ions at the electrolyte/electrode interface. This problem can be avoided by using AC techniques. Electrochemical Impedance spectroscopy (EIS) has proved to be a powerful technique for characterizing many electrical properties of materials, including the complex impedance of a specimen as a function of frequency and electronic effects at electrode interfaces. One of the great advantages of this method is the possibility of identifying the impedance contributions caused by defects within the materials such as vacancies as well as grain boundaries and interfaces.

The general approach of EIS is to apply an electrical stimulus (voltage or current) to electrodes and observe the response as a function of temperature, partial gas pressure, and applied static voltage or current bias [122]. Electrochemical impedance spectroscopy measurement is generally used to understand phenomena such as ionic/electron transport, activation energy, grain boundary resistance, mass transport rates, chemical reaction rates surface, diffusion effects, and redox reactions [122,123]. EIS can also study the influence of an external stimulus (elevated temperature in this work) on the conductivity of an electrode-electrolyte system [125,126].

In the latter half of the 19th century, Heaviside coined the words inductance, capacitance, and impedance, and laid a mathematical foundation for circuit analysis [123]. Nernst built upon his work and became the father of EIS by applying the Wheatstone bridge to measure the dielectric constants of aqueous electrolytes in 1894 [123].



Figure 2. 12. Fundamental concepts of electrochemical impedance spectroscopy [123].

Later in 1969, Bauerle was the first to apply EIS technique to solid-state electrolytes [124]. Since then, investigations into single and polycrystalline materials with EIS have increased rapidly, especially because of the evolution of solid-state batteries and more efficient fuel cells [127,128]. Impedance data can be represented as impedance or as admittance, which is the inverse of impedance. Admittance is used to examine high frequency behavior found in solid state systems, whereas impedance emphasizes low frequency phenomena such as mass transfer and gas reactions [123].

Impedance is the ratio of a voltage signal to a current signal, and it can have complex and real components. To obtain the impedance of a specific system, alternating voltage v(t) = V sin ( $\omega t$ ) signal is applied, followed by measure of the current response  $i(t) = I \sin (\omega t + \theta)$  where the impedance Z(w) = v(t) / i(t). Impedance is a frequency dependent transfer function consisting of the ratio of potential over current [126]. A phase angle ( $\theta$ ) quantifies lag or lead of i(t) with respect to v(t), as shown in figure 2.12. The impedance is given by  $Z(\omega) = Z_{real} + jZ_{imag}$  where the complex number  $j = \sqrt{-1}$  [123,129].



Figure 2. 13. Theoretical modeling of the electrochemical impedance spectroscopy (Nyquist plot) and equivalent circuit of 8 mol% YSZ, measured at 300 °C [124].

Impedance spectroscopy is a useful method to study gas adsorption since gas interactions are accompanied by redox reactions where electron exchange alters the impedance complex resistance. The impedance can be represented in the complex plane at each frequency by a vector whose absolute value magnitude represented by the length of the vector as defined by the Pythagoras relation,  $|Z| = [(Z_{real})^2 + (Z_{imag})^2]^{1/2}$ , and the angle that the vector makes with the horizontal x-axis is the phase angle ( $\theta$ ) [124]. This quantity also represents the lag or lead of the followed response current at any specific frequency. Based on basic trigonometric calculations, the phase angle is defined on the complex plane as  $\theta = \tan^{-1} (Z_{real} / Z_{imag})$ . The phase angle is used to probe gas reactions because it is very sensitive to the system parameters [123]. When the input voltage and output current are in phase, then the phase angle is zero and there is no imaginary component of the impedance. For this case, the impedance consists of only pure resistance aligned with the real axis [124,125].



Figure 2. 14. Impedance spectrum of YSZ thin film with a thickness of 200 nm. At frequencies below 1 Hz is clearly visible the contribution of the electrode.

EIS requires examining the measured impedance at several frequencies ranging from 1 MHz to 1 Hz. Equivalent circuit analysis is often useful to assist the understanding of the physical/chemical processes. A Nyquist plot represents impedance data on what is called the complex impedance plane plot. It was also named a Cole – Cole plot. A Nyquist plot is usually customized by plotting the impedance components as  $-Z_{imag}$  (y-axis) vs  $Z_{real}$  (x-axis) as shown in figure 2.13. The impedance spectroscopy rarely involves inductance but usually involves capacitance [124]. The number of arcs in a Nyquist plot is related to relaxation processes involved in the frequency dependent response to an input sinusoidal voltage signal. Most crystalline solids exhibit one arc, some exhibit two arcs, and few exhibit three arcs [122,123,130] In most cases, the third arc is too small to be visible and, in some cases, the second arc only appears as temperature is decreased [122]. In this thesis and in papers published in the literature [123,131-133], there is evidence of overlapping arcs, making it not easy to separate out the different relaxation processes.



Figure 2. 15. Ideal circuit elements used to interpret a Nyquist plot.

For example, figure 2.13 shows a typical impedance spectrum from a zirconia-based system displaying three arcs along the real axis. The first two arcs arise from grain and grain boundary resistance, which is usually visible at high frequency, and the overlapping first and second arcs can be interpreted in terms of charge transfer at the grain boundaries. The third arc (at low frequency) arises from diffusion or electrochemical reactions that occur at the electrode.

The low frequency arc may exhibit distortion depending on many parameters such as the electrode material, the preparation of the electrode, and the art of attaching the electrode to the RF cables. As frequency approaches infinity, the resistance of YSZ films represents the approaching value limit of the real component of impedance. As frequency approaches 0 Hz, the impedance approaches a real value that represents the sum of the resistances associated with the intrinsic physical and chemical characteristics of YSZ substance [122,123].



Figure 2. 16. Constant phase element on a Nyquist plot.

From the impedance spectroscopy and equivalent circuit fitting, the resistance and capacitance of YSZ grains and grain boundaries can be obtained [134].

A typical impedance spectrum scan (Nyquist Plot) from a YSZ film is shown in figure 2.14. For all the YSZ samples measured in this thesis, only one semicircle in the Nyquist plot and a small contribution from the platinum electrodes at low frequency is visible. This data was recorded with the sample at 500°C and over six decades of frequencies as indicated. The high frequency portion of the arc results from conductivity processes within YSZ grains and grain boundaries, whereas the low frequency arc region is derived from interfacial processes at the electrodes including charge transfer and electrochemical reaction. The recorded data taken in this thesis showed a very poorly defined low frequency arc region probably due to a low-quality connection between the Platinum pads and the rf cables.



Figure 2. 17. A Cole element (RQ) forms a depressed semicircle in a Nyquist plot.

The functionality of the YSZ thin film, electrode, interface, and gas interaction can be modeled by an equivalent circuit using ideal circuit element resistors (R), inductors (L), and capacitors (C) [122]. On a Nyquist plot, the resistors, capacitors, and inductors have an impedance response that coordinates with the axes defined in figure 2.15. For a resistor, the voltage and current are in phase, meaning that the phase angle is zero ( $\Theta = 0^{\circ}$ ) and resistance can be read directly from the x-axis. For a capacitor, voltage lags current by 90° (phase angle  $\Theta = -90^{\circ}$ ) resulting in impedance along the negative imaginary axis (y-axis upward on a Nyquist plot). Conversely, for an inductor, voltage leads current by 90° (phase angle  $\Theta = +90^{\circ}$ ) resulting in impedance along the positive direction of the imaginary y-axis. Since the impedance due to both capacitance and inductance is a product of an imaginary number, neither can be directly read from the Nyquist plot. The resistance arises from several sources: ion transport in the YSZ thin film, charge transfer across grain boundaries, and reactions at electrodes [122-124]. The capacitance is primarily created across an interface, for example by adding Pt nanoparticles to the YSZ film surface or from reaction products upon hydrogen exposure [122,123]. Inductance is rarely important and, if measurable, is often attributed to electrode contacts and the RF cables [122,125].

Constant phase element (CPE) is a general circuit element approach that is useful to model the input voltage and response current over a range of frequencies 1MHz to 1Hz [123,135]. In the complex impedance plane, the impedance output from resistors, capacitors, and inductors are ideally aligned with the axes of the Nyquist plot. The physical explanation of a CPE can be ambiguous [122,132]. One interpretation of a CPE is a non-ideal capacitor, which is apparent by examining the formula for impedance:  $Z = 1/[(j\omega)^{\varphi}Q]$ , where Q is a CPE parameter. When the phase angle exponent takes on a value  $0 \le 0 \le 1$ , then Q is related to double layer capacitance [122,132]. When  $\varphi = 1$ , the CPE is a capacitor and then its impedance is identical to that of a capacitor:  $Z = 1/(j\omega C)$ . Notice that neither the phase angle,  $\Theta$ , nor the phase angle exponent ( $\varphi$ ), nor the CPE coefficient depend on frequency [123,135]. On a Nyquist plot, a single CPE has an impedance response of a straight line that makes an angle equal to  $\varphi^{*}(-90)^{\circ}$  with the x-axis, where  $\varphi$  is the phase angle exponent [132]. The angle that the CPE forms with the real axis is negative due to the inversion of the imaginary axis. When  $\varphi = 1$ , the phase angle is -90° and the CPE overlaps the ordinate, which is the same as a capacitor. The same conclusion can be applied for a CPE representing a non-ideal inductor when  $-1 \le \phi \le 0$ . When  $\phi = -1$ , the CPE is an inductor: Z =  $1/[(j\omega)-1T] = j\omega/T$ , as L = 1/T. In this case, on a Nyquist plot the CPE aligns with the  $Z_{imag}$  axis inductor. The same conclusion can also be applied for a resistor, where  $\varphi = 0$ . For the case of a resistor, Z = 1/T = R only the real component [123,135].

Although mathematically the CPE could represent a range of types of non-ideal circuit elements, in the case of electrochemical sensors, a CPE usually approximates a capacitor on account of the geometry of sensors. The cause of non-ideal capacitive behavior is time-constant dispersion resulting from distributed physical properties. For example, a distribution of relaxation times can be caused by inhomogeneities in an electrode-material system [123,135]. Other examples are the heterogeneity of the surface such as grain boundaries, crystal faces, and surface roughness. All that causes the reactivity and electrical properties to vary, resulting in not a single time constant, but rather a distribution of time constants [123,135]. This action can also be noticed during mass transfer [123,135]. Varying oxide composition results in heterogeneous properties that can cause time-constant dispersion [123,135]. Figure 2.16 shows that a CPE with the symbol (Q) can be used in conjunction with a resistor as a part of a Cole-Cole circuit element. Thus, a Cole-Cole element consists of a resistor (R) in parallel with a CPE (Q). Sometimes it is referred to as simply a Cole element, whereas Barsoukov and Macdonald refer to this element as a "ZARC" [123,135]. This circuit combination results in a depressed arc on a Nyquist plot, as shown in figure 2.17 [122,132]. Through modeling of the CPE, the center part of an arc can be adjusted relative to the real x-axis, and the width of the depressed arc is the sample resistance, R. A Cole-Cole element can be used to model grain boundaries that display a distribution of time constants and can also be used to represent interfacial or electrode surface processes such as adsorption and chemical reactions [123,135].

Figure 2.19 shows an example of a typical Nyquist plot for an impedance-based sensor with its corresponding CPE equivalent circuit. The interface element represents a physical or chemical process, and the arcs are represented by CPE element, with a unique time constant.



Figure 2. 18. Hydrogen sensing configuration.

The sensing behavior is attributed to changes in resistance at the interface between the YSZ thin film and gas adsorption species [131,136]. However, the exact sensing mechanism of impedance – based sensors is still poorly understood as most of the physical processes that impact the impedance spectrum take place at low frequencies [40].

Figure 2.19 shows an impedance spectrum measured from a YSZ thin film decorated with platinum nanoparticles exposed to two gases at 500°C: Air (orange) and 96%  $N_2 - 4\%$  H<sub>2</sub> (blue). This Nyquist plot shows the resistive and capacitive contributions of impedance where the high frequency locus in the arc provides information on kinetically controlled phenomena and the low frequency locus in the arc is sensitive to mass transfer events (i.e., gas adsorption) [137]. Hydrogen exposure leads to an inward shift of the low frequency arc resulting in a phase angle change. The modulus represents the length of the vector from the origin to an impedance value at a specific frequency and the phase angle is the arctangent of the ratio of the capacitive contribution of the impedance to the resistive component at a specific frequency [134,138].



Figure 2. 19. Example impedance spectroscopy data acquired from a YSZ film (200 nm) decorated with Pt nanoparticles (10 nm) before and after exposure to hydrogen gas. Hydrogen adsorption causes an inward shift of the low frequency arc on the Nyquist plot.

Figure 2.20 shows the overall experimental setup that was used in this thesis for acquiring impedance spectroscopy data at elevated temperatures [139]. The impedance / gain – phase analyzer is a 1260A Frequency Response Analyzer made by Solartron Analytical / Ametek Scientific Instruments. Frequency Response Analysis (also referred to as Transfer Function Analysis) measures the magnitude and phase relationship between output and input waveforms as a function of frequency. SMaRT software is used to control the Solartron Analytical FRAs and Materials Interfaces. The measurement was carried out inside a purged quartz furnace tube supplied by MTI Corporation. The gas delivery system for the tube furnace delivered a constant flow of either 99.999% pure N<sub>2</sub> or a  $96\%N_2 : 4\%H_2$  mixture. A Eurotherm temperature controller with an Omega model series CN7600 was used to adjust and control the temperature of the furnace. Impedance spectra were measured over the range from  $400^{\circ}C - 600^{\circ}C$ .



Figure 2. 20. (a) Photograph of the experimental setup used for impedance spectroscopy measurements at elevated temperatures; (b) schematic cartoon showing a YSZ film with Pt nanoparticles and Pt contact pads; (c) overall configuration for carrying out H<sub>2</sub> gas dosing experiments.

#### CHAPTER 3

# NANOSTRUCTURE AND MORPHOLOGY OF YSZ FILMS DEPOSITED ON LANGASITE SUBSTRATES

### **3.1 Introduction**

Surface acoustic wave (SAW) technology based on piezoelectric langasite crystals can address multiple harsh-environment sensing needs such as monitoring temperature, pressure, torque, gas, or strain [140-142]. Due to the demands of these applications up to 1000°C, two major technological challenges need to be satisfied: (i) high temperature endurance and (ii) sensor stability after being subjected to multiple heating, cooling, and soaking cycles. Stable thin film materials for SAW sensor electrodes, interfacial layers, and capping layers have been investigated in the Frontier Institute for Research in Sensor Technologies (FIRST) over the past decade [143-145]. For example, co-deposited Pt/Al<sub>2</sub>O<sub>3</sub> [143-145], Pt/ZrO<sub>2</sub> [143-145], and Pt/Ni [143-145] electrodes have been successfully used on langasite SAW resonators to enable long term sensor operation.

This thesis project focuses on the investigation of yttria-stabilized zirconia (YSZ) films for use as a potential sensing layer on SAW sensor devices. YSZ films are well known to promote the adsorption of a wide variety of gases and molecules at temperatures up to 1000°C [83]. The high ionic conductivity of YSZ combined with high mechanical and chemical resistance also make it a promising material for use as a solid electrolyte in gas sensors and solid oxide fuel cells [138]. By introducing oxygen vacancies into the YSZ lattice via yttria doping, the oxygen ion conductivity dominates at temperatures above ~500°C compared to the relatively low electronic conductivity.

Added trivalent Y<sup>3+</sup> cations replace tetravalent Zr<sup>4+</sup> cations for charge compensation, and one oxygen vacancy is created per two Y atoms. Distortions around the vacancy and an overall lattice expansion decrease the average O–O repulsion, stabilizing the thermodynamically stable high temperature YSZ cubic phase down to room temperature at concentrations above 7.5 mol% Y<sub>2</sub>O<sub>3</sub> [146,147]. To date, various physical and chemical methods have been employed to prepare YSZ thin films, including radio frequency (RF) sputtering, DC reactive sputtering, pulsed laser deposition (PLD), electrophoretic deposition (EPD), spraying techniques, spin coating, chemical vapor deposition (CVD) and atomic layer deposition (ALD) [148-150].

Among them, RF sputtering is a very attractive process that is frequently utilized for the production of dense, crack-free, homogeneous YSZ films over large area substrates [148-150]. The nanostructure and properties of the films are strongly influenced by the deposition conditions, so that finely tuning the process parameters is required to reach optimum performance. The RF power is an important sputtering parameter since it directly affects the deposition rate and hence adatom mobility on the film growth surface. If the RF power is too high, thermal stresses induced on the target can lead to localized cracks on the target [148-150].

An important factor to consider with thin films is the adhesion to the substrate, which in turn affects mechanical behavior of the interface. In particular, the film–substrate interface mismatch may lead to significant strain because of the difference in thermal expansion coefficients [148-150]. Interfacial strain usually leads to cracking and delamination, but intrinsic film stress resulting from the thin film deposition process can in some cases be beneficial for promoting good film-substrate adhesion.

#### **3.2 Deposition Parameters for YSZ Thin Film Growth**

The sputtering parameters used in depositing YSZ films have a major influence on the structural characteristics, defects, and electrical properties. The dominant deposition parameters that influence film nanostructure are substrate temperature during growth, the energy of incident ion and neutral fluxes, the deposition rate, and the target reactivity with reactive process gases [151]. In this thesis work, the YSZ films were grown on langasite substrates using the RF magnetron sputtering deposition method, and of the five relevant sputtering parameters, two were fixed and three were varied. The fixed parameters were a total gas pressure of 6 mTorr in the sputter chamber and an Ar: $O_2$  gas composition ratio of 95:5. The 5%  $O_2$  gas component was added to the sputter plasma to ensure that as-deposited films were not oxygen deficient. The three variable parameters used during the experiments were deposition rate, substrate temperature, and substrate biasing. In particular, YSZ films were deposited at 30°C, 400°C and 700°C growth temperatures and at deposition rates of 0.03 nm/s, 0.05 nm/s and 0.07 nm/s. For the substrate biasing experiments, voltages of -300V, -100 V, +100 V and +300 V were used, and the YSZ films were grown at 30°C at 0.07 nm/s. In the RF sputtering process, sputtered atoms initially have much higher kinetic energy (and speed) than ambient gas atoms; therefore, the gases can be regarded as stationary. However, as sputtered atoms proceed along their pathway, they experience collisions with ambient gases and are decelerated until they are equilibrated with the gases. This is called the "thermalization" of sputtered atoms. Modes of the transport process of sputtered atoms before and after the thermalization are usually called "ballistic" and "diffusive," respectively, and they are significantly different with regard to the energy of atoms reaching the substrate, the arrival flux (deposition rate), and their profiles [152].

In our work, the deposition rate and the substrate temperature were found to have a major effect on film crystallinity. The film deposition rate is dependent on the applied RF power in the plasma and an increased deposition rate requires increased target voltage to achieve a higher plasma density. This leads to a higher ion flux, which in turn increases the target current [151]. The deposition rate is also inversely proportional to the deposition pressure: when higher pressures are applied, it involves a shorter mean free path, because there is a higher number of particles in the argon plasma, which act as obstacles to the ejected target particles in their trajectory to the substrate. However, in our experiments, we fixed the total pressure to sustain a constant deposition rate and hence controlled film thickness [153,154]. At higher RF power, the argon ions become more energetic and hence can release higher energy to the target atoms during sputtering. When the working gas pressure is relatively low (e.g., such as 6 mTorr used in this study), these highly energetic atoms from the target will experience few collisions and can reach the substrate with high energy. XRD results reported in the literature suggest that it is difficult to obtain crystalline films with other than (111) YSZ film texture even after post deposition annealing [155]. One way to investigate the ion energy effects in the deposition flux is to apply either a positive or negative substrate bias [156]. High energetic electrons impinging on the film growth surface can also be influenced by a bias voltage and directly affect film crystallinity [157]. The substrate bias influences the energy of ions impinging on the substrate sheath potential near the edge of the plasma near the substrate [158]. It is believed that a negative bias can attract more positive ions to bombard the sample surface, leaving behind a dense structure. When a positive bias voltage is applied to the substrate, the energy of bombarding ions decreases but the energy of incident electrons on the growing film greatly increases [158,159].

# **3.3 Characterization of As-Deposited YSZ Films**

This section presents the collected results concerning elemental composition, crystallographic structure, and film morphology of as-deposited YSZ films. It will be shown that the deposition rate, substrate temperature, and substrate biasing can be used to influence the YSZ film properties.

# 3.3.1 Film Compositional Analysis

For composition analysis of the YSZ thin films, XPS was conducted using a pass energy of 20 eV, a resolution of 0.1 eV, and with binding energies referenced to O 1s: 529 eV and carbon C 1s: 284.5 eV (if present). Figure 3.1 shows an example of an XPS spectrum from a 200 nm thick YSZ film deposited onto langasite at 30°C. Shake-up structure, multiplet splitting, and plasmon loss structure features can complicate the XPS spectra, and this means that fitting parameters such as peak widths and asymmetries need to be carefully considered during XPS curve-fitting [161]. XPS spectra were fitted using CasaXPS software [160,162,163], and all samples nominally showed the same film composition as shown by the average composition of 16 films shown in figure 3.1, as discussed below. The other film properties changed significantly as a function of the deposition parameters.

For XPS peak fitting, the new line shape (LF) with Tougaard background subtraction in CasaXPS was used for electron binding energy and asymmetry analysis, respectively [162,163]. An extension to the Lorentzian Asymmetric (LA) lineshape was used to introduce a further parameter, the purpose of which is to limit the range of the asymmetric tail. The challenge with asymmetric peaks is matching a lineshape to the data shape after a background is removed, while

still maintaining a functional form for the lineshape suitable for measuring the intensity of the transition [92,162,163]. For asymmetric lineshapes, the challenge is to both model the data and allow the measurement of peak areas, therefore the new lineshape,  $LF(\alpha, \beta, \omega, m)$ , uses the same functional form as the LA lineshape, but introduces a damping parameter,  $\omega$ , to force the tail to go to zero at the integration limits [92,162,163]. It is worth noting that the asymptotic form of the LA and LF lineshapes is equivalent to the asymptotic form of the theoretical Doniach-Sunjic asymmetric lineshape.

All the peak fittings were performed after applying a Tougaard background correction [164] and using the proper area relation between the doublets and a fixed spin-orbit splitting [160]. The deviation in as-deposited film stoichiometry is small as evidenced by a standard deviation in the Y/Zr ratio of 0.12-0.15 atomic %. Figure 3.1 shows several plasmon excitation peaks, which are caused by collective oscillations of the conduction band electrons during the photoelectron emission process. These plasmon energy loss features appear at regular intervals and can be observed on the high binding energy side of all the photoelectron peaks in the spectrum of figure 3.1 [165,166].

# 3.3.2 XRD Analysis of Crystal Structure

XRD was used to analyze the lattice parameter, film crystallographic texture, crystallite size, and strain within the as-deposited YSZ films. It was observed that the main XRD peak measured in a  $\theta$ -2 $\theta$  gonio scan, figure 3.2, corresponding to cubic YSZ (111) planes parallel to the surface, was shifted towards larger d-values compared to the values measured from a YSZ bulk single crystal standard, which provides evidence for out-of-plain (compressive) strain in the films.



Figure 3. 1. XPS spectrum from a YSZ film deposited at 30°C. The atomic concentrations and binding energies for each element averaged for 16 different YSZ films are shown Table 3.1 in comparison to measurements from a (111) YSZ single crystal standard. Both the measured Y/Zr ratio and the observed Zr3d and Y3d binding energies were nominally the same for all the as-deposited YSZ films.

Table 3. 1. Atomic co	oncentration and X	PS binding of	energies for Y	SZ measured	values fi	rom an
8-YSZ single crystal	compared to avera	ige value det	ermined from	16 film depo	sitions at	t 30°C.

Atomic Concentration (%)	Zr (3d)	Y (3d)	O (1s)
(Y <sub>2</sub> O <sub>3</sub> ) <sub>0.08</sub> (ZrO <sub>2</sub> ) <sub>0.92</sub>	29.11	5.06	65.82
Ave. Film Composition (16 films deposited at 30°C)	28.5±1.4	4.7±0.9	66.7±1.8
Binding Energies	181.1 ± 0.5	155.9 ± 0.3	529.0

Figure 3.2 shows that the highly textured (111) oriented grains were primarily observed for all YSZ films. Other crystallite orientations including (200), (220) and (311) can also be present depending on the exact deposition parameters. Films with other grain orientations coexisting with (111) were those deposited at high deposition temperature (700°C) and high deposition rate (0.07 nm/s), which gave the most intense (220) peak, and films deposited at low deposition temperature (30°C) and low deposition rate (0.03 nm/s), which exhibited the most intense (311) peak. These other grain orientations can influence the film characteristics such as film roughness, film strain, crystallite size, and in-plane ionic conductivity, but the dominant (111) crystallites have the highest impact on these film properties. Grazing-incidence XRD results shown in figure 3.4 are consistent with (111) YSZ film texture since the off-axis planes are seen in the GIXRD scan. YSZ films deposited at low deposition temperature (30°C) and low deposition rate (0.03 nm/s) have a large (200) component which has also been observed for YSZ film growth at room temperature on other substrates [167-170].

