RUBY THIN FILM PRESSURE SENSORS

By

Eric M Straley

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Chemical Engineering–Master of Science

2018

ABSTRACT

RUBY THIN FILM PRESSURE SENSORS

By

Eric M Straley

As the population rises, it is important that society adopts a more environmentally friendly energy landscape. Currently, solid oxide fuel cells (SOFCs) are a promising technology due to high energy efficiency, power density, and fuel flexibility. However, SOFCs are held back by high costs which are due, in part, to high operating temperatures. It is the principle research goal in the SOFC community to decrease these operating temperatures and current research studies suggest that strain engineering SOFC materials can help. Current studies are hamstrung by the lack of ability to determine stress *in-situ* thus performance improvements due to strain cannot be isolated. A method to easily measure non-hydrostatic stress is needed to make strain engineered SOFCs a reality. Fluorescent stress sensors have been used to measure non-hydrostatic stress, but the accuracy of these measurements have never been evaluated. The work here uses ruby thin films as non-hydrostatic, fluorescent stress sensors and uses curvature-determined stress to evaluate the accuracy of these new sensors.

Highly oriented ruby thin films were deposited onto single crystal sapphire and yttria-stabilized zirconia (YSZ) substrates using pulsed-laser deposition. The resulting ruby/YSZ samples achieved a fluorescence determined stress of ~1.9 GPa while the ruby/sapphire samples achieved ~0.05 GPa. Stress determination from sample curvature measurements confirmed the results of the fluorescence stress measurements, indicating that the ruby piezospectroscopic tensor, which had previously been experimentally validated up to 0.9 GPa, is accurate up to nearly 2 GPa. This work concludes that ruby thin films are an effective sensor for measuring biaxial stress; thus, strain engineering a variety of thin film devices is now a possibility.

ACKNOWLEDGEMENTS

This work was financially supported by National Science Foundation (NSF) Award Number CBET-1254453

There are many people who I would like to thank for their help and support along the way. First, I'd like to thank my graduate committee members. To my advisor, Dr. Jason Nicholas, thank you for your guidance and support throughout my time at MSU, I truly appreciate the opportunity that you gave me. To Dr. Tim Hogan, thank you for your guidance and expertise in teaching me pulsed-laser deposition and thin-film growth. Dr. Susannah Dorfman, I am grateful for your expertise in all-things fluorescence spectroscopy related. Finally, thank you to Dr. Yue Qi for your support. I have also received help in my experiments from Karl Dersch and Dr. Per Askeland. Without them, none of this would have been possible.

I would like to thank my past and present research-group mates: Dr. Ted Burye, Yuxi Ma, Quan Zhou, Yubo Zhang, Brandon Bocklund, and Lindsay Fricano. I truly appreciate all the recommendations and friendly conversations along the way.

Finally, I would like to thank my friends and family. I am forever grateful to my parents and sister for their unwavering support in these last 4 years. To the wonderful friends that I've met at MSU: thank you for all the amazing memories and for keeping me sane during my time in East Lansing.

TABLE OF CONTENTS

| LIST OF TABLESv |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| LIST OF FIGURES |
| KEY TO ABBREVIATIONS |
| CHAPTER 1 – MOTIVATION AND OVERVIEW11.1 SOLID OXIDE FUEL CELLS11.2 STRAIN ENGINEERING21.3 STRESS MEASUREMENT31.4 HYPOTHESIS AND AIM OF THIS WORK4 |
| CHAPTER 2 – LITERATURE REVIEW |
| CHAPTER 3 – EXPERIMENTAL TECHNIQUES.133.1 SAMPLE PREPARATION AND CHARACTERIZATION.133.2 STRESS DETERMINATION FROM FLUORESCENCE163.3 STRESS DETERMINATION FROM CURVATURE.18 |
| CHAPTER 4- EVALUATION OF RUBY THIN FILM PRESSURE SENSORS |
| CHAPTER 5- CONCLUSIONS |
| APPENDIX |
| BIBLIOGRAPHY |