The film texture and crystallite orientation of YSZ films was analyzed using XRD pole figures. Figure 3.3 shows pole figures measured from YSZ films set up to measure diffraction from (200), (111), (220) and (311) Miller planes within films with primarily (111) crystallographic texture. Due to the cubic symmetry of the YSZ crystal, the (200), (220) and (311) poles should occur at angles of 45°, 54.7°, and 60.5° in the pole figures, respectively. The pole figures acquired from a (111) oriented YSZ single crystal (1<sup>st</sup> row in figure 3.3) are consistent with a single crystal orientation with a (111) pole at 0° and diffraction from the other planes at the expected radial angles with distinct diffraction beams from a single in-plane orientation. For the YSZ films, a ring is present in the pole figures (2<sup>nd</sup> row of figure 3.3) indicates that the YSZ crystallites are primarily oriented with (111) planes parallel to the surface, but with random in-plane configurations.

The (311) pole figures shown in the 3<sup>rd</sup> row of figure 3.3 clearly shows differences in the in-plane crystallite alignment for films grown at 30°C versus 600°C. It is interesting to note that all the pole figures show a peak at 0° and this can be explained by diffraction from bremsstrahlung radiation wavelengths that satisfy the (111) diffraction condition.

The width of peaks in XRD gonio spectra can be analyzed to extract information about crystallite size and lattice strain. Crystallite size is a measure of the size of coherently diffracting domains and this crystallite size is not generally the same as the grain size of polycrystalline aggregates seen in SEM imaging [114].

Lattice strain can be either uniform throughout a film or non-homogeneous around crystal imperfections, such as with hillock formation [114], which causes peak broadening and a shift in the  $2\theta$  peak position, respectively. The average crystallite size within a thin film perpendicular to the surface can be determined by the X-ray line broadening method using the well-known Scherrer equation:

$$D = \frac{K\lambda}{\beta_D \cos\theta}$$
(3.1)

where D is the crystallite size in nanometers,  $\lambda$  is the wavelength of the radiation (0.154056 nm for CuK<sub>a</sub> radiation), K is a constant related to the shape of the grain (K ~ 0.9 for spherical grains),  $\beta_D$  is the peak width at half-maximum intensity in radians and  $\theta$  is the Bragg angle [114,171]. Full width of half maximum (FWHM) values of XRD peaks include a combination of both instrument and sample dependent effects, and to decouple these contributions, it is necessary to measure a standard material such as silicon to determine the instrumental broadening [114].



Figure 3. 2. XRD gonio scans from as-grown YSZ films. All peaks can be attributed to cubic YSZ. The intensity of (111) peak increases with increasing growth temperature, consistent with enhanced crystallinity. The (200) crystallite orientation only exists in films deposited at 30°C with 0.03 and 0.05 nm/s rates.



Figure 3. 3. XRD pole figures for different Miller planes measured from a YSZ single crystal (1<sup>st</sup> row) and from an as-deposited YSZ film grown on langasite at 30°C (2<sup>nd</sup> row). Also, a (311) pole figure is compared for a YSZ film deposited at 30°C and at 600°C (3<sup>rd</sup> row). There are no features from the LGS substrate because the LGS single crystal was cut to a Euler angle that does not correspond to a low-index Miller plane.

The Scherrer method gives a crystallite size estimate, but it also makes a major assumption that there is no peak broadening contribution due to film strain. An alternative approach, which takes into account both the size and strain effects, is the Williamson–Hall (WH) method [171]. In this method, D and the microstrain are obtained from a so-called W-H plot ( $\beta_D \cos \theta$  versus  $\sin \theta$ ), since they are related to the peak broadening by,

$$\beta_{\rm D}\cos\theta = \frac{\lambda}{\rm D} + 4\varepsilon . \sin\theta$$
 (3.2)

The W-H method does not follow a  $1/\cos\theta$  dependency as in the Scherrer equation but instead varies with tan  $\theta$  [114]. This fundamental difference allows for a separation of reflection broadening when both microstructural causes (small crystallite size and microstrain) occur together [114] and the assumption is that size and strain broadening are additive components of the total integral breadth of a Bragg peak. For W-H analysis, the term ( $\beta_D \cos \theta$ ) is plotted with respect to  $(4\varepsilon \sin \theta)$  for the preferred orientation peaks [114,172] as shown in figure 3.3 (C) for YSZ films grown at 30°C and 0.07 nm/s deposition parameters. Accordingly, the slope and yintersect of the fitted line correspond to strain and crystallite size values were -1.15% and 7 nm, respectively. Films grown at low deposition temperature and high deposition rate, or high deposition temperature and low deposition rate exhibit a negative microstrain slope value. This behavior presumably is associated with the compressive film strain, which leads to the formation of a great quantity of defects, especially hillocks [172]. For YSZ films, the main constraint of grain growth is believed to be grain boundary energy, which depends mostly on the deposition parameters [173]. The average grain sizes in the film normal direction for 200 nm thick YSZ films deposited at 30°C, 400°C, and 700°C were 8, 10, 12 nm respectively as shown in figure 3.3. The inhomogeneous strain in figure 3.4 (E) shows positive or negative values based on tensile or compressive film characteristics. It can be observed that a common property in all films with positive strain is that they all have other grain orientations coexisting with the (111) grains.





Figure 3. 4. Characterization of 200 nm thick YSZ films (grown at 30°C and 0.07nm/s) to determine grain size and strain. (A) Gonio (2 $\theta$ ) scan (B) GIXRD scan, sample stage tilted 5° (C) Williamson – Hall plot. The negative slope is due to compression stress, while the positive slope reflects a tensile stress (D) 3D plot showing the grain (crystallite) size for different films versus the relevant parameters shown by the colors in the legend: deposition rate and deposition temperature (E) Strain analysis for as-deposited YSZ films grown under different conditions. Negative strain means compression perpendicular to the film, while positive strain means tensile.

#### **3.3.3 Analysis of Film Morphology**

The equiaxial compressive stress generated within a YSZ film on an LGS substrate from thermal coefficient of expansion mismatch can cause film material to extrude out of plane through the free surface. As a result, the film material can "squeeze out" through any defects or cracks in its protective oxide layer or passivation layer, producing a mound of extruded material, commonly known as a hillock [174]. Hillocks can cause reliability problems in surface acoustic wave sensors due to instability, deformation, and dispersion [174]. To obtain a highly reliable gas sensing layer, it is important to understand the formation mechanisms of hillocks and minimize their distribution in thin films [174]. The presence of hillock formation supports the fact that YSZ films are under compressive stress and the hillocks form when heated as a result of compressive stress relaxation [175]. Hillocks apparently form by diffusion from the surrounding areas in order to achieve local stress relaxation. The high elastic constants of YSZ films can sustain high compressive stresses even after heating, and these high compressive stresses provide a large driving force for hillock formation.

Figure 3.5 shows SEM images of YSZ films grown varying both deposition rate and deposition temperature. It is observable that: low deposition temperature (30°C) and high deposition rate (0.07 nm/s); or low deposition rate (0.03 nm/s) and high deposition temperature (400°C and 700°C) show hillock formation. The other films have less stress and have positive tensile strain. Many phenomena can affect the development of the surface morphology, such as adatom adsorption, nucleation and island forming. The island size typically depends on two parameters: the deposition rate (determined by sputtering power) and the diffusion rate (determined by growth temperature) [176].

The diffusion rate / sputtering power ratio determines the island size distribution, with the island density decreasing with a larger ratio. The roughness of YSZ films also depends on these parameters, increasing with sputtering power. Figure 3.5 shows a film roughness in addition to hillock formation. Films grown at low deposition temperature (30°C) and high deposition rate (0.07 nm/s), or high deposition temperatures (400°C, 700°C) and low deposition rate (0.03 nm/s) exhibit a surface roughness. The decrease in roughness for other films in figure 3.5 might be attributed to plasma energy and adatom mobility and suggested more homogeneous film growth.

To investigate surface roughness, XRR experiments were carried out. X-ray reflectivity (XRR) can be used to determine surface roughness, furthermore film density and film thickness. Information that can be accessed directly from the XRR plot includes film thickness and the critical angle. Further information on thickness and interface roughness can come from fitting (simulating) the XRR pattern. Figure 3.6 presents the fitted XRR patterns from a 40 nm YSZ film deposited on a langasite substrate at two different temperatures 30°C and 400°C, respectively.

Surface roughness will dampen XRR oscillations at higher angles [177,178]. Thus, a direct comparison of one XRR scan to another can immediately yield significant, qualitative results. Figure 3.6 shows that increasing the roughness damps the oscillations more quickly.



Figure 3. 5. SEM images from as-deposited YSZ films. Films grown with high deposition rate and low deposition temperature exhibit roughness and hillock formation. Films grown at low deposition rate and high deposition temperature show a rough surface with smaller hillocks.



Figure 3. 6. XRR spectra from 40 nm thick YSZ thin films deposited on LGS substrate at (A) 30°C and (B) 400°C. X'Pert Reflectivity software was used to fit the data in order to determine values for the roughness (R) and thickness (t) of the top layer and the roughness of the substrate/film interface.

This can be explained by the fact that as  $\omega$  increases, the XRR oscillates modulated by alternating constructive and destructive interference. Also, the period of this oscillation gives the thickness of the layers, and the magnitude is related to the density contrast. X'Pert Reflectivity software assisted with obtaining a quantitative result by constructing an adequate model of the thin film multilayer structure and performing a non-linear regression to fit the model to the data [177,178]. Figure 3.5 shows that with power increasing from 60 W (0.03 nm/s) to 140 W (0.07 nm/s), the film surface roughness increases for films grown at 30°C. However, when the power reaches 100 W (0.05 nm/s), there is a decrease of film roughness. In our experiments, the XRD stress analysis revealed that as the power decreased the tensile stress resulting from lattice mismatch at the YSZ film / LGS substrate interface is relieved, and then a decrease / increase in roughness [176].

# 3.4 Influence of Substrate Bias during YSZ Film Growth

Ion bombardment of the surface with high kinetic species during film growth by RF magnetron sputtering commonly induces high compressive stress by atomic-peening, defect generation, and/or grain boundary densification [179]. It is very important to manage the level of film stress for end-use technology applications. The substrate temperature and sputtering power are important as discussed before, but substrate bias can also be an effective parameter to influence film stress due to how it affects enhanced surface diffusion rates and film nucleation density [180]. The bias process can increase the kinetic energy of the species being deposited, through a mechanism known as re-sputtering, which increases both the adatom mobility during deposition and local substrate temperature. Both increasing substrate bias and substrate temperature has been shown to eliminate voids and consequently an increase in YSZ film density [181]. The negatively biased substrate could enhance the surface adatoms mobility, the number and density of nucleation sites, film density and columnar grain growth. High energetic electrons at this bias voltage could improve the particles bombardment, thereby inducing layer-by-layer growth and produce films with better quality compared to normal sputtering. Under optimum conditions, the positively charged Ar<sup>+</sup> ions will provide the necessary displacement energy to enhance the growth process towards layer growth. Film deposited at no bias voltage (figure 3.2) has a (111) orientation as it has the lowest surface energy. However, with a substrate bias voltage, residual strain competes with the surface energy to determine the orientation of the film during growth. The application of a bias voltage increases the surface mobility leading to the formation of a coating with more structural perfection, promoting closed packed structures in near-thermodynamic equilibrium conditions.

Thus, for high atomic mobility, the YSZ films are expected to grow along the (200) preferred orientation in addition to (111), corresponding to that with the lowest surface free energy and the highest number of atoms per unit area can be incorporated at low energy sites. These ion-bombardment effects explain why a (200) texture develops at high biases for samples deposited at room temperature, since (200) provides an easy channeling direction in YSZ, resulting in less sputtering and a lower defect concentration [158,182-185]. Under a positive bias, the plasma potential tends to move in the positive direction to equalize the electron and ion losses from the system, which increases the energy with which plasma species impact the target. The energies of impinging electrons during growth also increase which gives added energy to the film and increases local surface temperature. At higher positive biases, an additional glow discharge may form around the substrate and may cause re-sputtering of the surface atoms. It is possible that the electron bombardment energy during deposition can induce a higher thermal and growth stress due to excess sputtered atoms and high energy electrons bombarding the substrate [157,180,186].

XRD data in figure 3.7 from film deposited with a substrate bias show peaks with (111), (200), (220), (311) and (222) orientations. The (200) orientation exists in all the biased films. This (200) texture observed with bias voltages is most likely an ion-induced effect due to increased kinetic energies of bombarding positively charged particles. A mixed orientation of (111) and (200) orientations exist at a substrate bias of -/+ 300 V and these films were found to exhibit close to zero strain. The moderate biasing induces compressive stress because of the growth of (200) orientation, leading to expansion of the crystal lattice. It is also observed that ion bombardment modifies the state of stress in YSZ film from compressive to again tensile, along with the suppression of (200) orientation.

The ion impact of low energy ions mainly increases the kinetic energy of the adatoms which in term enhances adatom diffusion. It therefore has a similar effect as substrate heating during deposition which leads to larger grain sizes. Figure 3.8 shows the grain (crystallite) size of the as-grown biased films are larger than ones grown without a bias voltage [158,182-185,187]. The ion bombardment has a strong effect on the resulting film morphology and structure as shown in figure 3.8, and the bias voltage is a valuable parameter for the control of film growth [187]. An intrinsic stress is compressive for samples deposited on biased substrates, however there is no sign of hillock formation or buckling features.

The morphological properties of the YSZ films were characterized by SEM in order to better understand the effect of substrate biasing on their microstructure and electrical properties. Examples of the surface morphology of as-deposited YSZ films analyzed by SEM are shown in figure 3.8. A positive bias can especially increase secondary electron energy into the growth surface and thus enhance the local surface temperature. The increase of the temperature will cause higher surface diffusion rate and lead to the formation of larger grains [157,180,191]. When the depositing bias decreases to a negative value, a dense structure is formed in the film [160]. The low roughness values can be attributed to the biased ion bombardment which enhances the nucleation density and leads to uniform nucleation and promoted vertical growth.

We have found that the deposition rate can be used to control the crystallographic orientation of the grains and stress within YSZ films independently. High deposition rates during the initial nucleation stages result in (111) oriented films while low rates yield (200) oriented films.






Figure 3. 8. Strain and morphology of YSZ films grown with biases of -300V, -100V, +100V, +300V on a LGS substrate. The mean crystallite size and microstrain as determined from the Williamson-Hall method are shown.

# 3.5 Formation of (111) versus (200) Grain Orientations in As-Grown YSZ Films

XRD analysis of the YSZ films deposited during our work indicated the formation of primarily YSZ grains with preferred (111) orientation. However, YSZ films deposited at room temperature and under a substrate bias of -300V, -100V, +100V and +300V induced the formation of (200) oriented grains as well, as shown in figure 3.9.

This result suggests that film texture and stress can be induced by nucleating at one rate and then it can potentially change by carrying out subsequent growth at a different deposition rate. Figures 3.2 shows that YSZ films deposited at higher rate (0.07 nm/s) are (111) oriented, whereas those at lower growth rate (0.03 nm/s and 0.05nm/s) are (200) oriented. Figure 3.9 shows that increasing growth rate at low deposition temperature causes an increase in the magnitude of compressive stress in the (111) oriented films.

The YSZ films deposited at 30°C with the higher growth rate have a compressive film stress. According to a Thornton diagram [90] that summarizes different film growth modes versus deposition parameters, a high deposition rate and low growth temperature corresponds to a film grown in 'zone T' where different grain orientations nucleate and those with the fastest growth direction overgrow other grains.

Diffusion on the (111) plane presents the fastest growth direction, and thus (111) becomes the preferred out-of-plane preferential orientation of the film as shown in figure 3.9. Under deposition conditions for 'zone II' growth, the preferred grain orientation is governed by the lowest film surface energy. If additional energy is imparted to the film during growth by adding substrate bias and allowing higher surface diffusion, (200) oriented grains are formed. For films deposited at no voltage, the (200) peak shifts to lower 2 $\theta$  angle with increasing deposition rate (sputtering power) as shown in figure 3.9, which implies a change in stress for the YSZ films. As the deposition temperature is the same for all films, it can be inferred that film stress originates from intrinsic stress not thermal stress. For the films grown with no substrate bias at 30°C, weak peaks corresponding to (111) and (220) reflections appear indicating poor crystallinity and random orientation. In contrast, when a substrate bias was applied, the (200) peak appears [188,189]. It can be speculated that a large number of defects produced by the bombardment of more energetic ions due to the bias serve as sites for secondary nucleation and grain boundary migration, giving rise to a (111) growth orientation. An increase in bias voltage increases the number of renucleation sites, resulting in more grain growth in the (111) orientation. All biased films were grown at sputtering power of 140 W, Ar:O<sub>2</sub> (95:5) and pressure of 6 mTorr with biasing voltage varied between -300 and +300 V. The (200) peak intensity increased as the bias voltage was negatively increased, consistent with other reports [188,189]. The (111) plane has a lower surface energy compared to (100), which, in theory, should show a preferred orientation in this direction [190].

The argon ion density bombarding the growing film during the RF sputtering process can be easily controlled by changing the bias voltage applied to the biased substrate [188,189]. The lattice structures evolve under ion bombardment because of a lower sputtering yield for the more open directions, while the recrystallization mechanism due to ion-bombardment-induced lattice defects is more likely to explain the texture changes [191,192]. These ion-bombardment effects explain why a (200) texture is formed at high biases for samples deposited at room temperature, since (200) provides an easy channeling direction in YSZ, resulting in less sputtering and a lower defect concentration.

For the samples deposited at 400°C, the mixed texture of (111) and (220) at high bias during growth is expected due to the balance between surface energy minimization and ion-induced texturing [191,192]. It can be concluded that argon ion bombardment during deposition is vital to the growth of YSZ films with (200) preferred orientation.



Figure 3. 9. XRD gonio scans from films deposited at various deposition rates and bias voltages showing coexistence of (111) and (200) grain orientations.

AYSZ film deposited with a substrate bias of -300 V exhibited the strongest (200) preferred orientation as shown in figure 3.9. The (111) and (200) peaks coexist, but the relative intensity of (111) to (200) monotonically increases from positive to negative bias as observed in figure 3.9 and the peaks shift to lower angles as bias voltage is increased indicating compressive stress within the film. This phenomenon is often observed when thin films are grown under intense ion bombardment [188,189]. For films deposited without bias at lower deposition rate, the (200) peak did not exhibit a peak shift and had minimal strain.



Figure 3. 10. SEM images from as-deposited YSZ films on LGS substrate. YSZ films grown at 0.07 nm/s rate and 30°C deposition temperature. Films show a periodic repeatable arrangement of line patterns morphology on the surface. Images conducted from three different samples grown with the same deposition parameters.

# 3.6 Roughness of As-Grown YSZ Thin Films

As mentioned in Section 3.3, films deposited at high deposition rate and low deposition temperature (0.07 nm/s, 30°C) and/or low deposition rate and high deposition temperature (0.03 nm/s, 400°C, 700°C) exhibit roughness and hillock formation. This film morphology can be rationalized by differences in thermal expansion and phase energies of grains nucleating on the LGS substrate. Figure 3.10, SEM images of YSZ films deposited at 0.07 nm/s deposition rate and 30°C deposition temperature exhibit similar surface morphology with a grainy-like structure along with some white particles dispersed in a line pattern on the surface. Although this film shows roughness, hillock formation and line patterns, the thin film appears without cracks . One can speculate that high compressive film stress might lead to formation of the line patterns which precede hillock formation, another conjecture is that those lines are just a result of residual polishing damage for the langasite substrate.

# 3.7 Characterization of YSZ Thin Films Subjected to Post-Deposition Annealing Treatments

Following YSZ surface film deposition, the films were subjected to annealing treatments in air at 600°C, 800°C and 1000°C. Phenomena that were investigated include alloy segregation of yttria, overall film compositional changes, and the impact of surface roughness and hillock formation on grain size and strain. Overall, the goal was to assess the YSZ phase stability as a function of substrate bias and annealing temperature.

Analysis of the surface composition of YSZ films by XPS found that yttrium segregates to the surface of YSZ at elevated temperatures as shown in figure 3.11. The occurrence of surface segregation in YSZ films has been suggested depending on three factors: surface energy of the individual components, strain energy and the thermal energy [194,195]. The process of segregation is driven by the reduction of the surface free energy. Strain relaxation and the formation of a space-charge region associated with defects and aliovalent cations are considered to be the main contributions in the reduction.

The surface free energy of the YSZ surface is reported to change due to the increased Y<sub>2</sub>O<sub>3</sub> concentration. The driving force for impurity segregation is believed to be the lowering of surface or interfacial energy [196]. The surface energy of an element is directly related to its melting point; the lower the melting point, the lower is the surface energy. The melting points of yttrium and zirconium are 1509°C and 1852°C, respectively. Therefore, the surface energy of yttrium is likely to be lower than that of zirconium [194,195]. Moreover, the ionic radius of yttrium is about 16% larger than that of zirconium. So, the segregation of yttrium to the surface is expected to occur to reduce the overall surface and strain energy of the system [194,195].



Figure 3. 11. XPS high resolution spectra from as-deposited and annealed YSZ thin films.

The segregation of  $Y_2O_3$  to the surface region may be driven by a combination of strain relaxation and a different local bonding in the lattice [196]. Yttria cations, which are aliovalent in the ZrO<sub>2</sub> lattice, segregate to the grain boundaries (GBs) in yttria–zirconia ceramics by a mechanism which combines the elastic misfit effect (since the dissimilarity between the ionic radii of the Zr<sup>4+</sup> (0.92 Å) and Y<sup>3+</sup> (1.16 Å) cations helps the latter to segregate) and the Coulombic interactions between the dopants and the oxygen vacancies which must be created for charge compensation [197-199].

It has been demonstrated that yttria and oxygen vacancies tend to co-segregate together, and this co-segregation of oxygen vacancies with yttrium cations is electrically and energetically favorable [197-199]. Yttria segregation is partially responsible for a number of exceptional mechanical and (especially) electrical properties exhibited in the yttria–zirconia system.



Figure 3. 12. Ratio of Y/Zr in YSZ films as measured by XPS as function of the annealing conditions for films grown at different deposition rates and temperatures.

The XPS spectra in figure 3.12 illustrate changes in the Zr 3d and Y 3d peaks as yttria segregation occurs. The binding energies of the Y  $3d_{5/2}$  and Zr  $3d_{5/2}$  components are at 156 eV and 181 eV, respectively, indicating the presence of the fully oxidized  $Zr^{4+}$  state, as expected in YSZ. The oxygen peak was used as reference peak for as-deposited YSZ films, and oxygen and carbon peaks were the reference peak for annealed YSZ films. Binding energies of Zr and Y show a slight peak shift (+0.5 eV to +0.8 eV) which might be due to the ion size difference. Stabilizing the zirconia by adding 8 mol% Y<sub>2</sub>O<sub>3</sub> causes a rearrangement among the nearest neighboring ions, which might give rise to a lattice deformation producing lattice strains that could explain this shift in binding energies [175,193]. The segregation-induced surface enrichment can be observed already at 600°C and increase with annealing temperature in air as shown in figure 3.12.

Similar Y segregation behavior was observed in all films similar to that reported for a YSZ crystal annealed at 1100°C [200].

For either negative sample bias or positive sample bias, the YSZ composition changes minimally. The positive substrate bias attracts more electrons than negative bias to come to the substrate and neutralize argon ions, which then become less chemically reactive [183,201]. Usually, when sputtering is adopted as the depositing method, a denser structure with less macro defects can be obtained [160,201].

The Y/Zr ratio of the as-deposited films falls between 0.12 - 0.16 for films with applied bias. It is interesting to note that sputtering shows a dependence on substrate bias voltage as the biased films deposited at room temperature are highly stoichiometric [202].

Our data indicate that the substrate bias limits yttria segregation and leads to the coexistence of (200) and (111) grains that appear to significantly reduce film stress, figure 3.13.

Investigation of YSZ films grown with different deposition parameters, all showed that after heating at 1000°C for 10 hours in air, the yttrium concentration reached a steady-state value. The surface composition of the YSZ thin film remained the same after annealing at 1000°C for 10 hr. At lower annealing temperatures of 600°C and 800°C, shorter annealing times (one hour) were needed for the stabilization of the Y (3d)/ Zr (3d) atomic ratios, as shown in figure 3.14.



Figure 3. 13. Ratio of Y/Zr in YSZ films as measured by XPS as function of the post-deposition annealing conditions for films grown at  $30^{\circ}$ C under different substrate bias conditions. The substrate bias hinders yttrium segregation towards the surface.



Figure 3. 14. Ratio of Y/Zr in YSZ films as measured by XPS for films deposited at different temperatures (30°C, 400°C, 700°C) and then annealed at 600°C, 800°C, and 1000°C in air.

### 3.8 Comparison of the Sample Set of YSZ Thin Films

Figure 3.15 shows XRD gonio scans measured from films grown with different deposition rates and deposition temperatures both as-grown and after annealed to 1000°C. Peaks shifts and broadening indicate changes in crystallite size and film strain. Peaks shift to lower angles in asdeposited films compared to the position for an unstrained powder standard, due to compressive strain. The annealing temperature treatments shift the peaks to higher angle as strain is relieved.

The crystallite sizes, determined for the different substrate temperatures and deposition rates as shown in figure 3.16, increase with increasing deposition temperature. Increased temperature, in turn, increases the diffusion coefficient of incoming adatoms on the substrate, relaxes compressive stress, and increases crystallite size within the films [139]. The estimated grain sizes determined from the Williamson-Hall method are 25-35 nm after annealing. This limited grain growth (<100 nm) can be attributed to the moderate annealing temperature and dopant  $Y^{3+}$  addition. In addition to the grain size, the grain growth by thermal treatment also causes a decrease of the grain boundary density [203].

YSZ film strain versus annealing temperature as determined from the Williamson – Hall method is shown in figure 3.17. It is found that the compressive stress in the as-sputtered YSZ films begins to decrease in magnitude at temperatures >600°C, reaches nearly zero stress at a temperature between 800°C and 1000°C, and becomes tensile and decrease in magnitude at higher temperatures. The strain decreases with increasing substrate temperature, because of thermal annealing. The improvement of crystallinity leads to a reduction in defect density inside the films which involves network relaxation. The strain is also an indication of the crystalline quality of YSZ film. A decrease in strain indicates an improvement of the crystallinity of the film [204].

Figure 3.18 shows SEM images from a YSZ film grown at 30°C and 0.07nm/s, both asdeposited and after annealing at 800°C and 1000°C. After annealing, the hillocks get enlarged and finally fracture making a pinhole – defects. Changes in microstructure as a result of grain growth and hillock formation usually stabilize after a series of thermal cycles. The history of film stress versus temperature attains a steady-state hysteresis loop which does not vary significantly from cycle to cycle thereafter. Hillocks represent permanent damage to the film material which is not relieved upon temperature reversal.

The as-deposited films exhibit no voids, and upon annealing, grain growth and hillock (bubble) formation occur. Hillocks as large as 1  $\mu$ m in diameter were observed after annealing at 1000°C. The formation of these bubbles was attributed to more than one reason: the lattice mismatch between the film layers and the LGS substrate orientation, the sputtered particle free surface energy, the difference in the thermal expansion coefficient between YSZ and LGS and compressive stress for films deposited at low deposition temperature (30°C) and high deposition rate (0.07 nm/s).



Figure 3. 15. XRD gonio scans from as-grown and annealed YSZ films. Peaks shift and broadening indicate changes in crystallite size and film strain. Peaks shift to lower angles in as-deposited films compared to the position for an unstrained powder standard, due to compressive strain. The annealing temperature treatments shift the peaks to higher angle as strain is relieved.



Figure 3. 16. 3-D plot showing YSZ crystallite size (a) as-deposited (b) annealing up to 1000°C. Crystallite sizes were calculated by the Williamson – Hall method.



Figure 3. 17. YSZ film strain versus annealing temperature as determined from the Williamson – Hall method. It is found that the compressive stress in the as-sputtered YSZ film starts to decrease in magnitude at a temperature higher than 600°C, reaches zero stress at a temperature between 800 and 1000°C, and becomes tensile and decrease in magnitude at higher temperatures. The annealing temperature simply becomes too low to completely relieve the compressive residual stress induced by sputtering [28].



Figure 3. 18. Films grown at low deposition temperature (30°C) and high deposition rate (0.07 nm/s) show that the free surface of YSZ film is not perfectly flat and exhibit hillock formation.

Figure 3.19 shows SEM images from the YSZ films deposited at different temperatures and after annealing at 1000°C. Films deposited at 700°C and 0.03 nm/s, and films deposited at 30°C and 0.07 nm/s exhibit hillock formation, and films grown under the other conditions do not have visible hillocks. XRD gonio scans (figure 3.20) reveal shifts and narrowing of diffraction peaks after annealing at 1000°C due to grain growth and strain. The diffraction peak shifts to lower angle theta in as-deposited films compared to the standard polycrystalline powder peak position which signifies lattice contraction with compressive strain. With an increase in annealing temperature, the peaks shift to higher two-theta indicating some tensile strain. For the biased YSZ films, the (111) and (200) diffraction peaks gradually increased in sharpness and intensity as annealing temperature increased due to grain growth (see figure 3.21). It was found that the highly (111) and (200) oriented crystallite textures remained after annealing at 1000°C. The amount of film strain is very dependent on the substrate bias. Figure 3.22 shows that films grown without bias had much larger strain than those grown using bias. The morphologies of these films as observed by SEM are shown in figure 3.23.





0.03 nm/s





Figure 3. 19. SEM images for as-grown and annealed YSZ thin films. Films deposited at high deposition temperature (700°C) and low deposition rate (0.03 nm/s), and films deposited at low deposition temperature (30°C) and high deposition rate (0.07 nm/s) exhibit hillock formation. However, rest of the films have a range of stress process between compression and tensile stress. Images are for films annealed at 1000°C in air for one hour.





Figure 3. 20. XRD gonio scans from as-grown YSZ thin films and the same films after annealing at 1000°C in air for 1 hour. The YSZ films were all deposited at 30°C, a rate of 0.07 nm/s and with a 95:5 Ar:O<sub>2</sub> ratio but with biases of -300V, -100V, +100V and +300V.



Figure 3. 21. XRD crystallite size of as-deposited YSZ films and after annealing at 1000°C in air for different substrate biases.



Figure 3. 22. Film strain in as-grown and annealed YSZ films is determined by the XRD Williamson-Hall method.



Figure 3. 23. SEM images from as-grown YSZ thin films (upper row) and films annealed at 1000°C in air for 1 hour (lower row) for different substrate biasing conditions. All films were deposited at a deposition temperature of 30°C and deposition rate of 0.07 nm/s.

# 3.9 Impedance and Ionic Conductivity of YSZ Films

The ionic conduction in YSZ proceeds via a vacancy hopping mechanism wherein an oxygen vacancy exchanges position with an  $O^{2-}$  ion at a neighbor anion site. The presence of  $O^{2-}$ - vacancy pairs is crucial to the YSZ conductivity. The concentration of Y<sub>2</sub>O<sub>3</sub> plays an important role in determining the ionic properties of YSZ, because the dopant  $Y^{3+}$  cations replace the host  $Zr^{4+}$  cations in the zirconia lattice to create empty oxygen sites or oxygen vacancies  $V_0^{\bullet\bullet}$  [206]. YSZ with 8 mol%  $Y_2O_3$  is widely considered to be an optimized fast-ion conductor [207]. The maximum ionic conductivity in zirconia-based systems is observed when the concentration of acceptor-type dopants is close to the minimum value that is necessary to completely stabilize the cubic fluorite-type YSZ structure [211]. This maximum conductivity has been observed in  $ZrO_2$  – 8 mol % Y<sub>2</sub>O<sub>3</sub> crystals, in which charged oxygen vacancies associate with Zr<sup>4+</sup> so that seven-fold local coordination around Zr<sup>4+</sup> is stabilized in cubic symmetry [170,171], and consequently oxygen atoms are displaced from high-symmetry positions characteristic of the cubic phase, which provides their enhanced diffusion mobility [208]. Six yttrium atoms can be introduced substitutionally at random sites of the cation sublattice and these defects (denoted as  $Y'_{Zr}$  in Kröger - Vink notation) are negatively charged. Therefore, three oxygen vacancies are also created as charge-compensating defects of positive effective charge  $V_0^{\bullet\bullet}$ . The incorporation reaction in Kröger-Vink notation is the following:

$$Y_2 O_3 \xrightarrow{ZrO_2} 2Y'_{Zr} + V_0^{\bullet \bullet} + 3O_0^X$$
(3.3)

where  $O_0^X$  denoting oxygen atoms at normal lattice sites [209,210].

Due to Coulombic and elastic attractive forces between the individual  $Y'_{Zr}$  and  $V_0^{\bullet\bullet}$  defects, the oxygen vacancies existed as two manners:  $Y'_{Zr} V_0^{\bullet\bullet}$  and  $V_0^{\bullet\bullet}$ . The formation of defects associates binds some oxygen vacancies to yttrium ions, making the oxygen vacancies unavailable for conduction. It was suggested that  $Y'_{Zr}$  is more likely to occur because of the expected random distribution of  $Y'_{Zr}$  [211]. Since oxygen transport in these materials is controlled by free vacancies, it is necessary to quantify the population of free vacancies explicitly as a function of temperature [211].

AC impedance spectroscopy was used in this thesis work to investigate the transport properties of YSZ films with respect to properties such as crystallite size and orientation, strain, and nanomorphology. Figure 3.24 shows impedance spectra (Nyquist plots) from a 200 nm thick YSZ film deposited on LGS substrate at 400°C. The resistivity of the film decreases (semicircles shrink) as expected for ionic conduction with the increase in temperature from 400 to 750°C. The ionic conductivity is related to the free oxygen vacancy presence in YSZ; an increase in the free oxygen vacancies leads to increased ionic conductivity and a lower activation energy [212]. According to electrochemical impedance theory, the highest frequency impedance arcs in a Nyquist plot (imaginary-part impedance Z" versus real-part impedance Z' obtained from frequency sweep) are associated with conduction within the YSZ film between the two platinum electrodes [213].

One concern in the conductivity measurements of thin films is the influence of the substrate on the total resistance. Since the thin films were deposited on an insulating LGS substrate, the electrode configuration was selected to obtain measurements of the current flow in the plane parallel to the substrate surface. In this case, the total resistance involves the superposition of film, interface, and substrate contributions.



Figure 3. 24. Typical impedance spectra (Nyquist plots) from 200 nm thick YSZ film deposited on LGS substrate at 400°C. The resistivity of the film decreased (semicircles shrink) as expected for ionic conduction with the increase in temperature from 400 to 750°C. The high stray capacitance value observed in the in-plane configuration of the YSZ film makes it impossible to separate the contribution between grain and grain boundary resistance, which effectively reduces the Nyquist plot to a single arc. The total conductivity of the YSZ film exponentially increases with increase in temperature attributed to the thermal enhancement of oxide migration in the conduction mechanism [216]. The electrochemical impedance spectra were fitted using EC-Lab software.

However, if the substrate resistance is significantly higher than that of the film and interface, the total resistance will be determined by film and/or interface [214-216]. The resistance of a bare LGS substrate was measured under the same identical conditions as the YSZ/LGS samples and was found to have a value about five to six orders less than that of YSZ.

Changes in film structure and composition may also have a substantial influence on conductivity. For example, impurity segregation to the grain boundary during heat treatment constricts the ion migration pathway, reducing the electrical conductivity as inferred from impedance spectroscopy [221].

For the as-grown and thermally annealed YSZ films, the oxygen deficiency due to segregation of oxygen vacancies on dislocations, forms a positively charged dislocation core in YSZ. Due to electrostatic interaction between positively charged dislocations and oxygen vacancies, positively charged oxygen vacancies might deplete near the dislocation, while negatively charged carriers are accumulated.

The concentration deviation of the oxygen vacancy in the vicinity of dislocations from the bulk value will lead to the formation of a space charge region, as suggested in the space charge model for a grain boundary in YSZ [207,217,219]. Space charge effect is a nano ionic size effect which shows up when sample dimensions are comparable to the extension of the space-charge region, which means it depends on the synthesis and thermal treatments.

The scale for charge inhomogeneities determines the size of the space-charge region at an interface or grain boundary [207,217]. With oxygen vacancies being the predominant charge carriers, the grain boundaries of YSZ present a blocking effect to the ionic transport across the specific grain-boundary conductivity of YSZ depending on film synthesize parameters.

GB's blocking effect has a significant influence on the total conductivity, GB's blocking effect has been recognized to come from two aspects: GB impurity phase and space charge effect. The space charge effect is an intrinsic effect, which is believed to play a dominant role in GB's blocking effect. However, the grain-boundary blocking effect disappears at high enough temperatures (e.g.,  $> 400^{\circ}$ C) or high enough dopant concentration (e.g., 8% Y<sub>2</sub>O<sub>3</sub>) [218,220].

The relationship between the conductivity and film thickness can be interpreted as a superposition of surface/ interface and bulk related contributions. The interaction between these depends on many parameters including material morphology, the volume fraction occupied by the interfacial area, as well as the relaxation time and the activation energy for each transport process.

The observed behavior is not related to changes in the bulk conductivity but rather to increasing surface/ interface contributions with increase in temperatures [223]. To elucidate the effects of thicknesses and grain sizes on the electrical conductivities of YSZ films clearly and accurately, it is necessary and beneficial to eliminate the contribution from the film/ substrate interface region and obtain the real electrical conductivities of YSZ film itself [205,217].

The contribution of the substrate to the total resistance represented by parallel connected resistances of film, interface and substrate is negligible [214,217,222]. The observed relationship between the conductivity and film thickness can be explained as a superposition of YSZ/LGS surface/interface and YSZ lattice conductivities [214,217,222]. The film resistance value obtained with best fitting results were normalized and correspondingly converted into conductivity. These values as a function of thickness were found to increase when the film thickness decreased.

The behavior can be explained by consideration of the sample geometry. Based on the electrode configuration, the film thickness (d) affects the electrode cross-section area such that the resistance should exhibit the following behavior:

$$R = \frac{1}{\sigma} \frac{a}{bd} \tag{3.4}$$

where  $\sigma$ , a and b are the conductivity of the sample, distance between electrodes and electrode width normal to the current flow, respectively [214,216,217,222].

This surface/interface contribution can be attributed to grain boundary, space charge or YSZ/LGS interface effects, while lattice conductivity should not be dependent upon the thickness [214,216,217,222].



Figure 3. 25. Impedance pattern (Nyquist plot) for YSZ films as function of thickness. Two different thicknesses 15 and 200 nm YSZ films deposited at the same temperature (400°C), same deposition rate (0.07 nm/s) and same substrate (LGS) for each film. Film with less thickness 15 nm (orange plot) show a lower ionic conductivity compared to the thicker film 200nm (red plot) which exhibit higher ionic conductivity. Impedance measurement temperature for both films (500°C). The electrochemical impedance spectra were fitted using EC-Lab software.

It is obvious that the electrical conductivities of YSZ films tend to increase with the increment in film thickness after the interfacial effects are eliminated [205,217]. Based on the space charge effect theory, the grain-boundary region of polycrystalline YSZ ceramic consists of a grain-boundary core and two adjacent space-charge layers. The grain-boundary core of YSZ is positively charged probably due to the oxygen deficiency or the oxygen vacancy enrichment there [205,217]. The oxygen vacancies are depleted in the space-charge layers and the grain-boundary regions are blocking the oxygen-ion conduction, leading to a low conductivity of the grain boundary region.

Thus, the conductivities of YSZ films increase with the increment in film thickness, opposite to the trend of the apparent conductivity [205,217]. The effect of YSZ film thickness on the increase/decrease of the ionic conductivity value of the sputtered films have been plotted in figure 3.25.

#### 3.10 Ionic Conductivity of As-Grown and Annealed YSZ Thin Films

Generally, for an ionic conductivity measurement in the in-plane direction, four conduction paths are possible: bulk lattice conduction, grain boundary conduction, surface or film/substrate interface conduction, and substrate conduction. As mentioned earlier, langasite is a wide band gap insulator with high impedance, which is three/four orders of magnitude higher than the YSZ film even at elevated temperatures. The interface conduction becomes dominant only film thicknesses < 50nm and so film/substrate interface can also be ignored for our 200 nm thick films. Regarding bulk vs. grain boundary conduction, the grain size in the conduction path (i.e., in-plane) is less than 100 nm, so the bulk lattice and the grain boundary contributions cannot be deconvoluted in the semi-circle Nyquist plots. However, in impedance spectra, the ionic conductivity and apparent activation energy can be extracted [170,171].

To determine the effect of the grain boundary on the electrical properties of nanocrystalline YSZ thin films, electrochemical impedance spectroscopy (EIS) was conducted in the temperature range of 350°C to 600°C. Figure 3.26 shows the representative Nyquist plots from as-deposited and annealed films measured at 500°C. All samples exhibited one semicircle after annealing at 600°C and 800°C in air for one hour. EC-Lab software was used to fit the spectra arcs.

The intercepts of the impedance curves with the real axis in the high frequency and mid frequency regions can be used to calculate the total resistance.

In the ideal case, the frequency response of the grain polarization can be modeled by a resistor capacitor (RC) pair in parallel. A parallel RC element represents a lossy capacitor with a typical relaxation time which corresponds to the process. A constant phase element (CPE) is typically used to model experimental data instead of a simple capacitor. A CPE is equivalent to a distribution of capacitors in parallel; as such, it accounts for the nanostructure inhomogeneities within the sample [135,224]. The impedance data for YSZ are well explained by a space charge model, in which the grain boundary consists of a grain boundary core and two adjacent space charge layers. In addition to that, cation phases have been often observed at the grain boundaries due to dopant segregation. It is believed that high resistive grain boundaries arise due to the depletion of positively charged oxygen vacancies within the negative space charge layers.

Results shown in figures 3.36 and 3.27 show the ionic conductivities versus film deposition conditions, and after annealing up to 1000°C. The enhanced ionic conductivity of the annealed YSZ films may be due to increased larger crystallite sizes with annealing. As-deposited and annealed films with attenuated space charge layers exhibit superior conductivities due to a grain boundary blocking effect [213,225].

To explain these results, it has been known that ions are depleted to form a space charge region in the vicinity of the grain boundary core in YSZ, leading to obstruction of ion transport across the grain boundaries and thus limiting the ionic conductivity [222]. This is why strain has a sizeable effect on the ionic conductivity of YSZ thin films, through modifying the volume available for oxygen-ion hopping, with compressive strain reducing conductivity and tensile strain enhancing it [222].

It can clearly be observed in figure 3.26 that the semicircles for the annealed YSZ film are smaller than that of the as-deposited one, indicating that the ionic conductance of the annealed film is higher than that of the as-deposited film. When the residual stress is shifted from compressive to tensile, the radius of oxygen vacancy will be increased, and the ionic conductivity will thus be enhanced [226]. However, it should be noted that the stress is analyzed at room temperature while the ionic conductivity is measured at 400 -600°C. Compressive stresses are relieved, at least to some extent upon annealing. It is observed that as the grain size increases, the grain boundary density decreases, an increase in ionic conductivity is observed. As the oxygen vacancy concentration in the grain-boundary core is higher, it is expected that the transport of oxygen vacancies along the grain-boundary core will be faster. It has already been postulated that the enrichment of oxygen vacancies in the grain-boundary core is responsible for the increase in ionic conductivity in 8YSZ. When the grain size decreases, the mechanism of electrical conductivities along the grain boundary will change because the thickness of the intergranular region decreases to a greater extent. This minimizes the segregation or impurity phase on the grain boundary to form the blocking layer [224]. This finding is consistent with the idea that segregation of yttrium and vacancies strongly depends on the size of the grains [217]. Tensile strain expands the lattice spacing and thus weakens the oxygen-cation bond strength, thereby greatly reducing the ion transport barrier. This will enhance the mobility of oxygen vacancies and increase the resulting conductivity. Compressive strain would function conversely [227]. For films deposited with a substrate bias, a significant increase in in-plane ionic conductivity was observed as compared to the corresponding sample deposited at ground potential. The increase in ionic conductivity suggests grain boundary migration (ionic species O2- migrate through grain boundaries) due to different grain sizes and/or grain boundary structures. It was observed that the grain size increased in samples deposited at high bias voltages. The variation in the ionic conductivities based on manipulating deposition parameters is shown in figure 3.26. Impedance spectra (A), (D), (G), (H) and (I) in figure 3.26 exhibit an enhancement in ionic conductivity after annealing. This can be explained based on the condition of each film. Film (A) grown with the most stressed surface including roughness and hillock formation. After annealing, the stress was relieved, and the film morphology and crystallographic structure transferred from the compressive to tensile status with an improvement in crystallite size. Films (D) and (G) grow with (200) phase where no hillock exists and both films have smother surface interference compared to other films. However, films show an improvement in the ionic conductivity after annealing. However, there was not a change in the Y/Zr atomic percentage, a similar result to that shown previously in figure 3.13. Having both (200) and (111) crystallite orientations might reduce the blocking and space charge effects due to oxygen depletion into the grain boundaries by increasing oxygen exchange and ionic channeling. Films (H) and (I) are just like film (A), both grown with compressive strain crystallographic structure. Annealing changed the compressive strain into tensile strain with a noticeable enhancement in ionic conductivity as well as crystallite size. Films (A), (D), (G), (H) and (I) have a minimal level of yttria segregation proportional to zirconia concentration as it was shown in figure 3.12. The remarkable change in crystallographic structure for less stable films (A), (H) and (I), and having (200) orientation did not show direct evidence for yttria segregation in XPS. Films (B), (C), (E) and (F) clearly show a decrease in the ionic conductivity after annealing. Those films were the most stable films before and after annealing and did not show any roughness or hillock formation, however they have yttria enrichment near the surface. The change in ionic conductivity in this case are shown in tables (C) and (D) of figure 3.27. Tables (D) show an inverse relationship between deposition rate and ionic conductivity at the same deposition temperature.



Figure 3. 26. Impedance spectra (Nyquist plots) measured at 500°C from as-grown (Orange) and annealed (Brown) YSZ thin films grown at different deposition rates and deposition temperatures. All films have the same thickness of 200 nm. Samples inside the blue box exhibit a decrease in ionic conductivity after annealing due to the effects of strain and yttria segregation, whereas other samples show an enhancement in the ionic conductivity after annealing.



Figure 3. 27. (A) and (B) represent a 3D scatter plot for the conductivities measured at 500°C for as-deposited and annealed YSZ films. Plots (C) and (D) show the conductivity values calculated from (A) and (B). Samples with a star legend indicate the highest values in ionic conductivity. Plot (E) illustrates the changes in film conductivity after annealing. Films grown at low temperature and low deposition rate exhibit the highest conductivity before and after annealing.



Figure 3. 28. Typical EIS spectra measured at 500°C (Nyquist plot) for YSZ films deposited by applying substrate bias at 30°C. This figure shows the ionic conductivity value after annealing biased films up to 1000°C in air for one hour.

# 3.11 Ionic Conductivity and Activation Energy of As-Grown and Annealed YSZ Films

Oxygen vacancies are the main charge carriers in YSZ. They comprise two types: those being free to migrate and those bound to  $Y^{3+}$  cations. The activation energy (E<sub>a</sub>) for the conductivity consists of the sum of dissociation energy, and migration energy. For 8-YSZ, the amount of oxygen vacancies and  $Y^{3+}$  ions on  $Zr^{4+}$  sites are high enough to generate the formation of dopant-vacancy associations over the whole temperature range and the activation energy are comprised of a dissociation energy and migration energy [210,211,228]. The carriers in the surface layer can move more freely than the internal ones because they have relatively high energy. Therefore, when they migrate, the energy barrier is lower than that of the internal atoms or ions. In other words, the activation energy of the surface carriers is lower than that of the internal ones. Therefore, the increased hopping rate is expected to result in a lower activation energy and higher ionic conductivity for YSZ films [210,211,228]. Long-range migration of oxygen ions takes place by thermally activated hopping to adjacent oxygen vacancies, with conductivity obeying an Arrhenius relationship. The ionic conductivity and activation energy value of the different YSZ films, figures 3.29 and 3.30, with respect the total conductivity was determined and plotted using an Arrhenius relationship (Nernst-Einstein relationship):

$$\sigma T = A \, e^{(-E_a/k_\beta T)} \tag{3.5}$$

where,  $E_a$  is the activation energy for oxygen ion migration,  $k_B$  is the Boltzmann constant, T is the absolute temperature, and A is the pre-exponential coefficient factor correlating closely with the amounts and the entropies of oxygen vacancy [213,216,217].

The activation energy was determined from the slope of the Arrhenius plots for the YSZ films. The corresponding Arrhenius plots in figures 3.29 and 3.30, ranging from 400 to 600°C, show the conductivities for all of the annealed YSZ films. The activation energy, which is closely correlated with the migration of oxygen ions, can then be estimated according to equation 3.5 [189,198].

Increasing conductivity at a given temperature would require increasing the prefactor and/or decreasing the activation energy  $E_a$ . The broad changes in activation energy of conductivity in air represent primarily changes in the ionic diffusion characteristics of thin films. The activation energy for oxygen ion migration observed in the YSZ films (figure 3.29) was found to agree well with activation energy typically reported for YSZ films [189,211,213,215,224,226,227,229].

The y-intercept (A) of Arrhenius plot of the annealed specimens is inversely related to film thickness, indicating an enhancement of the pre-exponential factor. This could be caused by more oxygen vacancies existing along the interface and/or higher state of disorder of the vacancy for thinner films and the tensile residual stress.

It should be emphasized that thermal annealing is able to eliminate dislocations near the interface formed during deposition, enhancing film crystallinity, and lowering the activation energy [226]. Grain size alone is not a suitable parameter to discuss processing-related differences in diffusion of ionic charge carriers for thin films.



Figure 3. 29. (A) and (B) Arrhenius plots for as-grown and annealed YSZ films, respectively, measured in a temperature range of 400  $-600^{\circ}$ C under ambient air. (C) Activation energy values calculated from the Arrhenius plot slope. (D) Legend indicating the deposition parameters employed with each sample as each color represent a unique deposition temperature and deposition rate sputtering condition. The total activation energy of the film's increases/decrease with increase in temperature is attributed to the tensile/compression strain and the grain size effect [216].



Figure 3. 30. Arrhenius plot of the ionic conductivity measured in a temperature range of  $400 - 600^{\circ}$ C under ambient air. The lattice tensile / compressive strain and yttria segregation / space charge affect the activation energy that is calculated from the slope of the Arrhenius plot. It was found to be that the activation energy reduced from 1.28 to 0.9 eV for a YSZ film deposited at  $30^{\circ}$ C then annealed to  $1000^{\circ}$ C (green plot) and increased from 0.88 to 1.3 eV for a YSZ film deposited at  $700^{\circ}$ C then annealed to  $1000^{\circ}$ C (black plot).

The enhancement of the ionic conductivity might result from both the tensile strain and the space-charge effects. The variation in total conductivity of YSZ films deposited under the different conditions and their associated activation energy, suggests that the mechanistic aspect of conductivity largely depends on thin film synthesis and processing, with the total film conductivity substantially decreasing with increasing grain boundary area due to the depletion of oxygen vacancies by the negative space-charge layer. In this regard, the increase in the degree of (111) preferred film orientation will enhance the overall ionic conductivity by reducing the grain boundary resistance [216]. In addition, the ionic conductivity is also affected by defects and residual stresses inevitably formed during deposition and easily modified by subsequent annealing.
#### **3.12 Chapter Summary**

This chapter has been focused on results that were acquired from YSZ films deposited on langasite substrates. The YSZ (8% Y<sub>2</sub>O<sub>3</sub>-92% ZrO<sub>2</sub>) films were deposited on LGS (langasite - La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub>) using RF magnetron sputtering. Parameters such as deposition rate, deposition temperature, and substrate biasing were utilized to dictate film structure, strain and nanomorphology. Results from characterization, crystallographic structure and roughness were used to understand film functionality in terms of stability, yttria segregation and ionic conductivity.

The YSZ film crystal structure was probed by XRD, and the surface composition was investigated by XPS before and after high temperature treatments up to 1000°C in an air furnace. Film impedance experiments were carried out to characterize the high temperature surface reactivity of the YSZ thin films in the range 400-600°C.

As-deposited films at low deposition temperature ( $30^{\circ}$ C) and high deposition rate (0.07 nm/s), as well as film deposited at high deposition temperature ( $700^{\circ}$ C) and low deposition rate (0.03 nm/s) were not very stable, were rough, and exhibited hillock formation. Williamson – Hall experimental method was used to determine the crystallite size and strain for all of the YSZ films. XRR and SEM revealed film roughness and the influence of deposition parameters on film stability. The use of substrate bias (-300 V to +300 V) induced (200) oriented YSZ crystallites that help eliminate hillock formation.

YSZ films were annealed at 600°C, 800°C and 1000°C for 1 h in air to simulate the working temperatures that are of interest for YSZ-based gas sensors. Annealing enhances the YSZ crystallinity, enlarges the grain size, and reduces the level of compressive film strain.

Results from impedance spectroscopy showed that introducing oxygen vacancies into the YSZ lattice makes it a thin film material with high ionic (and very low electronic) conductivity at high temperatures, providing the basis for its use in gas sensors. Added trivalent  $Y^{3+}$  replaces tetravalent  $Zr^{4+}$  and for charge compensation, one oxygen vacancy is created per two Y atoms. These vacancies form the basis for the high oxygen ion conductivity at high temperatures. Measurements of ionic conductivity and activation energies were obtained from as-grown and annealed YSZ films. The presence of (200) crystallites lead to an increase in ionic conductivity presumably due to fast oxygen diffusion in strained films. Yttria segregation increases the activation energy and influences conductivity in as-grown and annealed films. The results of this chapter form the basis for understanding YSZ films containing Pt nanoparticles and H<sub>2</sub> interactions with Pt/YSZ thin materials discussed in Chapters 4 and 5.

#### **CHAPTER 4**

# CHARACTERISTICS OF YSZ FILMS WITH CATALYTIC PT NANOPARTICLES

# 4.1 Heterogenous Catalysis of Metal Nanoparticles on Oxide Supports

Oxide surfaces decorated with metal nanoparticles are well known for their catalytic activity, and as heterogeneous catalysts they find wide technological interest and applicability in catalysis, photonics, plasmonic, and sensing, among other areas [230-234]. Generally, the utilization of metal nanoparticles in applications is faced with a challenge of poor stability over time on the catalyst substrate since the nanosized metal particles eventually coalesce and grow at high operating temperatures. Important characteristics commonly determined for supported nanoparticle catalysts are the identity and composition of the phases, the particle size distribution, and how ionic conductivity changes under reaction conditions [230-234].

To maximize catalytic performance and reduce the loading of the expensive noble metals, the optimum catalytic activity per unit costs typically translates into synthesizing catalysts with very high dispersions, corresponding to particle sizes close to 1 nm in diameter. One way to produce such particles or ensembles is by "agglomeration" of a thin metal film in which there is an uncovering of the substrate or dewetting of an initially continuous film. The underlying forces that separate a thin film into small islands can also lead to agglomeration of very small metal particles into coarser aggregates or patches. The overall driving force for agglomeration is the minimization of the surface free energy of the metal film, of the metal oxide and of the metal–metal oxide interface [230-234].

Hydrogen (H<sub>2</sub>) gas is important in many industrial processes and various applications. For instance, it is the leading propellant used in spaceships and in commercial and military launch vehicles. In addition, hydrogen is an ecofriendly resource for many applications in scientific research and industry [235-239]. When hydrogen is present in concentrations up to 4 vol.% (40,000 ppm), it is an explosive mixture with air which has huge safety implications. Hence, there is a genuine and urgent need for reliably sensing H<sub>2</sub> at in the ppm range and above. Conventional hydrogen-gas sensors based on metal oxides (In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, ZnO, and TiO<sub>2</sub>) have reasonable sensitivities towards reducing gases, however these films face challenges like response time, slow and incomplete recovery time, and their high-temperature performance at approximately 400°C and above is a significantly poor [236-239]. Excellent monitoring and leak detector systems are still needed to detect H<sub>2</sub> gas with high accuracy and selectivity, fast response, and thermal stability.

The response/recovery time of H<sub>2</sub> sensors based on conductivity / resistivity primarily depends on the kinetic absorption, absorption energy, and diffusion length of the target gas and sensing material. Several strategies have been employed to enhance their performance, such as doping. Noble catalysts, such as palladium (Pd), platinum (Pt) and gold (Au), have been used to enhance H<sub>2</sub> absorption kinetics [235-239]. Palladium (Pd) is considered to be very promising because of its superior hydrogen solubility at room temperature. However, Pd films and nanoparticles are susceptible to undergo defect formation and structural transformations in H<sub>2</sub> gas concentrations and Pd film buckling can occur leading to long term instability [235-239]. Platinum (Pt) nanoparticles are also well-known catalysts, and they potentially could be more stable in terms of film morphology compared to Pd especially after long-term operation above 500°C. Aggregation of Pt films and nanoparticle formation often depends on Pt thickness, annealing temperature, and annealing time [232,240,241].

In this thesis research, Pt nanoparticles were dispersed on the surface of YSZ films. This chapter discusses properties of the Pt/YSZ thin films including synthesis and annealing, and Chapter 5 addresses reactivity of Pt/YSZ thin films towards H<sub>2</sub> gas.

#### 4.2 Deposition of Pt on top of YSZ films

Pt films of 1, 3, 5, and 10 monolayer equivalent thickness were deposited onto YSZ films at either room temperature or at 400°C by using electron-beam evaporation, as discussed in Section 2.2. Following synthesis of the Pt/YSZ samples, they were transferred under vacuum for immediate XPS analysis. The XPS peaks were deconvoluted to determine the peak areas and the binding energies belonging to the different bonding states of platinum. The peak area of 4f7/2 and 4f5/2 components were fixed at a 4:3 ratio, and theoretical spin orbit splitting of  $3.33 \pm 0.5$  eV was always true. The BE of Pt 4f7/2 component was corrected for sample charging referencing to O 1s at 529.0 eV. Pt 4f7/2 peaks were observed at  $69.4 \pm 0.2$  eV, while no peaks were observed for PtO (or Pt(OH)<sub>2</sub>) and PtO<sub>2</sub> after annealing. Peaks of Pt 4f7/2 and Pt 4f5/2 were shifted by ~1.2 and ~3 eV, respectively, relative to Pt metal. The position of the Pt 4f7/2 peaks was independent of the deposition temperature for 30 or 400 °C. The Pt 4f peak in the Pt/YSZ composites shows a gradual shift towards lower BE with decreasing thickness. The Pt4f7/2 exhibits a tendency to shift to lower BEs as the size of the NPs decrease suggesting a particle size effect on the position of the core level peak. Similar shift towards lower BE of the Pt 4f peak have been reported for several Pt/metal oxide composite systems [163,164,242-246]. The shift of the Pt 4f core level peak ( $\sim 1 \text{ eV}$ ) to the higher binding energies is an indication of an enhanced electron density of Pt nanoparticles when they are interfaced with YSZ [163,164,242-246].



Figure 4. 1. XPS spectra from YSZ film with and without Pt nanoparticles (NPs), all grown on LGS substrate. The inset shows the enlarged area of the core-level Pt 4f spectra.

The crystalline characteristics of the as-deposited Pt/YSZ samples were investigated using x-ray diffraction as summarized in figure 4.2, which shows GIXRD scans for 10 nm thick Pt thin films deposited on YSZ at either 30°C or 400°C. The major peaks at  $2\theta = 39.76^{\circ}$ , 46.24°, and 67.45°, correspond to (111), (200), and (220) of platinum, respectively (PDF card 00-004-0802). The strongest peak appears at 2Theta = 39.76°, revealing that the Pt NPs were mainly oriented with (111) parallel to the YSZ film surface, but other orientations were present as well. The Pt crystallite size estimated from the Scherrer equation:  $D = K\lambda/\beta \cos \theta$ , where D is the average length of the crystallite,  $\beta$  is the broadening of the line in units of 2 $\theta$  ( $\theta$  is Bragg diffraction angle) and K is the shape factor (0.9). Figure 4.2 shows the deposited at 30°C and Williamson – Hall plot in figure (iii) presents the negative slope as a result of compression strain and hillock formation.



Figure 4. 2. XRD patterns from 10 nm Pt on 200 nm YSZ film (i) GIXRD scan - Grown at 30°C; (ii) GIXRD scan - Grown at 400°C; (iii) W-H plot - Grown at 30°C (iv) W-H plot - Grown at 400°C. YSZ film deposit at 30°C are highly stressed due to hillock formation. Pt major peak is (111) plus two less intensity peaks at (200) and (220).

Film (ii) presents both YSZ and Pt layers deposited at 400°C and Williamson – hall plot in figure (iv) presents the flat slope means film has no stress. Pt crystallite size summarized in figure 4.8. Figure 4.2 used 10 nm Pt due to the strong peak intensity compared to 1,3, and 5 nm. Williamson – Hall method used to calculate the nonhomogeneous strain and crystallite size for YSZ films because of the poly crystallinity that required to create a W-H plot , while Scherrer method used to calculate the strain and crystallite size of Pt nanoparticles due to exist of only one leading peak (111) specifically for 1,3 and 5 nm thicknesses, figure 4.8. The SEM images for as-deposited P/YSZ films in figure 4.7 exhibit a continuous Pt layer on both stressed films (deposited at 30°C) and non-stressed films (deposited at 400°C). The SEM images of the as-deposited Pt/YSZ films did not show any sort of aggregation on the surface of Pt.

#### 4.3 Thermal treatments of Pt/YSZ films

Post-deposition annealing plays an important role in Pt nanoparticle creation, since fast enough diffusion is needed for the thermodynamically driven agglomeration process to occur. However, annealing of YSZ films also leads to yttria segregation as discussed in Section 3.7. Figure 4.3 shows XPS data illustrating the segregation of yttria after annealing YSZ films up to 1000°C for 1 hour in air with and without the Pt nanoparticles present. The graph also elucidates a saturation in the amount of yttria segregation after 10 hours annealing at 1000°C (see Section 3.7). The two temperatures of 600°C and 800°C were used to promote Pt agglomeration and form Pt nanoparticles. Figure 4.3 clearly shows that the amount of yttria segregation is reduced when Pt is present on the surface. It was also found that annealing above 800°C causes the Pt nanoparticles to start dissociating and diffusing into the YSZ films so no reliable data could be obtained in that range.

The Pt 4f7/2 and Pt 4f5/2 XPS peaks measured from annealed films are mainly composed of metallic Pt and Pt oxides (PtO and/or PtO<sub>2</sub>) after the air annealing treatment as shown in Figure4.4. For films annealed at 600°C, a contribution appeared at 69.4eV (4f7/2) and 72.9 eV (4f5/2), both corresponding to Pt and there was a low intensity Pt oxide peak. As the annealing temperature was further increased from 600 to 800°C, the peak intensities of Pt oxide decreased, while the peaks associated to metallic Pt increased. Some Pt–O bonds can still be detected after annealing at 600 °C; some of which could be attributed to the bonding of platinum to the YSZ surface oxidized upon the thermal annealing in air. In figure 4.3, the increment in Y/Zr atomic percent ratio with annealing exhibit an indicative of surface Y segregation and oxidation that is likely to occur under annealing conditions.



Figure 4. 3. XPS analysis of YSZ film composition after annealing for 1 hour in air at each temperature. Pt nanoparticle agglomeration on the surface of YSZ limits yttria segregation.

However, films with Pt shows a drop in the atomic percent ratio compared to YSZ film without Pt [243,245]. The smaller augmentation of Y/Zr atomic percentage ratio with Pt nanoparticles present on YSZ surface may be rationalized by the Pt:Y surface atomic proportion. It is evident that experimentally determined Pt:Y atomic ratio deviates from the expected target atomic percent composition Pt:Y = 24:4 if we assumed that Pt added without oxidation status and with Zr and O<sub>2</sub> contribution being slightly lower. This anticipation will not be true for Pt/YSZ films with span of Pt thicknesses and dissimilarities of Pt nanoparticles agglomeration, such a disparity could be expressive of Pt:Y ratio variation and that yield Y/Zr less with annealing [243,245].

For all the annealed samples the O 1s spectra was fixed at 529 eV. The Pt 4f level shifts to a higher or lower BE depending on the change in interfacial composition, charge transfer direction (chemical shift) and NPs quantum size effect [247].

Positive shifts in the binding energy of Pt 4f core levels were observed for a 10 nm Pt sample by up to 1.5 eV as annealing was increased to 800°C as observed in Figure 4.5. The shift to higher binding energy can be explained by changes in electron transfer between the oxide and Pt nanoparticle during XPS analysis [161]. The interaction of Pt atoms and the YSZ matrix can change significantly depending on the way the Pt is arranged in relation to the matrix. Such shifts may be attributed to size-dependent final state effects as well as to NP/support interactions. The positive shift could suggest a relative tendency for electronic transfer from the Pt atoms to the oxide matrix with temperature increase, due to the progressive change from dispersed Pt atoms/smaller agglomerate to increasingly larger Pt nanoparticles [161,163,243,248,249].

With an increase in Pt thickness, the Pt 4f peak is positioned close to the BE of bulk platinum (71eV), suggesting the progressive enlargement of the clusters with the increase in Pt concentration and the existence of Pt–Pt "bulk-like" bonds in the Pt 4f XPS spectrum.

The high binding energy peak in Figure 4.4, located around 77.5 eV, is characteristic of Ptoxide in the hydroxide form, possibly  $Pt(OH)_3$  in good agreement with the literature [161]. This peak is only detected for the sample with the highest Pt content, and it is interpreted based on the existence of oxygen in the chamber after YSZ deposition [161].



Figure 4. 4. XPS spectra from10 nm Pt on 200 nm YSZ grown at 400°C and then annealed at 600°C and 800°C in air. Pt 4f binding energy shifts occur due to Pt agglomeration.

To investigate the influence of the annealing temperature on the nanomorphology of the agglomerated nanoparticles on the Pt/YSZ surface, the samples with Pt were annealed at 2 different temperatures, 600°C and 800°C for one hour in air. In contrast to the as-deposited samples, no Pt(OH)<sub>3</sub> compound was detected in the Pt 4f region. As the temperature increases it is expected that Pt(OH)<sub>3</sub> decomposes into metallic Pt figure 4.4 shows only Pt 4f peak present in the surface spectrum [161,163,243,248,249]. As can be seen in Figure 4.5, the Pt 4f peak has a positive shift of ~1.2 eV for the films annealed up to 800°C compared to the as-deposited films. The origin of these shifts can be either an initial state effect (local variations in film stoichiometry) or final state effect (screening effects) of the photoemission process. The surface morphology and crystal structure of the Pt NPs supported on the YSZ films after annealing were studied as a function of the Pt NPs size by using scanning electron microscopy (SEM) and gonio X-ray diffraction.



Figure 4. 5. Pt 4f <sub>7/2</sub> binding energy versus Pt coverage and annealing temperature.

Figure 4.6 shows both secondary electron (shadowing) and backscatter (Z-contrast) SEM images from 1, 3, 5, and 10 nm thick Pt films prepared by e-beam evaporation at either 30°C or 400°C, and then subsequently annealed at 800°C for one hour. The images show the formation of Pt nanoparticles via the agglomeration mechanism, and that size of the Pt NPs depends on the amount of Pt on the surface. From the Gonio scan data in Figure 4.7, it can be observed that the Pt films have preferential growth along the (111) direction. with higher (111) peak intensity at 400°C compared to 30°C. The FWHM value decreases with increasing annealing temperature, which relates to the increase of the NP size. The larger Pt NPs exhibit a distinguishable narrower XRD features than the smaller NPs and the average size of the Pt NPs increases with increasing Pt film thickness and increasing post annealing temperature as shown by data in figure 4.8. Crystallites size was calculated by Scherrer equation method from Pt (111) peak.



Figure 4. 6. SEM images from Pt/YSZ films after annealing in air, showing agglomeration and recrystallization. Pt/YSZ films grown on LGS at different temperatures: 30°C (Top) and 400°C (Bottom). YSZ film thickness is ~200nm. All films were annealed at 800°C in air for 1 hour. Both secondary electron and backscattering electron images are shown.



Figure 4. 7. XRD Gonio patterns from 10 nm Pt / 200 nm YSZ films. The upper XRD pattern is for  $30^{\circ}$ C and the lower XRD pattern is for  $400^{\circ}$ C. The YSZ and Pt films were grown at either  $30^{\circ}$ C or  $400^{\circ}$ C. The SEM images show stages of the Pt agglomeration process.



Figure 4. 8. Pt crystallite size growth (nm) versus annealing temperature for different Pt film thicknesses.

#### 4.4 Ionic conductivity of Pt/YSZ Films in N<sub>2</sub> environment

The chemical properties of the Pt NPs changed with the number of atoms and could be significantly influenced by interaction with the metal-support. This can be explained in terms of ionic conductivity in this section. So, it is allowed to expect partial interaction between Pt atoms and YSZ atoms, depending on Pt NPs size as it clearly shows in figure 4.9. Figure 4.9 presents the Nyquist plot of 1, 5 and 10 nm Pt nanoparticles deposited on YSZ films at 30°C and 400°C. To compare with YSZ films without Pt, Nyquist plot added to each plot. Figure 4.9 shows how the metal-support interaction depends mainly on the nanoparticle size, in addition to the combination of nanoparticle and support. Impedance scan measurements are conducted at 500°C for all films.

Figure 4.10 presents the ionic conductivity values collected from fitting Nyquist arcs in figure 4.9. EC-Lab software utilizes to fit Nyquist arc and calculate the values of ionic conductivity with its standard deviation. Figure 4.10 presents a noticeable enhancement in ionic conductivity with enlarging Pt nanoparticles size. Also, another remarkable notice is within the same Pt nanoparticle size, Pt/YSZ film deposited at 400°C exhibit higher value in the ionic conductivity compared to Pt/YSZ deposited at 30°C. This behavior in variation in ionic conductivity is noticed mainly for thicker nanoparticles 5 and 10 nm. However other thicknesses 1 and 3 nm did not show a change in the ionic conductivity value based on changing deposition temperature. Ionic conductivity data of YSZ films without Pt is also added to figure 4.10 to compare with Pt films and show the effect of compression/ tensile strain and yttria segregation for annealed YSZ films. This variation in the ionic conductivity from figure 4.10, can be explained by thin film agglomeration. Pt agglomeration is governed by the available diffusion mechanisms of the metal film and, therefore, accelerated with increasing temperature depending on Pt thickness.

The diffusion process takes place by the migration of Pt particles across YSZ surface followed by coalescence with other particles. The intrinsic thermodynamic instability of thin metal films on oxidic thin film/substrates exhibit a difference of free energy per unit area where the Pt thickness will be a function of metal particles isolation on an oxide surface. The variation in Pt deposition temperature, the annealing process condition and the agglomeration state significantly affects the ionic conductivity of Pt/YSZ films [250,251].

Figure 4.11 shows a difference in the ionic conductivity for 10nm of Pt deposited on YSZ at two deposition temperatures 30°C and 400°C, then both annealed at 600°C and then at 800°C to form Pt nanoparticles. The region in the metal oxide which is depleted of electrons is characterized by bending of the valence and conduction bands, and the metal–metal oxide interface electrostatic potential in the depletion region depends on the distance from the interface.

The presence of Pt NPs has improved the electron transport process by reducing the charge-transfer resistance across the Pt/YSZ interface. This is due to the better inter grain connectivity and creation of more conducting pathways in the YSZ by the metal Pt NPs. The number of electrons transferred to the interface is the product of the charge density and the volume of the depletion region.

The transfer of electrons from the support to the metal particles, or vice versa, also influences the electron structure of the support at the outer edge of the metal particle and this part of the support can be either depleted or enriched in electrons.



Figure 4. 9. Impedance spectra measured at 500°C from 200 nm YSZ films decorated with Pt nanoparticles for different Pt coverages and annealed to 800°C to form the agglomerated Pt NPs. (i) Pt/YSZ deposited at 30°C. (ii) Pt/YSZ deposited at 400°C.



Figure 4. 10. Ionic conductivity of YSZ and Pt/YSZ films determined from Nyquist plots. The ionic conductivity for each of the films is shown after annealing at 800°C for 1 hr in air. Data is shown for Pt/YSZ films deposited at both 30°C and 400°C.



Figure 4. 11. Impedance spectra (Nyquist plots) from 200 nm YSZ decorated with 10 nm Pt nanoparticles. (i) Pt/YSZ (both) deposited at 30°C then annealed to 800°C for 1 hr in air. (ii) Pt/YSZ (both) deposited at 400°C then annealed to 800°C for 1 hr in air. SEM images are added to illustrate the Pt agglomeration in each set of films. Both films used for 4%  $H_2 / 96\% N_2$  experiment.

The affected region of the support, as concluded from the magnitude of the depletion length can be quite large and might respond differently to various adsorbates [252,253], and this will be discussed further in Chapter 5 relating to the 4% H<sub>2</sub> experiments. Figure 4.12 shows relative difference in the ionic conductivity of Pt/YSZ samples as a function of Pt thickness as defined by [254],

$$\frac{\Delta\sigma}{\sigma} = \frac{\sigma_{Pt/YSZ} - \sigma_{YSZ}}{\sigma_{YSZ}}$$
(4.1)



Figure 4. 12. Relative difference in the ionic conductivity of YSZ films decorated with Pt nanoparticles with respect to a YSZ film without Pt nanoparticles. The Pt/YSZ samples with 10 nm Pt were used in the  $H_2$  exposure experiments discussed in Chapter 5.

The conductance of agglomerated Pt film on YSZ film was found to scale with the nanoparticle surface area, as the SEM images show in figure 4.6. Figure 4.11 shows the difference between SEM images. Films deposited at 400°C exhibit a larger nanoparticle surface area compared to films deposited at 30°C within the same magnification ratio. It can be postulated that the total conductance of Pt/YSZ is additively composed of a conductance tracing back to grain boundaries and a conductance due to the agglomerated Pt nanoparticles, and this in turn depends strongly on the Pt film nanostructure [251].

### 4.5 Chapter Summary

Pt nanoparticles on YSZ films were created by depositing 1, 3, 5, or 10 nm Pt films on YSZ and then annealing at 800°C in air to form agglomerated Pt NPs. The Pt/YSZ samples were synthesized at deposition temperatures of both 30°C and 400°C.

XPS spectra show that Pt 4f peak intensity is proportional to Pt thickness for as-deposited films and there is evidence for Pt-oxide species. After the 800°C annealing treatment, the Pt 4f peak shifts to higher binding energy, there is less yttria segregation compared to Pt-free YSZ, and there is no evidence for Pt oxide species. The amount of Pt 4f peak shifting varies according to nanoparticles size and the annealing temperature. These results are explained in terms of charge transfer, initial and final binding states, and Pt nanoparticle size.

XRD patterns demonstrate that Pt nanoparticles form primarily with a preferred (111) orientation, but a few other orientations are also present. GIXRD confirms the nanocrystalline nature of the as-deposited Pt films, and the Pt nanoparticles grow in size with the annealing treatment as demonstrated by a decrease in FWHM of the Pt (111) peak. These Pt nanoparticles were observed by SEM to be regularly spaced with a uniform size distribution, with the separation between NPs being linearly dependent on their average size.

Impedance spectroscopy (EIS) results are in agreement with the XPS, XRD and SEM results. Three characteristics can be concluded: ionic conductivity is proportional to the Pt NPs size, ionic conductivity depends on nanoparticle crystallographic structure and morphology, and the ionic conductivity is function of Pt thickness. The Pt/YSZ samples synthesized with 10 nm Pt have the overall highest conductivities, and these samples were used for 4% H<sub>2</sub> exposure experiments discussed in Chapter 5.

#### **CHAPTER 5**

# INFLUENCE OF HYDROGEN EXPOSURE ON IONIC CONDUCTIVITY OF YSZ AND PT/YSZ FILMS

## 5.1 Hydrogen Interactions with YSZ Films

Most metal oxide-based gas sensors are faced with the challenge of achieving high sensitivity and selectivity towards specific gases. Several different strategies have been applied including mixed oxides and addition of gold (Au), platinum (Pt) or palladium (Pd) nanoparticles to target detection of specific gases based on catalysis spillover effects [255-257]. The presence of Pt has been shown to result in chemical sensitization where H<sub>2</sub> is converted to 2H by split-over and spill-over conversion mechanisms [255-257]. Strong metal-support interactions (SMSI) were originally posed by Tauster et al. [258,259] for group VIII metals on reducible metal oxides (TiO<sub>2</sub> and  $Nb_2O_5$ ) where H<sub>2</sub> reduction of the metal oxide support occurs through three major routes: (i) spill-over of the activated hydrogen species from the Pt; (ii) direct injection of electrons to the metal oxide support from hydrogen adsorbed on the Pt surface: and (iii) direct reduction of the metal-metal oxide interface by molecular H<sub>2</sub> [258,259]. The transfer of electrons from metals to metal oxides depends on their Fermi levels. Recent DFT calculations on a Pt nanoparticle- metal oxide nanoparticle predicts electron transfer from Pt to metal oxide, consequently forming oxygen vacancies and oxidizing Pt upon contact. The oxidized Pt then can be converted easily back into metallic Pt in the presence of H<sub>2</sub> [255,258-260]. Pt NPs either dissociate the H<sub>2</sub> molecule and then hydrogen atoms spill over to the metal oxide and diffuse until they reach a reaction site (active oxygen surface species) or promote the transfer of charge carriers between the gas molecule and the metal oxide via the Pt/YSZ interface (Fermi level control) [255,260].

Both these mechanisms eventually translate into changes in the ionic conductivity as will be shown by data in the next section.

Figures 5.1 and 5.2 show impedance spectroscopy spectra (Nyquist plots) measured at 500°C for as-deposited and annealed YSZ films without any Pt additions. The YSZ film thickness was controlled and fixed to be 200 nm for all the samples. Figure 5.1 shows results for YSZ films grown with different deposition rates and deposition temperatures, and Figure 5.2 shows results for YSZ films grown using substrate bias as discussed in chapter 3.

For all these YSZ films, there is a negligible change in film resistance upon exposing to 4%H<sub>2</sub> at 500°C. The as-deposited spectra (orange points) and annealed spectra (brown points) do not undergo any noticeable change when exposing to the 4%H<sub>2</sub> (white points). This result was found over the entire range of impedance scan temperatures from  $400^{\circ}$ C -  $600^{\circ}$ C. The negligible change in ionic conductivity can be explained in three ways: (i) there is an absence of a created depletion layer or space charge layer upon H<sub>2</sub> chemisorption; (ii) very few dissociated H atoms are created to diffuse over the YSZ surface to form hydroxyl OH– ions with the O<sup>2-</sup> anions; and (iii) the Fermi level of the Pt is lower than that of YSZ meaning that electrons are transferred from the YSZ to the Pt. Equations (5.1) and (5.2) summarize the proposed interaction of H<sub>2</sub> with the surface of a YSZ film that does not have Pt,

$$H_2 + \mathcal{O}_{YSZ\ Surface}^{2-} \to H_2O \uparrow + 2e^- \tag{5.1}$$

$$2e^{-} + 0_2 \rightarrow 20^{-}$$
 (5.2)

# 5.2 Hydrogen Interactions with Pt/YSZ Films

The spillover mechanism for catalysis is well documented and attributed to catalytic dissociation of molecular hydrogen on a transition metal catalyst followed by transport and further diffusion onto an oxide support surface [258,259,261]. It has been reported that the size of the catalytic Pt nanoparticles on a YSZ film surface noticeably affects H<sub>2</sub> adsorption and surface reactivity [258,259,261]. The  $H_2$  reactions mechanism can be understood by considering two well accepted models involving Fermi energy levels and chemical spillover [17,80,262-264]. When noble metal nanoparticles contact an oxide substrate, their Fermi levels become aligned and the metal acts either as an electron donor or acceptor on the oxide surface causing the energy bands to bend. The electron depletion layer or the hole depletion layer at the interface influences the concentration of carriers and their mobility. In this case, the baseline resistance of the other overall film changes, and sensor response can be improved. For the spillover mechanism, the noble metal acts as an electron acceptor on the oxide surface, which contributes to an increase of the depletion layer. Therefore, the change in resistance is larger, leading to increased sensor response. The Pt energy levels act as a mediator in the charge transfer process of the YSZ-H<sub>2</sub> interface resulting in widening of the depletion layer width [17,80,262-264]. It is also important to note that when noble metal nanoparticles are present on the surface of an oxide, the number of adsorption sites increases due to increased surface area of the nanoparticles, thereby increasing the amount of gas adsorption. The ionic conductivity of a Pt/YSZ film is a good indicator of H<sub>2</sub> chemisorption since it reflects the influence of the band bending and spillover effects. In experiments carried out in this thesis, 4%H<sub>2</sub> gas exposures were carried out under conditions of 'quasi-equilibrium' where steady-state conductivities were measured.



Figure 5. 1. Impedance spectroscopy spectra (Nyquist plots) measured at 500°C from 200 nm thick YSZ thin films synthesized with different deposition temperatures (x-axis) and deposition rates (y-axis). All films were annealed at 1000°C for one hour in air to stabilize YSZ films. As-grown samples (Orange) and annealed samples (Brown) were then exposed to 4%H<sub>2</sub> (White) at 500°C. None of the samples show a noticeable change in ionic conductivity upon exposure to H<sub>2</sub>. Note that samples B, C, E and F show a decrease in ionic conductivity due to yttria segregation as discussed in chapter 3.



Figure 5. 2. Impedance spectroscopy spectra (Nyquist plots) from YSZ films deposited using different bias voltages (Brown) (A) -300V (B) -100V (C) +100V (D) +300V. All films were grown at 30°C and annealed to 1000°C in air for one hour. Exposing to hydrogen (White) at 500°C did not change the ionic conductivity of the YSZ films.

The kinetics of  $H_2$  adsorption were not studied since the delivery of the  $H_2$  dosing could not be controlled in real time within the experimental apparatus; instead, conductivities were measured after long holds at a given temperature to obtain a steady-state values of conductivity. Electrochemical impedance spectroscopy (EIS) was used to investigate hydrogen interactions with Pt/YSZ films. In such measurements, contributions to the conductivity from the Pt/YSZ films can be observed including effects from crystallites, grain boundaries, electrode contacts, and other associated elements in the apparatus. Figure 5.3 shows a 'Nyquist plot,' acquired at 500°C by scanning frequencies between 1 MHz and 1 Hz. Generally, separate arcs can be observed in Nyquist plots arising from grains, grain boundaries and the Pt pads contacts as discussed in section 2.5 [124]. To achieve a single semicircle from the prescribed components, as shown in Figure 5.3, the time constant  $\tau$  associated all these components must be nearly the same.

The measured impedance spectra were fitted using EC-Lab software. The total impedance Z' of the device structure can be derived from the complex impedance contribution of the grains, grain boundaries, and the electrode contacts, respectively. The grain resistance can be estimated from the interception of the arc at high frequency with the real axis. Every individual semicircle has its own unique relaxation frequency (the frequency at the top of the arc), which can be represented as  $\omega_{max}RC = \omega_{max} \tau = 1$ , where R and C represent the resistance and capacitance of the equivalent circuit and  $\tau$  represents the relaxation time that depends only on the intrinsic properties of the material [256,265]. The effect of hydrogen gas on the impedance behavior of the Pt/YSZ films with different Pt coverages is apparent in figure 5.3. It is observed that when the Pt nanoparticles gradually increased from 1 to 10 nanometers, the diameter of the arc decreased. The Z" maximum values were smaller than the half values of the Z' maximum, demonstrating the contribution from the constant phase elements (CPEs) in the equivalent circuit [256,265]. The bestfitted value for capacitance was obtained by replacing C with a CPE, which frequently is used to describe the behavior of inhomogeneous YSZ and Pt/YSZ films. The impedance of Pt/YSZ decreases upon exposure to H<sub>2</sub>. Thus, it can be concluded that the hydrogen concentration significantly affects the grain boundary resistance which facilitates its detection; this is further discussed later in this section. However, the variation in the film capacitance is not significant suggesting that the hydrogen gas mainly affects the surface charge region of Pt/YSZ grain boundaries [256,265]. The H<sub>2</sub> gas sensing characteristics of the Pt/YSZ films were determined by exposing them to a 4%H<sub>2</sub> / 96%N<sub>2</sub> gas mixture and using pure N<sub>2</sub> as a background normalization gas. Prior to start of the gas sensing measurements, pure N<sub>2</sub> was purged through the quartz furnace tube to maintain normal ambient pressure and prevent sample oxidation inside the quartz tube.



Figure 5. 3. Impedance spectroscopy spectra (Nyquist plots) measured at 500°C from Pt/YSZ films. The left column are spectra from Pt/YSZ films deposited at 30°C and then annealed at 800°C, while the right column are spectra from Pt/YSZ films deposited at 400°C and then annealed to 800°C. The open points and solid (colored) points data are from N<sub>2</sub> and H<sub>2</sub> exposure, respectively.



Figure 5. 4. Pt/YSZ film ionic conductivity at 500°C versus Pt thickness after the 800°C annealing treatment. These experiments were carried out in pure  $N_2$  (shaded bars) or in 4%H<sub>2</sub> / 96%N<sub>2</sub> (unshaded bars).



Pt thickness (nm)

Figure 5. 5. The change in the ionic conductivity for Pt/YSZ films upon exposure to 4%H<sub>2</sub>/96%N<sub>2</sub> at 500°C. The 10 nm Pt sample deposited on YSZ at 400°C followed by annealing at 800°C shows the largest response upon H<sub>2</sub> exposure.

Afterwards, a 4%:96% H<sub>2</sub>:N<sub>2</sub> mixture was introduced into the quartz tube at a constant flow rate of 2 sccm controlled by a manual mass flow controller.

The film conductivities were measured as a function of Pt nanoparticle size at temperatures between 400°C - 600°C as shown in Figure 5.4 and Figure 5.5. The change of ionic conductivity is defined and expressed as:

$$\frac{\Delta\sigma}{\sigma} = \frac{\sigma_{(Pt/YSZ)H_2} - \sigma_{Pt/YSZ}}{\sigma_{Pt/YSZ}}$$
(5.3)

where  $\sigma_{(Pt/YSZ)H2}$  and  $\sigma_{Pt/YSZ}$  is the conductivity of Pt/YSZ films in the present and absence of the H<sub>2</sub> gas [253,266]. As mentioned, the fundamental H<sub>2</sub> sensing mechanism on an oxide surface has been well identified in terms of the depletion layer and space charge models. However, to fully understand the catalytic impact promoted by decorating YSZ surface with Pt NPs, it is crucial to further investigate the nature of H<sub>2</sub> interaction with YSZ films.

The YSZ surface is proposed to be covered with either atomic ( $O^-$ ) species above 400°C or molecular ( $O_2$ ) species below 400°C, that subsequently reacts with atomic hydrogen and nitrogen [20,79,80,266]. The presence of Pt NPs appears to have a great influence on the catalytic oxidation of H<sub>2</sub>. By decorating the YSZ surface with Pt, hydrogen molecules can dissociate, and the adsorbed H<sup>+</sup> species can spillover to the YSZ film surface, thereby inducing conductance changes caused by the injected electrons.

A schematic illustration of the  $H_2$  sensing process mechanism on YSZ is shown in Figure 5.6, indicating the different reactions happening on the surface of a Pt-decorated YSZ film. The interaction of  $H_2$  gas with the YSZ film can be broken up in this model into the following reactions steps [20,79,80,266]:



Figure 5. 6. A schematic illustration of the  $H_2$  sensing mechanism, indicating the types of reactions happening on the surface of a Pt-decorated YSZ film.

When Pt/YSZ films are exposed to  $H_2$  gas, the  $H_2$  molecules can react with oxygen species. Pt nanoparticles play an important role in this reduction reaction process as the hydrogen molecules first react with the oxygen species on Pt particles, equation (5.6). The Pt NPs can react with  $H_2$ , by breaking the H - H bond and bind directly with atomic H, in a process known as splitover, equation (5.7). The atomic hydrogen species on the Pt nanoparticles then spillover to the YSZ surface around Pt nanoparticles to react with oxygen species, equation (5.8). These H atoms can then diffuse over the active surface area of YSZ to form hydroxyl OH<sup>-</sup> ions after reacting with O<sup>-</sup>, equation (5.9). Afterwards, these OH<sup>-</sup> groups are again approached by incoming flux of H atoms and this reduction reaction will generate  $H_2O$ , equation (5.10). Finally, the ionic conductivity gets further promoted by release of free electrons into the conduction band of YSZ, equation (5.8).

In this reaction process, the Pt nanoparticles on the YSZ surface reduce the adsorption energies for H<sub>2</sub> gas. Pt will enhance YSZ surface ionization reaction performance by lowering the activation energy for adsorption and chemical reaction. These low adsorption energies will make more H<sub>2</sub> molecules adsorb on Pt nanoparticles and dissociate into atomic hydrogen, which is an efficient process. This enhancement in catalytic activity by the 'spillover effect' causes fast response towards H<sub>2</sub> [20,79,80,266]. According to equations (5.4) to (5.10), the reduction reaction process releases electrons into the conduction band of YSZ and consequently, the conductivity increases. In terms of using this functionality on a SAW sensor device, the higher conductivity should impact the velocity of a SAW wave and change center frequency of SAW gas sensor device. These experiments would be very useful to carry out in future work.



Figure 5. 7. The reversibility of the impedance spectroscopy spectra (Nyquist plots) for 200 nm YSZ film with 5 nm Pt upon repeated change between 4%H<sub>2</sub>/96%N<sub>2</sub> and 100%N<sub>2</sub> exposures. The green, blue, and sky-blue scans exhibit the location of the Nyquist plot when exposed to hydrogen, while the orange and red scans represent the Nyquist plot location when exposed to the background gas (nitrogen). Each individual plot is an average of 15 scans and the data was acquired at 500°C.

# 5.3 Reversibility of Pt/YSZ Film Conductivity with Repeated H<sub>2</sub> / N<sub>2</sub> Exposures

The Pt/YSZ thin films were exposed to several cycles of 4%H<sub>2</sub> / 96%N<sub>2</sub> gas exposure followed by pure N<sub>2</sub> to determine if their conductivity response behavior was reversible. The gas exposure process was repeated three times for each gas and impedance spectra were acquired by averaging 15 scans (3 min/scan) while the gas was present. Figure 5.8 shows the overall procedure for the H<sub>2</sub> dosing experiments which were run at 500°C, 550°C, and 600°C. Figure 5.7 shows an example of impedance spectra results from a Pt/YSZ sample with 5 nm of Pt measured at 500°C. Clearly the spectrum reversibly changes with and without the hydrogen present. This result suggests that the Pt/YSZ film nanostructure was stable during these tests and did not change versus time at the 500°C test temperature. The conductivity data for all three test temperatures are shown in Figure 5.8.



	100% N2	4% H2-N2
Dep. Temp. 30°C		
Dep. Temp. 400°C		

Figure 5. 8. The change in ionic conductivity of Pt/YSZ films upon switching between  $96\%N_2$  / 4% H<sub>2</sub> and 100% N<sub>2</sub> at temperatures between 500°C and 600°C. Each sample was exposed to the gas for 315 minutes.



Figure 5. 9. Impedance spectroscopy spectra from a PT/YSZ film (Pt 10 nm and deposition temperature 400°C) exposed to three different gases at 500°C: hydrogen (4%H<sub>2</sub>/96%N<sub>2</sub>), oxygen (air),and nitrogen (100%N<sub>2</sub>). The order for these gas exposures is set as oxygen (air)  $\leftrightarrow$  nitrogen (100%N<sub>2</sub>)  $\leftrightarrow$  hydrogen (4%H<sub>2</sub>/96%N<sub>2</sub>).

The highest conductivity changes upon  $H_2$  exposure occur at the 600°C test temperature. Also, Pt/YSZ films synthesized at 400°C are more sensitive than samples grown at 30°C. If the samples are heated above 600°C, film morphology begins to change, and the films are no longer stable.

# 5.4 Oxygen Interactions with YSZ and Pt/YSZ Films

The experiments presented in this chapter thus far were all carried out in  $4\%H_2$  -96%N<sub>2</sub> and N<sub>2</sub> environments. The role of oxygen in the environment is of high importance especially in relation to gas sensors that typically need to operate in air (O<sub>2</sub> + N<sub>2</sub> gas). Figure 5.9 shows Nyquist plots for Pt/YSZ film (Pt 10nm and deposition temperature 400°C) that was first exposed to N<sub>2</sub> (orange), then to  $4\%H_2$  -96%N<sub>2</sub> (blue) followed by exposure to air (green) all at 500°C. The results indicate that the conductivity shifts in between the hydrogen, the oxygen, and the nitrogen curves.

Oxygen molecules in the air will be adsorbed on Pt nanoparticles, then will dissociate into atomic oxygen (the same spilt-over mechanism as for hydrogen). The atomic oxygen will capture an electron from YSZ (equation 5.2) leading to an increase in the width of the electron depleted layer. Oxygen species on the surface ( $O^{2-}$  or/and  $O^{-}$ ) will subsequently spillover to the YSZ surface. The decrease in the conductivity when exposed to oxygen compared to hydrogen may be due to the fact that oxygen ions can act like electron trap centers, which result in reduction in conduction band electrons of YSZ layer [20,79]. In addition, there is an absence of the second electron that is generated upon hydrogen exposure.

# 5.5 Chapter Summary

Three major outcomes have emerged from the  $H_2$  gas exposure experiments on the Pt/YSZ samples as discussed in this chapter:

(i) Pure YSZ films without Pt can be produced to have different nanostructures, but all YSZ films exposed to hydrogen in the range 400°C - 600°C exhibit negligible change in the impedance spectra and ionic conductivity. From this result, it is believed that the interaction of  $H_2$  with YSZ surface is minimal, and in the experiments, there was not enough free O<sup>-</sup> on the YSZ surface to chemically react with hydrogen.

(ii) When Pt nanoparticles decorate a YSZ film surface, hydrogen exposure induces a large change in film conductivity. Pt NPs lower the H<sub>2</sub> adsorption energy and facilitate the interaction between H<sub>2</sub> and YSZ surface via the spillover effect. The size of the Pt nanoparticles and the thermal history of the Pt/YSZ play an important role in controlling the over-all ionic conductivity.

A Pt film deposit at 400°C then annealed to 800°C to cause agglomeration into Pt nanoparticles shows higher conductivity compared to a Pt film deposit at 30°C then annealed to 800°C, which might be explained by the depth of Pt penetration into the YSZ film for the two cases.

(iii) The response of a Pt/YSZ film exposed to 4%H<sub>2</sub> -96%N<sub>2</sub> and then to pure N<sub>2</sub> is reversible at 500°C. The reversibility is an indication that the nanostructure and nanomorphology of the Pt/YSZ films is stable between 400°C - 600°C.
## **CHAPTER 6**

## **CONCLUSIONS AND FUTURE WORK**

# **6.1 Conclusions**

The conclusions of this thesis can be divided into three sections based on the results presented in Chapters 3-5.

# <u>Section 1</u>: Synthesis, nanostructure, morphology, and high temperature stability of YSZ films on langasite substrates

Synthesis of YSZ films by RF magnetron sputtering is an effective means to grow homogenous films with defined alloy composition. YSZ films with 200 nm thickness were deposited on langasite (LGS) single crystal substrates, and depending on deposition parameters, the YSZ films contained primarily either (111) oriented grains or a mixture of (111) and (200) grain orientations. For applications in high temperature sensors and other electronics, the crystallinity of YSZ films is significantly important, as it dictates high temperature stability and electrical conductivity. The compressive / tensile strain levels within the YSZ films, determined using the Williamson – Hall XRD method, were found to be dependent on deposition rate, substrate temperature and substrate bias, which influence the crystallinity, roughness, and hillock formation. Other deposition parameters, such as plasma pressure (6 mTorr) and Ar:O<sub>2</sub> ratio (95:5), were fixed for all of the films reported in this thesis and are believed to be of lesser importance for impacting film nanostructure.

An important result found in this work was that adding a substrate bias during the RF magnetron sputtering process can be advantageous for producing smooth, dense YSZ films at room temperature. For films deposited with no bias, SEM images revealed that films grown with a proportional ratio between deposition rate and deposition temperature (0.03 nm/s:30°C, 0.05 nm/s: 400°C, 0.07 nm/s:700°C) were also less rough and did not show hillock formation compared to other films grown at [low deposition rates and high deposition temperature] or [high deposition rate and low deposition temperature]. Post-deposition annealing treatments up to 1000°C in air for one hour caused growth of YSZ crystallites and a noticeable reduction in strain.

SEM images show that films that contained hillocks from the deposition process roughened during annealing, with some evidence for fracture of the hillock features. For the smoother films that did not contain hillocks, negligible roughening was seen after annealing.

Annealing YSZ films up to 1000°C causes yttria segregation, where the surface becomes enriched in yttrium compared the 8mol% Yttria Stabilized-Zirconia (YSZ) bulk film composition, as measured by XPS and consistent with other data in the literature. This yttria segregation reaches a steady-state limit after extended annealing times (> 10hours) and plays an important role in lowering the ionic conductivity, reducing compressive strain, and increasing the activation energy for charge transport within the YSZ films. For YSZ films deposited using a substrate bias, the amount of yttria segregation was less than for unbiased films, and this may be related to the presence of both (111) and (200) oriented YSZ crystallites in the biased films.

All YSZ films regardless of deposition parameter and annealing treatments exhibited a wide span in ionic conductivity based on impedance spectroscopy measurements acquired in a  $N_2$ -purged tube furnace over the range 400 – 600°C.

Films grown at room temperature, and then annealed up to 1000°C, show an increase in ionic conductivity which may be attributed to enhanced crystallinity, increased crystallite size, and minimal tensile strain. Other films with a large amount of yttria segregation or compressive strain show a decrease in ionic conductivity.

YSZ films grown with a biased substrate at room temperature (30°C) and low deposition rate (0.03 nm/s) showed the highest ionic conductivities after annealing. The activation energies for ionic diffusion, measured from the slopes of the conductivity curves, were found to be correlated with roughness, yttria segregation, and compression / tensile strain in the as-grown and annealed YSZ films.

#### Section 2: Synthesis, agglomeration, and characterization of Pt nanoparticles on YSZ films

Platinum nanoparticles were synthesized on the surface of YSZ films by in-situ deposition of 1, 3, 5, or 10 nm thick Pt films on the surface of YSZ films immediately after they were grown, and then using post-deposition agglomeration of the Pt film to create the Pt nanoparticles. E-beam evaporation was used to deposit the Pt at either 30°C and 400°C and agglomeration occurred during thermal annealing at 600°C and 800°C.

The annealing process on these Pt/YSZ samples caused the XPS Pt 4f peak to shift to higher binding energy due to the formation of the nanoparticles, and the amount of yttria segregation was less than that for Pt-free YSZ films. XRD analysis indicated that the Pt nanoparticles form with a preferred (111) crystallite orientation, and SEM images illustrate that the surface morphology consists of near regularly spaced Pt nanoparticles with a fairly uniform size distribution and interparticle separation linearly dependent on the average size. Electron impedance spectroscopy (EIS) results of film conductivities measured between 400°C-600°C, are consistent with the collected results from XPS, XRD and SEM. The ionic conductivity was found to be proportional with the size of the Pt nanoparticles and depends on their crystallographic orientation.

Charge transfer, interface depletion layer and grain boundary conductivity, all integral to the catalytic mechanism of metal-support-interactions, play an important role in the mobility of oxygen vacancies and overall charge transport. The Pt/YSZ films with the 10 nm Pt coverage yielded the largest changes in conductivity of all the samples, and these 10 nm Pt/YSZ samples were used for subsequent exposures to a 4% H<sub>2</sub> / 96% N<sub>2</sub> gas mixture.

#### Section 3: Changes in ionic conductivity of YSZ and Pt/YSZ films upon exposure to hydrogen

Impedance spectra from YSZ thin films that do not have any added Pt were measured between 400°C - 600°C, and none of the spectra from the pure YSZ films exhibited any changes when switching between pure N<sub>2</sub> and 4% H<sub>2</sub> / 96% N<sub>2</sub> gas exposures. This result suggests that the interaction of H<sub>2</sub> with a YSZ surface does not markedly influence the conduction band, since there are not enough O<sup>-</sup> species on the surface to chemically react, leading to minimal hydrogen adsorption.

When Pt nanoparticles are added as catalysts on the YSZ surface, the surface becomes very reactive towards hydrogen. It is believed that the Pt nanoparticles lower the adsorption energy and facilitate the interaction between  $H_2$  and the YSZ surface according to the well-known catalytic spillover effect. The size and crystallographic orientation of the nanoparticles play an important role in controlling the over-all ionic conductivity.

Pt/YSZ films with Pt nanoparticles created by Pt deposition at 400°C followed by annealing to 800°C have higher conductivity than for Pt deposition at 30°C and annealing at 800°C. This might be explained by differences in the amount of Pt diffusion into the YSZ films, which in turn will affect the depletion region.

The conductivity changes between exposure to pure  $N_2$  versus exposure to 4%  $H_2$  / 96%  $N_2$  was found to be reversible for Pt/YSZ films measured in the range 400°C - 600°C. This attribute of the Pt/YSZ films has important ramifications for gas sensor technology.

The next step for advancing the technology readiness level of Pt/YSZ hydrogen sensing films should be to carry out response studies to  $H_2$  exposures using the different types of Pt/YSZ films developed in this thesis to assess their overall performance and stability as a working surface acoustic wave (SAW) sensor.

### 6.2 Future Work

As demonstrated in this thesis, the properties of YSZ thin films grown on langasite substrates are dependent on the deposition parameters as well as post-deposition processing parameters. The current work has focused on deposition temperature, deposition rate, and substrate biasing as a means to influence the crystallographic stability, electronic stability, and ionic conductivity of Pt/YSZ films. Other parameters such as the O<sub>2</sub>:Ar ratio in the sputtering plasma and total sputtering pressure can also influence Pt/YSZ film properties. Investigations of these other parameters is warranted, but it is expected that they will be less important than temperature, rate, and bias in influencing the films.

In this work, the YSZ and Pt/YSZ films were grown on single crystal langasite (LGS) piezoelectric substrates. Thin film piezoelectrics, such as AlN or ScAlN, have many advantages over langasite, and thus it will be of interest to study the conductivity of Pt/YSZ films synthesized on top of ~1 micrometer thick piezoelectric AlN and ScAlN thin films.

The same film deposition and processing parameters that have been used to grow the Pt/YSZ films on langasite would be a good starting point for extending investigations to these thin film piezoelectric materials. Experiments could be carried out on the Pt/YSZ films alone, as well as with Pt/YSZ films integrated onto surface acoustic wave resonator (SAWR) sensor device platforms.

The reversibility in ionic conductivity of Pt/YSZ films when switching between  $H_2$  and  $N_2$  exposure is an important result from this thesis. However, the measured responses of the films to the target gases were carried out under quasi-equilibrium conditions, so that kinetic effects were minimized.

A highly controlled gas delivery system would be needed in order to observe dynamics during gas dosing to assess the important gas sensor properties of sensor response time and longterm reproducibility. Adding oxygen-containing gases into the gas dosing experiments will also need to be investigated to probe aspects of selectivity of Pt/YSZ films towards hydrogen in the presence of other interfering gases.

#### REFERENCES

- [1] U.S. Energy Information Administration. Monthly energy review, August 2021. DOE/EIA-0035(2021/8). <u>http://www.eia.gov/totalenergy/data/monthly</u>.
- [2] A. Ghosh, C. Zhang, S. Q. Shi, and H. Zhang, "High-Temperature Gas Sensors for Harsh Environment Applications: A Review," *Clean - Soil, Air, Water*, vol. 47, no. 8. Wiley-VCH Verlag, 01-Aug-2019.
- [3] T. Liu, X. Zhang, L. Yuan, and J. Yu, "A review of higherature electrochemical sensors based on stabilized zirconia," *Solid State Ionics*, vol. 283, pp. 91–102, 2015.
- [4] Michael Fitzgerald, "Sensing the Future Before It Occurs," MITSloan Management Review, December 20, 2012. <u>https://sloanreview.mit.edu/</u>
- [5] M. A. Huque, B. J. Blalock, C. Su, R. Vijayaraghavan, S. K. Islam, and L. M. Tolbert, "SOI-Based Integrated Circuits for High-Temperature Applications," 2011 Twenty-Sixth Annual IEEE Applied Power Electronics Conference and Exposition (APEC), Fort Worth, TX, USA, 2011, pp. 836-843, doi: 10.1109/APEC.2011.5744692.
- [6] Y. S. H. Najjar, "Hydrogen safety: The road toward green technology," *International Journal of Hydrogen Energy*, vol. 38, no. 25. Elsevier Ltd, pp. 10716–10728, 21-Aug-2013.
- [7] M. P. Da Cunha, "Wireless sensing in hostile environments," *IEEE International Ultrasonics Symposium (IUS)*, Prague, Czech Republic, 2013, pp. 1337-1346, doi: 10.1109/ULTSYM.2013.0342.
- [8] S. Zhang and F. Yu, "Piezoelectric materials for high temperature sensors," *Journal of the American Ceramic Society*, vol. 94, no. 10, pp. 3153–3170, Oct. 2011.
- [9] D. W. Greve, T. L. Chin, P. Zheng, P. Ohodnicki, J. Baltrus, and I. J. Oppenheim, "Surface acoustic wave devices for harsh environment wireless sensing," *Sensors (Switzerland)*, vol. 13, no. 6, pp. 6910–6935, Jun. 2013.
- [10] H. P. Phan, D. V. Dao, K. Nakamura, S. Dimitrijev, and N. T. Nguyen, "The Piezoresistive Effect of SiC for MEMS Sensors at High Temperatures: A Review," *Journal of Microelectromechanical Systems*, vol. 24, no. 6, pp. 1663–1677, 2015.

- [11] T. T. Pham, H. Zhang, S. Yenuganti, S. Kaluvan, and J. A. Kosinski, "Design, Modeling , and Experiment of a Piezoelectric Pressure Sensor Based on a," *IEEE Transactions on Industrial Electronics*, vol. 64, no. 11, pp. 8484–8491, 2017.
- [12] T. Dinh, H. P. Phan, A. Qamar, P. Woodfield, N. T. Nguyen, and D. V. Dao, "Thermoresistive Effect for Advanced Thermal Sensors: Fundamentals, Design Considerations, and Applications," *Journal of Microelectromechanical Systems*, vol. 26, no. 5, pp. 966–986, Oct. 2017.
- [13] R. A. Miller, H. So, T. A. Heuser, and D. G. Senesky, "High-temperature ultraviolet photodetectors: A review," *arXiv*, pp. 1–41, 2018.
- [14] C. Zhang, S. Kaluvan, H. Zhang, G. Wang, and L. Zuo, "A study on the Langmuir adsorption for quartz crystal resonator based low pressure CO2 gas sensor," *Measurement: Journal of the International Measurement Confederation*, vol. 124, pp. 286–290, Aug. 2018.
- [15] C. Zhang, S. Kaluvan, H. Zhang, and G. Wang, "PMN-PT based smart sensing system for viscosity and density measurement," *Measurement: Journal of the International Measurement Confederation*, vol. 101, pp. 15–18, Apr. 2017.
- [16] Habib F. Rashvand (Editor), Ali Abedi (Editor), "Wireless Sensor Systems for Extreme Environments: Space, Underwater, Underground, and Industrial," John Wiley & Sons Ltd, 1<sup>st</sup> edition, 2017.
- [17] Y. Luo, C. Zhang, B. Zheng, X. Geng, and M. Debliquy, "Hydrogen sensors based on noble metal doped metal-oxide semiconductor: A review," *International Journal of Hydrogen Energy*, vol. 42, no. 31.
- [18] A. Trinchi, S. Kandasamy, and W. Wlodarski, "High temperature field effect hydrogen and hydrocarbon gas sensors based on SiC MOS devices," *Sensors and Actuators, B: Chemical*, vol. 133, no. 2. pp. 705–716, 12-Aug-2008.Elsevier Ltd, pp. 20386–20397, 03-Aug-2017.
- [19] H. Gu, Z. Wang, and Y. Hu, "Hydrogen gas sensors based on semiconductor oxide nanostructures," *Sensors (Switzerland)*, vol. 12, no. 5. pp. 5517–5550, May-2012.
- [20] L. Yang, C. Yin, Z. Zhang, J. Zhou, and H. Xu, "The investigation of hydrogen gas sensing properties of SAW gas sensor based on palladium surface modified SnO2 thin film," *Materials Science in Semiconductor Processing*, vol. 60, pp. 16–28, Mar. 2017.

- [21] X. Liu, S. Cheng, H. Liu, S. Hu, D. Zhang, and H. Ning, "A survey on gas sensing technology," *Sensors (Switzerland)*, vol. 12, no. 7. pp. 9635–9665, Jul-2012.
- [22] W. J. Buttner, M. B. Post, R. Burgess, and C. Rivkin, "An overview of hydrogen safety sensors and requirements," *International Journal of Hydrogen Energy*, vol. 36, no. 3, pp. 2462–2470, 2011.
- [23] L. Boon-Brett *et al.*, "Identifying performance gaps in hydrogen safety sensor technology for automotive and stationary applications," *International Journal of Hydrogen Energy*, vol. 35, no. 1, pp. 373–384, Jan. 2010.
- [24] T. Hübert, L. Boon-Brett, G. Black, and U. Banach, "Hydrogen sensors A review," *Sensors and Actuators, B: Chemical*, vol. 157, no. 2, pp. 329–352, 2011.
- [25] G. Korotcenkov, S. Do Han, and J. R. Stetter, "Review of electrochemical hydrogen sensors," *Chemical Reviews*, vol. 109, no. 3, pp. 1402–1433, 2009.
- [26] A. Ayes, P. R. Ohodnicki, R. J. Lad, and M. P. Da Cunha, "Enhanced Hydrogen Gas Detection Using SAW Sensor Through Oxygen Pre-Treatment," *IEEE International Ultrasonics Symposium (IUS)*, Glasgow, UK, 2019, pp. 189-192, doi: 10.1109/ULTSYM.2019.8925669.
- [27] A. Ayes and M. P. Da Cunha, "Influence of Langasite Crystal Orientation on Hydrogen Gas Detection up to 400°C," *IEEE International Ultrasonics Symposium (IUS)*, Glasgow, UK, 2019, pp. 735-738, doi: 10.1109/ULTSYM.2019.8925871.
- [28] [A. Ayes, G. Bernhardt, and M. P. Da Cunha, "Removal of Stress Hillocks from Platinum-Alumina Electrodes Used in High-temperature SAW Devices," *IEEE International Ultrasonics Symposium (IUS)*, Glasgow, UK, 2019, pp. 727-730, doi: 10.1109/ULTSYM.2019.8925942.
- [29] G. Tortissier *et al.*, "Langasite based surface acoustic wave sensors for high temperature chemical detection in harsh environment: Design of the transducers and packaging," *Sensors and Actuators, B: Chemical*, vol. 156, no. 2. pp. 510–516, Aug-2011.
- [30] I. Shrena, D. Eisele, E. Mayer, L. M. Reindl, J. Bardong, and M. Schmitt, "SAW-properties of langasite at high temperatures: Measurement and analysis," *3rd International Conference on Signals, Circuits and Systems (SCS)*, Medenine, Tunisia, 2009, pp. 1-4, doi: 10.1109/ICSCS.2009.5414173.

- [31] Walther Nernst, "Über die Elektrolytische Leitung Fester Körper bei Sehr Hohen Temperaturen," Zeitschrift für Elektrochemie, 6 (2), pp. 41-43,", 1899.
- [32] T. H. Etsell and S. N. Flengas, "The Electrical Properties of Solid Oxide Electrolytes," *Chemical Reviews*, vol. 70, no. 3, pp. 339-376, 1970.
- [33] N. Miura, T. Sato, S. A. Anggraini, H. Ikeda, and S. Zhuiykov, "A review of mixedpotential type zirconia-based gas sensors," *Ionics*, vol. 20, no. 7, pp. 901–925, 2014.
- [34] Charles C. Sorrell, Sunao Sugihara, and Janusz Nowotny, "Materials for Energy Conversion Devices," Woodhead Publishing, 1<sup>st</sup> edition, 2005.
- [35] X. Vendrell and A. R. West, "Electrical Properties of Yttria-Stabilized Zirconia, YSZ Single Crystal: Local AC and Long Range DC Conduction," *Journal of The Electrochemical Society*, vol. 165, no. 11, pp. F966–F975, 2018.
- [36] M. Gaudon, C. Laberty-Robert, F. Ansart, P. Stevens, and A. Rousset, "New chemical process for the preparation of fine powders and thin films of LSMx-YSZ composite oxides," *Solid State Sciences*, vol. 5, no. 10, pp. 1377–1383, 2003.
- [37] J. Nowotny, T. Bak, M. K. Nowotny, and C. C. Sorrell, "Charge transfer at oxygen/zirconia interface at elevated temperatures Part 1: Basic properties and terms," *Advances in Applied Ceramics*, vol. 104, no. 4, pp. 147–153, 2005.
- [38] N. M. Abdul-Jabbar, D. L. Poerschke, C. Gabbett, and C. G. Levi, "Phase equilibria in the zirconia–yttria/gadolinia–silica systems," *Journal of the European Ceramic Society*, vol. 38, no. 9, pp. 3286–3296, Aug. 2018.
- [39] J. P. Goff, W. Hayes, S. Hull, M. T. Hutchings, and K. N. Clausen, "Defect structure of yttria-stabilized zirconia and its influence on the ionic conductivity at elevated temperatures," Physical Review B, vol. 59, no. 22, pp. 14202-14219, 1999.
- [40] Serge Zhuiykov, "Electrochemistry of Zirconia Gas Sensors," Taylor & Francis Group, 1<sup>st</sup> edition, 2007.
- [41] I. R. Gibson, G. P. Dransfield, and J. T. S. Irvine, "Influence of yttria concentration upon electrical properties and susceptibility to ageing of yttria-stabilized zirconia," *Journal of the European Ceramic Society*, vol. 18, no. 6, pp. 661–667, 1998.

- [42] S. Zhuiykov, "Development of dual sulfur oxides and oxygen solid state sensor for `in situ' measurements," *Fuel*, vol. 79, no. 10, pp. 1255–1265, 2000.
- [43] R. Pornprasertsuk, P. Ramanarayanan, C. B. Musgrave, and F. B. Prinz, "Predicting ionic conductivity of solid oxide fuel cell electrolyte from first principles," *Journal of Applied Physics*, vol. 98, no. 10, 2005.
- [44] A. I. Ioffe, D. S. Rutman, and S. V Karyachov, "On the Nature of The Conductivity Maximum in Zirconia-Based Solid Electrolytes," *Electrochimica Acta*, vol. 23, no. 2, pp. 141-142, 1978.
- [45] "U. of Cambridge, Doitpoms, (2016). http://www.doitpoms.ac.uk/tlplib/fuelcells/sofc\_electrolyte.php," p. 2016, 2016.
- [46] S. C. Singhal, "Advances in solid oxide fuel cell technology," *Solid State Ionics*, vol. 135, pp. 305-313, 2000.
- [47] R. Jin, "The impacts of nanotechnology on catalysis by precious metal nanoparticles," *Nanotechnology Reviews*, vol. 1, no. 1. Walter de Gruyter GmbH, pp. 31–56, 01-Jan-2012.
- [48] R. V. Kazantsev, N. A. Gaidai, N. V. Nekrasov, K. Tenchev, L. Petrov, and A. L. Lapidus, "Kinetics of benzene and toluene hydrogenation on a Pt/TiO2 catalyst," *Kinetics and Catalysis*, vol. 44, no. 4, pp. 529–535, 2003.
- [49] S. J. Tauster, "Strong metal-support interactions," Accounts of Chemical Research, vol. 20, no. 11, pp. 389-394, 1987.
- [50] S. J. Tauster, S. C. Fung, and R. L. Garten, "Strong metal-support interactions. Group 8 noble metals supported on titanium dioxide," *Journal of the American Chemical Society*, vol. 100, no. 1, pp. 170-175, 1978.
- [51] Costas G. Vayenas, Symeon Bebelis, Costas Pliangos, Susanne Brosda, Demetrios Tsiplakides, "Electrochemical Activation of Catalysis Promotion, Electrochemical Promotion, and Metal-Support Interactions," Springer, 1<sup>st</sup> edition, 2002.
- [52] B. R. Cuenya, "Synthesis and catalytic properties of metal nanoparticles: Size, shape, support, composition, and oxidation state effects," *Thin Solid Films*, vol. 518, no. 12. pp. 3127–3150, 2010.

- [53] M. Y. Rezk, J. Sharma, and M. R. Gartia, "Nanomaterial-based co2 sensors," *Nanomaterials*, vol. 10, no. 11, pp. 1–18, 2020.
- [54] W. Maziarz, "TiO 2 /SnO 2 and TiO 2 /CuO thin film nano-heterostructures as gas sensors," *Applied Surface Science*, vol. 480, no. October 2018, pp. 361–370, 2019.
- [55] M. Graf, A. Gurlo, N. Bârsan, U. Weimar, and A. Hierlemann, "Microfabricated gas sensor systems with sensitive nanocrystalline metal-oxide films," *Journal of Nanoparticle Research*, vol. 8, no. 6, pp. 823–839, 2006.
- [56] [56] L. Filipovic and A. Lahlalia, "Review—System-on-Chip SMO Gas Sensor Integration in Advanced CMOS Technology," *Journal of The Electrochemical Society*, vol. 165, no. 16, pp. B862–B879, 2018.
- [57] K. Govardhan and A. Nirmala Grace, "Metal/Metal Oxide Doped Semiconductor Based Metal Oxide Gas Sensors—A Review," Sensor Letters, vol. 14, no. 8, pp. 741-750, 2016.
- [58] T. Zheng, J. He, Y. Zhao, W. Xia, and J. He, "Precious metal-support interaction in automotive exhaust catalysts," *Journal of Rare Earths*, vol. 32, no. 2, pp. 97–107, 2014.
- [59] J. A. Kurzman, L. M. Misch, and R. Seshadri, "Chemistry of precious metal oxides relevant to heterogeneous catalysis," *Dalton Transactions*, vol. 42, no. 41, pp. 14653–14667, 2013.
- [60] M. Sui, M. Y. Li, S. Kunwar, P. Pandey, Q. Zhang, and J. Lee, "Effects of annealing temperature and duration on the morphological and optical evolution of self-Assembled Pt nanostructures on c-plane sapphire," *PLoS ONE*, vol. 12, no. 5, 2017.
- [61] S. Kunwar, P. Pandey, M. Sui, Q. Zhang, M. Y. Li, and J. Lee, "Effect of Systematic Control of Pd Thickness and Annealing Temperature on the Fabrication and Evolution of Palladium Nanostructures on Si (111) via the Solid State Dewetting," *Nanoscale Research Letters*, vol. 12, pp. 1–14, 2017.
- [62] Anna Harley-Trochimczyk, Jiyoung Chang, Qin Zhou, Jeffrey Dong, Thang Pham, Marcus A. Worsley, Roya Maboudian, Alex Zettl, and William Mickelson, "Catalytic hydrogen sensing using microheated platinum nanoparticle-loaded graphene aerogel," *Sensors and Actuators, B: Chemical*, vol. 206, pp. 399–406, 2015.

- [63] Ivan I. Ivanov, Alexander M. Baranov, Vladislav A. Talipov, Sergei M. Mironov, Saba Akbari, Irina V. Kolesnik, Elena D. Orlova, Kirill S. Napolskii, "Investigation of catalytic hydrogen sensors with platinum group catalysts," *Sensors and Actuators, B: Chemical*, vol. 346, p. 130515, 2021.
- [64] Chun-Jern Pan, Meng-Che Tsai, Wei-Nien Su, John Rick, Nibret Gebeyehu Akalework, Abiye Kebede Agegnehu, Shou-Yi Cheng, and Bing-Joe Hwang, "Tuning/exploiting Strong Metal-Support Interaction (SMSI) in Heterogeneous Catalysis," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 74, pp. 154–186, 2017.
- [65] A.S. Ivanova, E.M. Slavinskaya, R.V. Gulyaev, V.I. Zaikovskii, O.A. Stonkus, I.G. Danilova, L.M. Plyasova, I.A. Polukhina, and A.I. Boronin, "Metal-support interactions in Pt/Al2O3 and Pd/Al2O3 catalysts for CO oxidation," *Applied Catalysis B: Environmental*, vol. 97, no. 1–2, pp. 57–71, Jun. 2010.
- [66] Miho Hatanaka, Naoki Takahashi, Toshitaka Tanabe, Yasutaka Nagai, Kazuhiko Dohmae, Yuki Aoki, Takeru Yoshida, and Hirofumi Shinjoh, "Ideal Pt loading for a Pt/CeO<sub>2</sub>-based catalyst stabilized by a Pt-O-Ce bond," *Applied Catalysis B: Environmental*, vol. 99, no. 1–2, pp. 336–342, 2010.
- [67] L. Deng, H. Miura, T. Shishido, S. Hosokawa, K. Teramura, and T. Tanaka, "Strong metalsupport interaction between Pt and SiO2 following high-temperature reduction: A catalytic interface for propane dehydrogenation," *Chemical Communications*, vol. 53, no. 51, pp. 6937–6940, 2017.
- [68] R. Strobel and S. E. Pratsinis, "Flame synthesis of supported platinum group metals for catalysis and sensors," *Platinum Metals Review*, vol. 53, no. 1, pp. 11–20, Jan. 2009.
- [69] J. Ohyama, A. Yamamoto, K. Teramura, T. Shishido, and T. Tanaka, "Modification of metal nanoparticles with TiO2 and metal-support interaction in photodeposition," ACS *Catalysis*, vol. 1, no. 3, pp. 187–192, Mar. 2011.
- [70] S. Bonanni, K. Aït-mansour, H. Brune, and W. Harbich, "Overcoming the Strong Metal -Support Interaction State : CO," vol. 2, no. 110, pp. 385–389, 2011.
- [71] L. Calvillo, V. Celorrio, R. Moliner, and M. J. Lázaro, "Influence of the support on the physicochemical properties of Pt electrocatalysts: Comparison of catalysts supported on different carbon materials," *Materials Chemistry and Physics*, vol. 127, no. 1–2, pp. 335– 341, 2011.

- [72] Kyungjung Kwon, Seon-ah Jin, Chanho Paka, Hyuk Chang, Sang Hoon Joo, Hyung Ik Lee, Jin Hoe Kim, and Ji Man Kim, "Enhancement of electrochemical stability and catalytic activity of Pt nanoparticles via strong metal-support interaction with sulfur-containing ordered mesoporous carbon," *Catalysis Today*, vol. 164, no. 1, pp. 186–189, 2011.
- [73] N. Yamaguchi, N. Kamiuchi, H. Muroyama, T. Matsui, and K. Eguchi, "Effect of reduction treatment on CO oxidation over Pt/SnO2 catalyst," *Catalysis Today*, vol. 164, no. 1, pp. 169–175, 2011.
- [74] D. Zagoraiosa, A. Athanasiadi, I. Kalaitzidou, S. Ntais, A. Katsaounis, A. Caravaca, P. Vernoux, and C.G. Vayenas, "Electrochemical promotion of methane oxidation over nanodispersed Pd/Co<sub>3</sub>O<sub>4</sub> catalysts," *Catalysis Today*, vol. 355, pp. 910–920, 2020.
- [75] B. L. Mojet, J. T. Miller, D. E. Ramaker, and D. C. Koningsberger, "A New Model Describing the Metal-Support Interaction in Noble Metal Catalysts," *Journal of Catalysis*, vol. 186, pp. 373–386, 1999.
- [76] X. Du *et al.*, "Size-dependent strong metal-support interaction in TiO2 supported Au nanocatalysts," *Nature Communications*, vol. 11, no. 1, 2020.
- [77] P. Vernoux *et al.*, "Ionically conducting ceramics as active catalyst supports," *Chemical Reviews*, vol. 113, no. 10, pp. 8192–8260, 2013.
- [78] M. Fee, S. Ntais, A. Weck, and E. A. Baranova, "Electrochemical behavior of silver thin films interfaced with yttria-stabilized zirconia," *Journal of Solid State Electrochemistry*, vol. 18, no. 8, pp. 2267–2277, 2014.
- [79] M. S. Barbosa, P. H. Suman, J. J. Kim, H. L. Tuller, J. A. Varela, and M. O. Orlandi, "Gas sensor properties of Ag- and Pd-decorated SnO micro-disks to NO<sub>2</sub>, H<sub>2</sub> and CO: Catalyst enhanced sensor response and selectivity," *Sensors and Actuators, B: Chemical*, vol. 239, pp. 253–261, 2017.
- [80] Zain Ul Abideen, Jae-Hun Kim, Jae-Hyoung Lee, Jin-Young Kim, Ali Mirzaei, Hyoun Woo Kim, and Sang Sub Kim, "Electrospun metal oxide composite nanofibers gas sensors: A review," *Journal of the Korean Ceramic Society*, vol. 54, no. 5, pp. 366–379, 2017.
- [81] R. Behanan, S. C. Moulzolf, M. Call, G. Bernhardt, D. Frankel, R. J. Lad, and M. Pereira da Cunha, "Thin films and techniques for SAW sensor operation above 1000°C," 2013

*IEEE International Ultrasonics Symposium (IUS)*, Prague, Czech Republic, 2013, pp. 1013-1016, doi: 10.1109/ULTSYM.2013.0260.

- [82] S. C. Moulzolf, D. J. Frankel, M. Pereira Da Cunha, and R. J. Lad, "High temperature stability of electrically conductive Pt-Rh/ZrO2 and Pt-Rh/HfO<sub>2</sub> nanocomposite thin film electrodes," in *Microsystem Technologies*, vol. 20, no. 4–5, pp. 523–531, 2014.
- [83] A. Maskay, A. Ayes, R. J. Lad, and M. P. Cunha, "Stability of Pt/Al2O3 -Based Electrode Langasite SAW Sensors with Al2O3 Capping Layer and Yttria- Stabilized Zirconia Sensing Layer," 2017 IEEE International Ultrasonics Symposium (IUS), Washington, DC, USA, 2017, pp. 1-4, doi: 10.1109/ULTSYM.2017.8092421.
- [84] J. Gong, Q. Chen, M. Lian, and N. Liu, "Environmental Influences on SMO Sensors' Performance," Sensors and Transducers, vol. 54, no. 4, pp. 310–319, 2005
- [85] K. M. Subramaniam, L. L. Rajeswara Rao, and N. Jampana, "Investigation of Annealing Induced Yttria Segregation in Sputtered Yttria-Stabilized Zirconia Thin Films," *Journal of the American Ceramic Society*, vol. 98, no. 10, pp. 3389–3397, 2015.
- [86] O. K. Alexeeva and V. N. Fateev, "Application of the magnetron sputtering for nanostructured electrocatalysts synthesis," *International Journal of Hydrogen Energy*, vol. 41, no. 5, pp. 3373–3386, 2016.
- [87] P. J. Kelly and R. D. Arnell, "Magnetron sputtering: A review of recent developments and applications," *Vacuum*, vol. 56, no. 3, pp. 159–172, 2000.
- [88] J. T. Gudmundsson, "Physics and technology of magnetron sputtering discharges," *Plasma Sources Science and Technology*, vol. 29, no. 11, 2020.
- [89] S. Berg and T. Nyberg, "Fundamental understanding and modeling of reactive sputtering processes," *Thin Solid Films*, vol. 476, no. 2, pp. 215–230, 2005.
- [90] J. A. Thornton, "The microstructure of sputter-deposited Coatings," *Journal of Vacuum Science & Technology A*, vol. 4, pp. 3059, 1986.
- [91] D. Spanjaard, C. Guillot, M. C. Desjonquères, G. Tréglia, and J. Lecante, "Surface core level spectroscopy of transition metals: A new tool for the determination of their surface structure," *Surface Science Reports*, vol. 5, no. 1–2, pp. 1–85, 1985.

- [92] D. Briggs and M. P. Seah, (editors), "Practical Surface Analysis," John Wiley and Sons, Chichester, 1983.
- [93] M. S. Farhan, E. Zalnezhad, and A. R. Bushroa, "Investigation of optical and structural properties of ion-assisted deposition (IAD) ZrO2 thin films," *International Journal of Precision Engineering and Manufacturing*, vol. 14, no. 11, pp. 1997–2002, 2013.
- [94] Terry L. Alford, Leonard C. Feldman, and James W. Mayer, "Fundamentals of Nanoscale Film Analysis," Springer New York, NY, 1<sup>st</sup> edition, 2007.
- [95] S. Oswald and R. Reiche, "Binding state information from XPS depth profiling: capabilities and limits," vol. 179, pp. 307–315, 2001.
- [96] S. Tougaard, "Surface nanostructure determination by x-ray photoemission spectroscopy peak shape analysis," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 14, no. 3, pp. 1415–1423, 1996.
- [97] R. Communication, A. Alshehabi, and J. Kawai, "Extrinsic and Intrinsic Contributions to Plasmon Peaks in Solids," *Zeitschrift für Naturforschung A*, vol. 71, no. 1, pp. 91–93, 2016.
- [98] H. K. Kim, D. Y. Jang, J. W. Kim, K. Bae, and J. H. Shim, "Ionic properties of ultrathin yttria-stabilized zirconia thin films fabricated by atomic layer deposition with water, oxygen, and ozone," *Thin Solid Films*, vol. 589, pp. 441–445, 2015.
- [99] W. Zhu, S. Nakashima, E. Marin, H. Gu, and G. Pezzotti, "Microscopic mapping of dopant content and its link to the structural and thermal stability of yttria-stabilized zirconia polycrystals," *Journal of Materials Science*, vol. 55, no. 2, pp. 524–534, 2020.
- [100] M. P. Seah, "A review of the analysis of surfaces and thin films by AES and XPS," Vacuum, vol. 34, no. 3–4, pp. 463–478, 1984.
- [101] M. Seah, I. Gilmore, and S. Spencer, "Quantitative XPS," Journal of Electron Spectroscopy and Related Phenomena, vol. 120, no. 1–3, pp. 93–111, 2001.
- [102] John F. Moulder, William F. Stickle, Peter E. Sobol, and Kenneth D. Bomben. Atomic Sensitivity Factors for X-ray Sources at 54.7. In Jil Chastain, editor, Handb. X-ray

Photoelectron Spectrosc., chapter Appendix F, page 253. Perkin-Elmer Corporation, Eden Prairie, Minnesota, 1992. ISBN 0-9627026-2-5.

- [103] Tanuma, Shigeo, and T. Kimura. "Quantitative Auger and X-Ray Photoelectron Analysis of Au-Cu Alloys with Three Kinds of Relative Sensitivity Factors." *Journal of Surface Analysis*, vol. 10, pp. 163-168, 2003.
- [104]C. D. Wagner, "Sensitivity factors for XPS analysis of surface atoms," *Journal of Electron Spectroscopy and Related Phenomena*, vol. 32, no. 2, pp. 99–102, 1983.
- [105]S. Tougaard, "Practical algorithm for background subtraction," *Surface Science*, vol. 216, no. 3, pp. 343–360, 1989.
- [106] P. W. H. Bragg and W. L. Bragg, "The Reflection of X-rays by crystals" *Proceedings of the Royal Society A*, vol. 88, pp. 428–438, 1913.
- [107]G. Hölzer, M. Fritsch, M. Deutsch, J. Härtwig, and E. Förster, "[Formula Presented] and [Formula Presented] x-ray emission lines of the [Formula Presented] transition metals," *Physical Review A - Atomic, Molecular, and Optical Physics*, vol. 56, no. 6, pp. 4554– 4568, 1997.
- [108]ICDD database, PDF-4+ (04-011-7881). International Centre for Diffraction Data, Newtown, PA, USA (2017).
- [109]ICDD database, PDF-4+ (00-004-0802). International Centre for Diffraction Data, Newtown, PA, USA (2017).
- [110] ICDD database, PDF-4+ (00-030-1468). International Centre for Diffraction Data, Newtown, PA, USA (2017).
- [111]E. Chason and P. R. Guduru, "Tutorial: Understanding residual stress in polycrystalline thin films through real-time measurements and physical models," *Journal of Applied Physics*, vol. 119, no. 19, 2016.
- [112] V. H. Smith and P. G. Simpson, "Crystallite size distributions from x-ray powder line profiles," *Journal of Applied Physics*, vol. 36, no. 10, pp. 3285–3287, 1965.

- [113]A. K. Deb and P. Chatterjee, "Estimation of lattice strain in alumina-zirconia nanocomposites by X-ray diffraction peak profile analysis," *Journal of Theoretical and Applied Physics*, vol. 13, no. 3, pp. 221–229, 2019.
- [114] A. Khorsand Zak, W. H. Abd. Majid, M. E. Abrishami, and R. Yousefi, "X-ray analysis of ZnO nanoparticles by Williamson-Hall and size-strain plot methods," *Solid State Sciences*, vol. 13, no. 1, pp. 251–256, 2011.
- [115]U. Pietsch, "Investigations of semiconductor surfaces and interfaces by X-ray grazing incidence diffraction," *Current Science*, vol. 78, no. 12, pp. 1484–1495, 2000.
- [116]B. K. Tanner, T. P. A. Hase, T. A. Lafford, and M. S. Goorsky, "Grazing incidence inplane X-ray diffraction in the laboratory," *Powder Diffraction*, vol. 19, no. 1, pp. 45–48, 2004.
- [117]N. Widjonarko, "Introduction to Advanced X-ray Diffraction Techniques for Polymeric Thin Films," *Coatings*, vol. 6, no. 4, p. 54, 2016.
- [118] Mario Birkholz, "Thin Film Analysis by X-ray Scattering," Wiley-VCH Verlag GmbH, Germany, 2006. ISBN 3-527-31052-5.
- [119] Jens Als-Nielsen and Des McMorrow, "Elements of Modern X-ray Physics," John Wiley & Sons, 2<sup>nd</sup> edition, 2011.
- [120]S. A. Veldhuis, P. Brinks, T. M. Stawski, O. F. Göbel, and J. E. Ten Elshof, "A facile method for the density determination of ceramic thin films using X-ray reflectivity," *Journal of Sol-Gel Science and Technology*, vol. 71, no. 1, pp. 118–128, 2014.
- [121]S. L. McArthur, "Thin films of Vanadium Oxide Grown on Vanadium metal," *Surface and Interface Analysis*, vol. 38, no. c, pp. 1380–1385, 2006.
- [122]Evgenij Barsoukov, and J. Ross Macdonald, "Impedance Spectroscopy: Theory, Experiment, and Applications," John Wiley & Sons, 2<sup>nd</sup> edition, 2005.
- [123] Mark E. Orazem, and Bernard Tribollet," Electrochemical Impedance Spectroscopy," John Wiley & Sons, 1<sup>st</sup> edition, 2008.

- [124]J. E. Bauerle, "Study of solid electrolyte polarization by a complex admittance method," *Journal of Physics and Chemistry of Solids*, vol. 30, pp. 3657-2670, 1969.
- [125]J. L. Hertz, A. Rothschild, and H. L. Tuller, "Highly enhanced electrochemical performance of silicon-free platinum-yttria stabilized zirconia interfaces," *Journal of Electroceramics*, vol. 22, no. 4, pp. 428–435, 2009.
- [126] R. Barfod, A. Hagen, S. Ramousse, P. V. Hendriksen, and M. Mogensen, "Break down of losses in thin electrolyte SOFCs," *Fuel Cells*, vol. 6, no. 2, pp. 141–145, 2006.
- [127]T. P. Heins, N. Harms, L. S. Schramm, and U. Schröder, "Development of a new Electrochemical Impedance Spectroscopy Approach for Monitoring the Solid Electrolyte Interphase Formation," *Energy Technology*, vol. 4, no. 12, pp. 1509–1513, 2016.
- [128] V. M. Huang, S. L. Wu, M. E. Orazem, N. Pébre, B. Tribollet, and V. Vivier, "Local electrochemical impedance spectroscopy: A review and some recent developments," *Electrochimica Acta*, vol. 56, no. 23, pp. 8048–8057, 2011.
- [129] R. Schmidt, W. Eerenstein, T. Winiecki, F. D. Morrison, and P. A. Midgley, "Impedance spectroscopy of epitaxial multiferroic thin films," *Physical Review B - Condensed Matter and Materials Physics*, vol. 75, no. 24, pp. 1–8, 2007.
- [130] J. Luo, D. P. Almond, and R. Stevens, "Ionic mobilities and association energies from an analysis of electrical impedance of ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> alloys," *Journal of the American Ceramic Society*, vol. 83, no. 7, pp. 1703–1708, 2000.
- [131]N. Miura, M. Nakatou, and S. Zhuiykov, "Impedancemetric gas sensor based on zirconia solid electrolyte and oxide sensing electrode for detecting total NOx at high temperature," *Sensors and Actuators, B: Chemical*, vol. 93, no. 1–3, pp. 221–228, 2003.
- [132]N. Miura, M. Nakatou, and S. Zhuiykov, "Impedance-based total-NOx sensor using stabilized zirconia and ZnCr2O4 sensing electrode operating at high temperature," *Electrochemistry Communications*, vol. 4, no. 4, pp. 284–287, 2002.
- [133] V. Balasubramani, S. Chandraleka, T. S. Rao, R. Sasikumar, M. R. Kuppusamy, and T. M. Sridhar, "Review—Recent Advances in Electrochemical Impedance Spectroscopy Based Toxic Gas Sensors Using Semiconducting Metal Oxides," *Journal of The Electrochemical Society*, vol. 167, no. 3, p. 037572, 2020.

- [134]S. W. Kim, Y. Lee, and G. M. Choi, "Electrical conductivity of Gd-doped ceria film at low temperatures (300-500 °c)," *Solid State Ionics*, vol. 262, pp. 411–415, 2014.
- [135] M. R. Shoar Abouzari, F. Berkemeier, G. Schmitz, and D. Wilmer, "On the physical interpretation of constant phase elements," *Solid State Ionics*, vol. 180, no. 14–16, pp. 922– 927, 2009.
- [136] P. K. Shukla, M. E. Orazem, and O. D. Crisalle, "Validation of the measurement model concept for error structure identification," *Electrochimica Acta*, vol. 49, no. 17–18, pp. 2881–2889, 2004.
- [137] V. Vivier and M. E. Orazem, "Impedance Analysis of Electrochemical Systems," *Chemical Reviews*, vol. 122, no. 12, pp. 11131–11168, 2022.
- [138]D. Eder and R. Kramer, "Impedance spectroscopy of reduced monoclinic zirconia," *Physical Chemistry Chemical Physics*, vol. 8, no. 38, pp. 4476–4483, 2006.
- [139] T. H. Yeh, R. De Lin, and J. S. Cherng, "Effects of residual stress and interface dislocations on the ionic conductivity of yttria stabilized zirconia nano-films," *Thin Solid Films*, vol. 574, pp. 66–70, 2015.
- [140] M. P. Da Cunha, "Wireless sensing in hostile environments," *IEEE International Ultrasonics Symposium, IUS*, pp. 1337–1346, 2013.
- [141]X. Jiang, K. Kim, S. Zhang, J. Johnson, and G. Salazar, "High-temperature piezoelectric sensing," *Sensors (Switzerland)*, vol. 14, pp. 144–169, 20-Dec-2013.
- [142]A. Maskay and M. Pereira da Cunha, "High-temperature static strain langasite SAWR sensor: Temperature compensation and numerical calibration for direct strain reading," *Sensors and Actuators, A: Physical*, vol. 259, pp. 34–43, 2017.
- [143]M. Pereira Da Cunha *et al.*, "Pt-Ni / Pt-Zr electrodes for stable SAW resonator operation during repeated temperature cycling up to 1000°C," *IEEE International Ultrasonics Symposium, IUS 2015*, pp. 6–9, 2015.
- [144] M. P. Da Cunha, R. J. Lad, T. Moonlight, G. Bernhardt, and D. J. Frankel, "High temperature stability of langasite surface acoustic wave devices," *Proceedings - IEEE Ultrasonics Symposium*, pp. 205–208, 2008.

- [145]S. C. Moulzolf, R. Behanan, T. Pollard, R. J. Lad, and M. P. Da Cunha, "Capacitively coupled IDT for high temperature SAW devices," *IEEE International Ultrasonics Symposium, IUS*, pp. 255–258, 2013.
- [146]P. Lackner, A. J. Brandt, U. Diebold, and M. Schmid, "Few-monolayer yttria-doped zirconia films: Segregation and phase stabilization," *Journal of Chemical Physics*, vol. 152, no. 6, 2020.
- [147] Y. Wang, C. Cai, L. Li, L. Yang, Y. Zhou, and G. Zhou, "Oxygen vacancy ordering induced displacements of cations in yttria-stabilized zirconia," *AIP Advances*, vol. 6, no. 9, 2016.
- [148]S. Sprio, S. Guicciardi, A. Bellosi, and G. Pezzotti, "Yttria-stabilized zirconia films grown by radiofrequency magnetron sputtering: Structure, properties and residual stresses," *Surface and Coatings Technology*, vol. 200, no. 14–15, pp. 4579–4585, 2006.
- [149]F. Smeacetto *et al.*, "Yttria-stabilized zirconia thin film electrolyte produced by RF sputtering for solid oxide fuel cell applications," *Materials Letters*, vol. 64, no. 22, pp. 2450–2453, 2010.
- [150]D. Golosov, S. Zavatskiy, S. Melnikov, "Physical and Electrical Properties of Yttria-Stabilized Zirconia Thin Films Prepared by Radio Frequency Magnetron Sputtering," vol. 53, no. 2, pp. 155-159, 2013.
- [151]U. Helmersson, M. Lattemann, J. Bohlmark, A. P. Ehiasarian, and J. T. Gudmundsson, "Ionized physical vapor deposition (IPVD): A review of technology and applications," *Thin Solid Films*, vol. 513, pp. 1–24, 2006.
- [152]T. Nakano, R. Yamazaki, and S. Baba, "Effects of atomic weight, gas pressure, and targetto-substrate distance on deposition rates in the sputter deposition process," *Journal of the Vacuum Society of Japan*, vol. 57, no. 4, pp. 152–154, 2014.
- [153]R. Rivera, T. Jorge, A. García, J. Bertomeu, and R. Rivera, "Deposition of Al <sub>2</sub> O <sub>3</sub> thin films by sputtering for c-Si solar cells passivation," pp. 1–10.
- [154]Y. Hamon *et al.*, "Influence of sputtering conditions on ionic conductivity of LiPON thin films," *Solid State Ionics*, vol. 177, no. 3–4, pp. 257–261, 2006.

- [155]H. Hidalgo et al., "Yttria-stabilized zirconia thin films deposited by pulsed-laser deposition and magnetron sputtering," Surface and Coatings Technology, vol. 205, no. 19, pp. 4495– 4499, 2011.
- [156]C. S. Chen, C. P. Liu, C. Y. A. Tsao, and H. G. Yang, "Study of mechanical properties of PVD ZrN films, deposited under positive and negative substrate bias conditions," *Scripta Materialia*, vol. 51, no. 7, pp. 715–719, 2004.
- [157] N. A. Rusli, R. Muhammad, S. K. Ghoshal, H. Nur, N. Nayan, and S. N. Jaafar, "Bias voltage dependent structure and morphology evolution of magnetron sputtered YSZ thin film: A basic insight," *Materials Research Express*, vol. 6, no. 10, pp. 106414, 2019.
- [158] J. Gao, H. Nakashima, J. Wang, K Iwanaga, D. Gao, K. Furukawa, and K. Muraoka "Effect of substrate bias on Si epitaxial growth using sputtering-type electron cyclotron resonance (ECR) plasma," *Japanese Journal of Applied Physics, Part 2: Letters*, vol. 38, no. 11B, pp. L1293-L1295, 1999.
- [159]Y. Zeng, Z. Tan, L. Zhou, M. Jiang, Y. Qiu, F. Fang, H. Huang, X. Zhang, and J. Jiand "Effects of bias voltage on fen films prepared by magnetron sputtering," *Materials Research*, vol. 18, pp. 115–119, 2015.
- [160] N. M. Figueiredo, N. J. M. Carvalho, and A. Cavaleiro, "An XPS study of Au alloyed Al-O sputtered coatings," *Applied Surface Science*, vol. 257, no. 13, pp. 5793–5798, 2011.
- [161] M. C. Biesinger, L. W. M. Lau, A. R. Gerson, and R. S. C. Smart, "Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn," *Applied Surface Science*, vol. 257, no. 3, pp. 887–898, 2010.
- [162] A. Lewera, L. Timperman, A. Roguska, and N. Alonso-Vante, "Metal-support interactions between nanosized Pt and metal oxides (WO 3 and TiO2) studied using X-ray photoelectron spectroscopy," *Journal of Physical Chemistry C*, vol. 115, no. 41, pp. 20153–20159, 2011.
- [163] R. Liu *et al.*, "A low-temperature synthesis of electrochemical active Pt nanoparticles and thin films by atomic layer deposition on Si(111) and glassy carbon surfaces," *Thin Solid Films*, vol. 586, pp. 28–34, 2015.

- [164]S. Sekimoto *et al.*, "Fiber-optic evanescent-wave hydrogen gas sensor using palladiumsupported tungsten oxide," *Sensors and Actuators, B: Chemical*, vol. 66, pp. 142–145, 2000.
- [165]S. Hajati and S. Tougaard, "Non-Destructive Depth Profiling by XPS Peak Shape Analysis," *Journal of Surface Analysis*, vol. 15, no. 3, pp. 220–224, 2009.

[166]<u>WWW.CASAXPS.COM</u>

- [167] P. Li, J. Carroll, and J. Mazumder, "Room temperature growth of biaxially aligned yttriastabilized zirconia films on glass substrates by pulsed-laser deposition," *Journal of Physics D: Applied Physics*, vol. 36, no. 13, pp. 1605–1608, 2003.
- [168] T. Kiguchi, T. J. Konno, H. Funakubo, O. Sakurai, and K. Shinozaki, "Columnar grain boundary coherence in yttria-stabilized zirconia thin film: Effects on ionic conductivity," *Journal of the Ceramic Society of Japan*, vol. 122, no. 1, pp. 72–77, 2014.
- [169] T. Kiguchi, Y. Kodama, T. J. Konno, H. Funakubo, O. Sakurai, and K. Shinozaki, "Chemical and structural effects on ionic conductivity at columnar grain boundaries in yttria-stabilized zirconia thin films," *Journal of the Ceramic Society of Japan*, vol. 122, no. 6, pp. 430–435, 2014.
- [170] M. Sillassen, P. Eklund, N. Pryds, E. Johnson, U. Helmersson, and J. Bøttiger, "Lowtemperature superionic conductivity in strained yttria-stabilized zirconia," *Advanced Functional Materials*, vol. 20, no. 13, pp. 2071–2076, 2010.
- [171]O. J. Durá and M. A. L. De La Torre, "X-ray diffraction line profile analysis of mechanically alloyed nanocrystalline YSZ," *Journal of Physics D: Applied Physics*, vol. 41, pp. 045408, 2008.
- [172]L. Mariscal-Becerra, R. Vázquez-Arreguín, U. Balderas, S. Carmona-Téllez, H. Murrieta Sánchez, and C. Falcony, "Luminescent characteristics of layered yttrium oxide nanophosphors doped with europium," *Journal of Applied Physics*, vol. 121, pp. 125111, 2017.
- [173]F. Nemla and D. Cherrad, "Metallic amorphous electrodeposited molybdenum coating from aqueous electrolyte: Structural, electrical and morphological properties under current density," *Applied Surface Science*, vol. 375, pp. 1–8, 2016.

- [174]S. J. Hwang, J. H. Lee, C. O. Jeong, and Y. C. Joo, "Effect of film thickness and annealing temperature on hillock distributions in pure Al films," *Scripta Materialia*, vol. 56, pp. 17– 20, 2007.
- [175]E. Shaffir, Y. Kauffmann, and I. Riess, "Void formation in gold films on yttrium-doped zirconia in the initial stage of de-wetting," *Acta Materialia*, vol. 79, pp. 59–65, 2014.
- [176]Y. Wang, D. Xu, Y. Li, and L. Liu, "Texture and morphology developments of Yttriastabilized zirconia (YSZ) buffer layer for coated conductors by RF sputtering," *Surface and Coatings Technology*, vol. 232, pp. 497–503, 2013.
- [177] A. Jafari, F. E. Christensen, S. Massahi, S. Svendsen, L. M. Vu, P. L. Henriksen, B. Shortt, M. Krumrey, L. Cibikc, E. Handick, and D. D. M. Ferreira, "X-ray reflectometry of a platinum coating as reference sample for the ATHENA coating development," *Optics for EUV, X-Ray, and Gamma-Ray Astronomy IX, Proceedings of S P I E - International Society for Optical Engineering*, vol. 11119, pp. 111191K-111191K-7, 2019.
- [178]S. A. Veldhuis, P. Brinks, T. M. Stawski, O. F. Göbel, and J. E. Ten Elshof, "A facile method for the density determination of ceramic thin films using X-ray reflectivity," *Journal of Sol-Gel Science and Technology*, vol. 71, pp. 118–128, 2014.
- [179]F. Cemin, G. Abadias, T. Minea, and D. Lundin, "Tuning high power impulse magnetron sputtering discharge and substrate bias conditions to reduce the intrinsic stress of TiN thin films," *Thin Solid Films*, vol. 688, p. 137335, 2019.
- [180]C.-S. Chen, C.-P. Liu, H.-G. Yang, and C.-Y. A. Tsao, "Influence of substrate bias on practical adhesion, toughness, and roughness of reactive dc-sputtered zirconium nitride films," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 22, no. 5, pp. 2041–2047, 2004.
- [181]J. E. Alfonso, J. Torres, and J. F. Marco, "Influence of the substrate bias voltage on the crystallographic structure and surface composition of Ti6Al4V thin films deposited by rf magnetron sputtering," *Brazilian Journal of Physics*, vol. 36, no. 3 B, pp. 994–996, 2006.
- [182]S. Rey-Mermet, Y. Yan, C. Sandu, G. Deng, and P. Muralt, "Nanoporous YSZ film in electrolyte membrane of Micro-Solid Oxide Fuel Cell," *Thin Solid Films*, vol. 518, no. 16, pp. 4743–4746, 2010.

- [183]C. Amaya, J. Caicedo, G. Bejarano, C. A. Cortés Escobedo, J. Muñoz-Saldaña, G. Zambrano, and P. Prieto, "Influence of bias voltage on the crystallographic orientation and morphology of sputter deposited yttria stabilized zirconia (YSZ) thin films," *Physica Status Solidi (C)*, vol. 4, no. 11, pp. 4288-4293, 2007.
- [184]N. Rösemann *et al.*, "Influence of bias voltage and oxygen flow rate on morphology and crystallographic properties of gas flow sputtered zirconia coatings," *Surface and Coatings Technology*, vol. 276, pp. 668–676, 2015.
- [185] M. Sillassen, P. Eklund, M. Sridharan, N. Pryds, N. Bonanos, and J. Bøttiger, "Ionic conductivity and thermal stability of magnetron-sputtered nanocrystalline yttria-stabilized zirconia," *Journal of Applied Physics*, vol. 105, no. 10, 2009.
- [186] D. G. Lim, G. S. Kang, S. I. Kwon, M. W. Park, and D. J. Kwak, "Influence of positive substrate bias on the electrical properties of ZnO:Al films prepared by DC magnetron sputtering," *Journal of the Korean Physical Society*, vol. 50, no. 6, pp. 1697–1700, 2007.
- [187]C. Zhang *et al.*, "The effect of substrate biasing during DC magnetron sputtering on the quality of VO2 thin films and their insulator-metal transition behavior," *Materials*, vol. 12, no. 13, pp. 1–14, 2019.
- [188] M. Fukutomi, S. Aoki, K. Komori, Y. Tanaka, T. Asano, and H. Maeda," Control of Y<sub>2</sub>O<sub>3</sub> -stabilized ZrO<sub>2</sub> thin film orientation by modified bias sputtering," *Thin Solid Films*, vol. 239, pp.123-126, 1994.
- [189]C. H. Liang and X. Qi, "Indium-tin-oxide thin films deposited on polyethyleneterephthalate substrates by substrate-biased RF magnetron sputtering," *Surface and Coatings Technology*, vol. 231, pp. 205–208, 2013.
- [190] A. Ul-Hamid, "The effect of deposition conditions on the properties of Zr-carbide, Zrnitride and Zr-carbonitride coatings-a review," *Materials Advances*, vol. 1, no. 5, pp. 988– 1011, 2020.
- [191]M. Sillassen, P. Eklund, M. Sridharan, N. Pryds, N. Bonanos, and J. Bøttiger, "Ionic conductivity and thermal stability of magnetron-sputtered nanocrystalline yttria-stabilized zirconia," *Journal of Applied Physics*, vol. 105, no. 10, pp. 3–8, 2009.
- [192]S. Sønderby, A. Nielsen, B. Christensen, K. Almtoft, J. Lu, J. Jensen, L. Nielsen, P. Eklund, "Reactive magnetron sputtering of uniform yttria-stabilized zirconia coatings in

an industrial setup," *Surface and Coatings Technology*, vol. 206, no. 19–20, pp. 4126–4131, 2012.

- [193]I. Espitia-Cabrera, H. D. Orozco-Hernández, P. Bartolo-Pérez, and M. E. Contreras-García, "Nanostructure characterization in single and multi layer yttria stabilized zirconia films using XPS, SEM, EDS and AFM," *Surface and Coatings Technology*, vol. 203, no. 3–4, pp. 211–216, 2008.
- [194] D. Majumdar and D. Chatterjee, "X-ray photoelectron spectroscopic studies on yttria, zirconia, and yttria-stabilized zirconia," *Journal of Applied Physics*, vol. 70, no. 2, pp. 988– 992, 1991.
- [195]D. Majumdar and D. Chatterjee, "X-ray photoelectron spectroscopic studies on yttriastabilized zirconia and its surface transformations," *Thin Solid Films*, vol. 206, no. 1–2, pp. 349–354, 1991.
- [196] M. de Ridder, R. van Welzenis, A. van der Gon, and H. Brongersma, "Subsurface segregation of yttria in yttria stabilized zirconia," *Journal of Applied Physics*, vol. 92, no. 6, pp. 3056–3064, 2002.
- [197] R. L. González-Romero and J. J. Meléndez, "Yttrium segregation and oxygen diffusion along high-symmetry grain boundaries in YSZ," *Journal of Alloys and Compounds*, vol. 622, pp. 708–713, 2015.
- [198] M. Yoshiya, K. Shimizu, and T. Oyama, "Oxide Ionic Conduction at Y 2 O 3 -Segregated ZrO 2 Grain Boundaries by Atomistic Simulation: Roles of Oxide Ion Vacancy," vol. 1, pp. 162–163, 2008.
- [199] J. Wang and H. Conrad, "Contribution of the space charge to the grain boundary energy in yttria-stabilized zirconia," *Journal of Materials Science*, vol. 49, no. 17, pp. 6074–6080, 2014.
- [200] Anthony Hughes, "Segregation in Single-Crystal Fully Stabilized Yttria-Zirconia," Journal of American Ceramic Society, vol. 78, no. 2, pp. 369, 1995.
- [201]S. Nezar, N. Saoula, S. Sali, M. Faiz, M. Mekki, N. Laoufi, and N. Tabete, "Properties of TiO<sub>2</sub> thin films deposited by rf reactive magnetron sputtering on biased substrates," *Applied Surface Science*, vol. 395, pp. 172–179, 2017.

- [202] A. A. Adjaottor, E. I. Meletis, S. Logothetidis, I. Alexandrou, and S. Kokkou, "Effect of substrate bias on sputter-deposited TiCx, TiNy and TiCxNy thin films," *Surface and Coatings Technology*, vol. 76–77, pp. 142–148, 1995.
- [203] J. Bae, Y. Lim, J. Park, D. Lee, S. Hong, J. An, and Y. Kim, "Thermally-Induced Dopant Segregation Effects on the Space Charge Layer and Ionic Conductivity of Nanocrystalline Gadolinia-Doped Ceria," vol. 163, no. 8, pp. 919–926, 2016.
- [204]C. Charpentier, P. Prod'homme, I. Maurin, M. Chaigneau, and C. P. I. Roca, "X-Ray diffraction and Raman spectroscopy for a better understanding of ZnO:Al growth process," *EPJ Photovoltaics*, vol. 2, 2011.
- [205]Q. Yang, Z. Lin, B. Meng, X. Zhu, F. Yang, and S. Wu, "Effects of Thickness on the Electrical Conductivity of Sputtered YSZ Film with Nanocrystalline Columnar Microstructure," *Journal Wuhan University of Technology, Materials Science Edition*, vol. 33, no. 6, pp. 1344–1349, 2018.
- [206]K. Bae, K. Son, J. Kim, S. Park, J. An, F. Prinz, J. Shim, "Proton incorporation in yttriastabilized zirconia during atomic layer deposition," *International Journal of Hydrogen Energy*, vol. 39, no. 6, pp. 2621–2627, 2014.
- [207] R. A. De Souza, M. J. Pietrowski, U. Anselmi-Tamburini, S. Kim, Z. A. Munir, and M. Martin, "Oxygen diffusion in nanocrystalline yttria-stabilized zirconia: The effect of grain boundaries," *Physical Chemistry Chemical Physics*, vol. 10, no. 15, pp. 2067–2072, 2008.
- [208] D. Agarkova, M. Borik, S. Bredikhin I. Burmistrov, G. Eliseeva, A. Kulebyakin, I. Kuritsyna, E. Lomonova, F. Milovich, V. Myzina, N. Tabachkova, "Phase compositions, structures and properties of scandia-stabilized zirconia solid solution crystals co-doped with yttria or ytterbia and grown by directional melt crystallization," *Solid State Ionics*, vol. 346, no. January, p. 115218, 2020.
- [209] A. G. Marinopoulos, "Protons in cubic yttria-stabilized zirconia: Binding sites and migration pathways," *Solid State Ionics*, vol. 315, no. March 2017, pp. 116–125, 2018.
- [210] W. Zhao, I. J. Kim, and J. Gong, "Influence of thickness on the electrical conductivity of YSZ electrolytes," *Journal of the Ceramic Society of Japan*, vol. 118, no. 1378, pp. 550– 554, 2010.

- [211]C. Zhang, C. Li, G. Zhang, X. Ning, C. Li, H. Liao, C. Coddet, "Ionic conductivity and its temperature dependence of atmospheric plasma-sprayed yttria stabilized zirconia electrolyte," *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, vol. 137, no. 1–3, pp. 24–30, 2007.
- [212] Min Nah Tong, Jon Binner, Christopher Munnings, Bala Vaidhyanathan, and Hirad Taherparvar, "Characterisation of Submicron-Grain Sized Yttria-Stabilized Zirconia Electrolyte for SOFCs," *Journal of Materials Science and Engineering A*, vol. 1, no. 2, pp. 177–183, 2011.
- [213] T. Hill and H. Huang, "Fabricating Pinhole-Free YSZ Sub-Microthin Films by Magnetron Sputtering for Micro-SOFCs," *International Journal of Electrochemistry*, vol. 2011, pp. 1–8, 2011.
- [214] I. Kosacki, C. M. Rouleau, P. F. Becher, J. Bentley, and D. H. Lowndes, "Surface/interfacerelated conductivity in nanometer thick YSZ films," *Electrochemical and Solid-State Letters*, vol. 7, no. 12, pp. 459–462, 2004.
- [215] A. Karthikeyan, C. L. Chang, and S. Ramanathan, "High temperature conductivity studies on nanoscale yttria-doped zirconia thin films and size effects," *Applied Physics Letters*, vol. 89, no. 18, 2006.
- [216] P. Arunkumar, R. Ramaseshan, S. Dash, and K. Suresh Babu, "Tunable transport property of oxygen ion in metal oxide thin film: Impact of electrolyte orientation on conductivity," *Scientific Reports*, vol. 7, no. 1, pp. 1–18, 2017.
- [217]O. Durá, M. López de la Torre, L. Vázquez, J. Chaboy, R. Boada, A. Rivera-Calzada, J. Santamaria, and C. Leon, "Ionic conductivity of nanocrystalline yttria-stabilized zirconia: Grain boundary and size effects," *Physical Review B Condensed Matter and Materials Physics*, vol. 81, no. 18, pp. 1–9, 2010.
- [218]X. Guo and R. Waser, "Electrical properties of the grain boundaries of oxygen ion conductors: Acceptor-doped zirconia and ceria," *Progress in Materials Science*, vol. 51, no. 2, pp. 151–210, 2006.
- [219]K.-W. Park, "Chemical characterization of dislocation in yttria-stabilized zirconia," arXiv, vol. 2, pp. 1–11, 2020.

- [220] P. Yan, T. Mori, A. Suzuki, Y. Wu, G. Auchterlonie, J. Zou, and J. Drennan, "Grain boundary's conductivity in heavily yttrium doped ceria," *Solid State Ionics*, vol. 222–223, pp. 31–37, 2012.
- [221] Mahmood Aliofkhazraei, Abdel Salam Hamdy Makhlouf (editors) "Handbook of Nanoelectrochemistry," Springer Cham, 2015. ISBN 978-3-319-15265-3.
- [222]E. Mills, M. Kleine-Boymann, J. Janek, H. Yang, N. Browning, Y. Takamura, and S. Kim "YSZ thin films with minimized grain boundary resistivity," *Physical Chemistry Chemical Physics*, vol. 18, no. 15, pp. 10486–10491, 2016.
- [223] I. Kosacki, C. M. Rouleau, P. F. Becher, J. Bentley, and D. H. Lowndes, "Nanoscale effects on the ionic conductivity in highly textured YSZ thin films," *Solid State Ionics*, vol. 176, pp. 1319–1326, 2005.
- [224]K. Rajeswari, M. B. Suresh, D. Chakravarty, D. Das, and R. Johnson, "Effect of nano-grain size on the ionic conductivity of spark plasma sintered 8YSZ electrolyte," *International Journal of Hydrogen Energy*, vol. 37, pp. 511–517, 2012.
- [225]B. Feng, R. Ishikawa, A. Kumamoto, N. Shibata, and Y. Ikuhara, "Atomic Scale Origin of Enhanced Ionic Conductivity at Crystal Defects," *Nano Letters*, vol. 19, no. 3, pp. 2162– 2168, 2019.
- [226] T. H. Yeh, R. De Lin, and J. S. Cherng, "Significantly enhanced ionic conductivity of yttria-stabilized zirconia polycrystalline nano-film by thermal annealing," *Thin Solid Films*, vol. 544, pp. 148–151, 2013.
- [227] J. Park, J. Ahn, K. Yoon, H. Kim, H. Ji, J. Lee, S. Han, and J. Son "Columnar Grain Size Effect on Cross-Plane Conductivity of Yttria-Stabilized Zirconia Thin Films," *Journal of The Electrochemical Society*, vol. 165, no. 9, pp. F671–F676, 2018.
- [228] W. Liu, G. Ou, L. Yao, H. Nishijima, and W. Pan, "Enhanced ionic conductivity in phase stabilized yttria-doped zirconia nanowires," *Solid State Ionics*, vol. 308, pp. 34–39, 2017.
- [229] M. M. Bućko, "Ionic conductivity of the yttria-stabilized-zirconia nanomaterials," 9th IEEE Conference on Nanotechnology, IEEE NANO 2009, vol. 8, pp. 543–546, 2009.

- [230] J. R. Gallagher *et al.*, "In situ diffraction of highly dispersed supported platinum nanoparticles," *Catalysis Science and Technology*, vol. 4, no. 9, pp. 3053–3063, 2014.
- [231]Y. Choi, S. Cha, H. Ha, S. Lee1, H. Seo, J. Lee, H. Kim, S. Kim, and W. Jung, "Unravelling inherent electrocatalysis of mixed-conducting oxide activated by metal nanoparticle for fuel cell electrodes," *Nature Nanotechnology*, vol. 14, no. 3, pp. 245–251, 2019.
- [232] M. Altomare, N. T. Nguyen, and P. Schmuki, "Templated dewetting: designing entirely self-organized platforms for photocatalysis," *Chemical Science*, vol. 7, no. 12, pp. 6865– 6886, 2016.
- [233]P. R. Gadkari, A. P. Warren, R. M. Todi, R. V. Petrova, and K. R. Coffey, "Comparison of the agglomeration behavior of thin metallic films on SiO2," *Journal of Vacuum Science* & *Technology A: Vacuum, Surfaces, and Films*, vol. 23, no. 4, pp. 1152–1161, 2005.
- [234] D. Schonvogel, J. H" ulstede, P. Wagner, I. Kruusenberg, K. Tammeveski, A. Dyck, C. Agert, and M. Warkb., "Stability of Pt Nanoparticles on Alternative Carbon Supports for Oxygen Reduction Reaction," *Journal of The Electrochemical Society*, vol. 164, no. 9, pp. F995–F1004, 2017.
- [235] J. Park, J. Mun, J. S. Shin, and S. W. Kang, "Highly sensitive two dimensional MoS2 gas sensor decorated with Pt nanoparticles," *Royal Society Open Science*, vol. 5, no. 12, pp. 1– 9, 2018.
- [236]Q. A. Drmosh and Z. H. Yamani, "Synthesis, characterization, and hydrogen gas sensing properties of AuNs-catalyzed ZnO sputtered thin films," *Applied Surface Science*, vol. 375, pp. 57–64, 2016.
- [237] Y. Pak, S. Kim, H. Jeong, C. Kang, J. Park, H. Song, R Lee, N Myoung, B. Lee, S. Seo, J. Kim, and G. Jung, "Palladium-decorated hydrogen-gas sensors using periodically aligned graphene nanoribbons," ACS Applied Materials and Interfaces, vol. 6, no. 15, pp. 13293–13298, 2014.
- [238]K. Hassan and G. S. Chung, "Catalytically activated quantum-size Pt/Pd bimetallic coreshell nanoparticles decorated on ZnO nanorod clusters for accelerated hydrogen gas detection," *Sensors and Actuators, B: Chemical*, vol. 239, pp. 824–833, 2017.
- [239] N. H. Ha, C. T. Long, N. H. Nam, N. T. Hue, N. H. Phuong, and H. S. Hong, "Characteristics of Hydrogen Sensor Based on Monolayer of Pt Nanoparticles Decorated

on Single-Layer Graphene," *Journal of Electronic Materials*, vol. 46, no. 6, pp. 3353–3358, 2017.

- [240]X. Jiao, C. Lin, N. P. Young, C. Batchelor-McAuley, and R. G. Compton, "Hydrogen Oxidation Reaction on Platinum Nanoparticles: Understanding the Kinetics of Electrocatalytic Reactions via 'nano-Impacts," *Journal of Physical Chemistry C*, vol. 120, no. 24, pp. 13148–13158, 2016.
- [241] M. Miu, I. Kleps, M. Danila, T. Ignat, M. Simion, A. Bragaru, and A. Dinescu "Electrocatalytic activity of platinum nanoparticles supported on nanosilicon," *Fuel Cells*, vol. 10, no. 2, pp. 259–269, 2010.
- [242] M. A. Raso, I. Carrillo, E. Mora, E. Navarro, M. A. Garcia, and T. J. Leo, "Electrochemical study of platinum deposited by electron beam evaporation for application as fuel cell electrodes," *International Journal of Hydrogen Energy*, vol. 39, no. 10, pp. 5301–5308, 2014.
- [243] A. Mosquera, D. Horwat, L. Vazquez, A. Gutiérrez, A. Erko, A. Anders, J. Andersson, and J. Endrino "Thermal decomposition and fractal properties of sputter-deposited platinum oxide thin films," *Journal of Materials Research*, vol. 27, no. 5, pp. 829–836, 2012.
- [244] N. T. Nguyen, J. E. Yoo, M. Altomare, and P. Schmuki, "Suspended' Pt nanoparticles over TiO2 nanotubes for enhanced photocatalytic H<sub>2</sub> evolution," *Chemical Communications*, vol. 50, no. 68, pp. 9653–9656, 2014.
- [245] R. Sandström, E. Gracia-Espino, G. Hu, A. Shchukarev, J. Ma, and T. Wågberg, "Yttria stabilized and surface activated platinum (PtxYOy) nanoparticles through rapid microwave assisted synthesis for oxygen reduction reaction," *Nano Energy*, vol. 46, no. January, pp. 141–149, 2018.
- [246] S. Ntais, R. J. Isaifan, and E. A. Baranova, "An X-ray photoelectron spectroscopy study of platinum nanoparticles on yttria-stabilized zirconia ionic support: Insight into metal support interaction," *Materials Chemistry and Physics*, vol. 148, no. 3, pp. 673–679, 2014.
- [247] Y. Sohn, D. Pradhan, A. Radi, and K. T. Leung, "Interfacial electronic structure of gold nanoparticles on Si(100): Alloying versus quantum size effects," *Langmuir*, vol. 25, no. 16, pp. 9557–9563, 2009.

- [248] A. Naitabdi, L. K. Ono, F. Behafarid, and B. R. Cuenya, "Thermal stability and segregation processes in self-assembled size-selected AuxFe1-x nanoparticles deposited on TiO<sub>2</sub> (110): composition effects," *Journal of Physical Chemistry C*, vol. 113, no. 4, pp. 1433–1446, 2009.
- [249]C. Riedl, A. Schmid, A. Nenning, H. Summerer, S. Smetaczek, S. Schwarz, J. Bernardi, A. Optiz, A. Limbeck, and J. Fleig, "Outstanding Oxygen Reduction Kinetics of La 0.6 Sr 0.4 FeO 3-δ Surfaces Decorated with Platinum Nanoparticles," *Journal of The Electrochemical Society*, vol. 167, no. 10, p. 104514, 2020.
- [250]Ulrich S. Schubert, Nicola Hüsing, "Synthesis of Inorganic Materials," 4<sup>th</sup> edition, Weinheim : Wiley-VCH, 2012. ISBN: 978-3-527-34457-4.
- [251]T. Ryll, H. Galinski, L. Schlagenhauf, P. Elser, J. Rupp, A. Bieberle-Hutter, and L. Gauckler, "Microscopic and nanoscopic three-phase-boundaries of platinum thin-film electrodes on YSZ electrolyte," *Advanced Functional Materials*, vol. 21, no. 3, pp. 565–572, 2011.
- [252]T. Ioannides and X. E. Verykios, "Charge transfer in metal catalysts supported on doped TiO2: A theoretical approach based on metal-semiconductor contact theory," *Journal of Catalysis*, vol. 161, no. 0218, pp. 560–569, 1996.
- [253]K. Umair, M. A. K. L. Dissanayake, and G. K. R. Senadeera, "Efficiency enhancement in SnO<sub>2</sub> based dye-sensitized solar cells by incorporating plasmonic gold nanoparticles," *Ceylon Journal of Science*, vol. 50, no. 5, pp. 341-347, 2021.
- [254] A. K. Mishra, C. Bansal, and H. Hahn, "Surface charge induced variation in the electrical conductivity of nanoporous gold," *Journal of Applied Physics*, vol. 103, no. 9, 2008.
- [255]S. Phanichphant, "Semiconductor Metal Oxides as Hydrogen Gas Sensors," *Procedia Engineering*, vol. 87, pp. 795–802, 2014.
- [256] V. Balasubramani, S. Chandraleka, T. S. Rao, R. Sasikumar, M. R. Kuppusamy, and T. M. Sridhar, "Review—Recent Advances in Electrochemical Impedance Spectroscopy Based Toxic Gas Sensors Using Semiconducting Metal Oxides," *Journal of The Electrochemical Society*, vol. 167, no. 3, p. 037572, 2020.

- [257]S. Sharma and M. Madou, "Review article: A new approach to gas sensing with nanotechnology," *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 370, no. 1967, pp. 2448–2473, 2012.
- [258]C. Sun, H. Li, and L. Chen, "Nanostructured ceria-based materials: Synthesis, properties, and applications," *Energy and Environmental Science*, vol. 5, no. 9, pp. 8475–8505, 2012.
- [259]K. Fujiwara, K. Okuyama, and S. E. Pratsinis, "Metal-support interactions in catalysts for environmental remediation," *Environmental Science: Nano*, vol. 4, no. 11, pp. 2076–2092, 2017.
- [260] M. Qadri, A. Diaz, M. Cittadini, A. Martucci, M. Cinta Pujol, J. Ferré-Borrull, E. Llobet, M. Aguiló and F. Díaz, "Effect of Pt nanoparticles on the optical gas sensing properties of WO3 thin films," *Sensors (Switzerland)*, vol. 14, no. 7, pp. 11427–11443, 2014.
- [261]B. Szafraniak, A. Kusior, M. Radecka, and K. Zakrzewska, "Impedance spectroscopy in h2 sensing with tio2/ sno2 nanomaterials," *Metrology and Measurement Systems*, vol. 27, no. 3, pp. 417–425, 2020.
- [262]S. Xue, S. Cao, Z. Huang, D. Yang, and G. Zhang, "Improving gas-sensing performance based on MOS nanomaterials: A review," *Materials*, vol. 14, no. 15, 2021.
- [263] A. Mirzaei, B. Hashemi, and K. Janghorban, "α-Fe<sub>2</sub>O<sub>3</sub> based nanomaterials as gas sensors," *Journal of Materials Science: Materials in Electronics*, vol. 27, no. 4, pp. 3109–3144, 2016.
- [264] V. B. Kamble and A. M. Umarji, "Achieving selectivity from the synergistic effect of Cr and Pt activated SnO2 thin film gas sensors," *Sensors and Actuators, B: Chemical*, vol. 236, pp. 208–217, 2016.
- [265] M. Kashif, M. E. Ali, S. M. U. Ali, U. Hashim, and S. B. Abd Hamid, "Impact of hydrogen concentrations on the impedance spectroscopic behavior of Pd-sensitized ZnO nanorods," *Nanoscale Research Letters*, vol. 8, no. 1, pp. 1–9, 2013.
- [266] S. Mourya, A. Kumar, J. Jaiswal, G. Malik, B. Kumar, and R. Chandra, "Development of Pd-Pt functionalized high performance H2 gas sensor based on silicon carbide coated porous silicon for extreme environment applications," *Sensors and Actuators, B: Chemical*, vol. 283, no. December 2018, pp. 373–383, 2019.

#### **BIOGRAPHY OF THE AUTHOR**

Firas Mahyob was born in Basrah, Iraq on September 14, 1979. He was raised in Karbala, Iraq. In 1991, he returned to Basrah where he graduated from Al-Markazia High school in 1997. He obtains his Bachelor's and Master's degrees in Physics from the University of Basrah in 2002 and 2007, respectively. After graduation, Firas was offered a job as Laboratory Supervisor in Basrah Oil Company (formerly South Oil Company). In Basrah Oil Company he worked with Eni/ ZFOD (Zubair Field Operating Division) in Al Zubair, Basrah, Iraq supervising staff shifts, reporting the routine laboratory analysis of crude oil, inspecting degassing station wells periodically, and organizing administrative tasks. In 2012, he awarded Higher Committee for Education Development in Iraq (HCEDIraq) Scholarship to pursue a PhD. HCEDIraq qualified by graduating with honors and ranking among STEM majors. In 2014, Firas moved to the United States to begin his PhD journey. He began his graduate studies at the University of Maine, Orono, Maine in the fall of 2015. Firas worked as both a teaching assistant for PHY 121 and PHY122 in the Department of Physics & Astronomy and a research assistant to Dr. Robert Lad in Frontier Institute for Research in Sensor Technologies (FIRST). His research interests include materials science, thin films fabrication and surface science technologies. During his time at the University of Maine, Firas received Graduate Trustee Tuition Scholarship (2019), Graduate Students Government (GSG) Travel Grant for APS March Meeting (2020) and Summer Dissertation Writing Fellowship (2020 and 2021). He is a member of the American Physical Society, The American Ceramic Society, and the Electrochemical Society. In 2022, Firas started his career in industry with Shimadzu Scientific Instruments as a Physical Measurements Technical Support Engineer. Firas is a candidate for the Doctor of Philosophy degree in Physics from the University of Maine in May 2023.