LIST OF TABLES

| Table 1: Summary table of pressure sensor metrics for materials considered for this work,adapted from Raju et al [38] |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Table 2: Piezospectroscopic coefficients of ruby fluorescence peaks [32] 11 |
| Table 3: Separate PLD conditions for the 5 ruby thin film samples [82] 21 |
| Table 4: Average and standard deviation of contour plots. Positive stress is compressive. Error bars are standard deviation of the stress contour plot or the manufacturer reported error the spectrometer used in this work, whichever number was greater |
| Table 5: Average curvature values for all samples. Error is standard deviation of the curvature measurements |
| Table 6: Curvature-determined stress values (MPa) for all samples. Error is from propagation of uncertainty in film thickness and curvature measurements |

LIST OF FIGURES

| Figure 1: Solid oxide fuel cell schematic |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Figure 2: Diagrams of the five d-electron orbitals [36] |
| Figure 3: Labeled image of PLD chamber14 |
| Figure 4: Labeled image of automated fluorescence test rig 16 |
| Figure 5: Schematic of multi-beam optical stress sensor. Adapted from [23] 19 |
| Figure 6: XRD data for ruby on a) sapphire substrate samples, and b) YSZ substrate samples. $A=\alpha$ -Al ₂ O ₃ . Y =YSZ peak. AS=Sillimanite (Al ₂ SiO ₅) Peaks indexed for α -Al ₂ O ₃ , YSZ, and Sillimanite using JCPDS card numbers 74-582, 70-4436, and 70-7052, respectively. Asterisks in 6a denote impurity phases present in the bare wafer [82] |
| Figure 7: Representative backscatter SEM image of ruby on YSZ [82] |
| Figure 8: Sample film thickness distributions, from SEM analysis [82] |
| Figure 9: SEM cross-sections of a) RY2 and b) RY3 film thickness abnormalities |
| Figure 10: ToF-SIMS depth profile of Cr through sample RS1 [82] 28 |
| Figure 11: R_1 Stress contour plots for a) RS1, b) RS2, c) RY1, d) RY2, and e) RY3. All stress values are in MPa. Compressive stress is positive |
| Figure 12: Representative profilometry of bare wafers and film/substrate samples for a) ruby/sapphire and b) ruby/YSZ samples |
| Figure 13: Comparison plot of a) R1 fluorescence-determined stress with MOSS-determined stress b) R1 fluorescence stress with profilometry determined stress c) R2 fluorescence-determined stress with MOSS stress and d) R2 fluorescence-determined stress with profilometry stress. The dashed 45-degree line is added to aid the eye [82] |

KEY TO ABBREVIATIONS

- CCD Charge-coupled device
- CTE Coefficient of thermal expansion
- DAC Diamond anvil cell
- MOSS Multi-beam optical stress sensor
- PLD Pulsed laser deposition
- RS Ruby on sapphire sample (usually followed by a number to identify the sample)
- RY Ruby on YSZ sample (usually followed by a number to identify the sample)
- SEM Scanning electron microscope
- SFP Stress free position, referring to ruby fluorescence peak position
- Sm:YAG Samarium doped yttria aluminum garnet
- SOFC(s) Solid oxide fuel cell(s)
- ToF-SIMS Time of flight secondary ion mass spectrometry
- XRD X-ray diffraction
- YSZ Yttria-stabilized zirconia

CHAPTER 1 – MOTIVATION AND OVERVIEW

1.1 SOLID OXIDE FUEL CELLS

As the world's population continues to rise, reducing dependence on fossil fuels is critical to preventing further environmental damage. Solid oxide fuel cells (SOFCs) are an enticing technology as they can achieve efficiencies in excess of 85% in combined heat and power applications[1]. SOFCs also offer the highest volumetric power density and the second highest gravimetric power density, second only to large scale gas turbines, of any energy generation technology[2]. As such, SOFCs are a good technology to help improve efficiency of processes that consume fossil-fuels. SOFCs running on a variety of fuels have also been demonstrated[3] which suggests that SOFCs could remain an import energy generation technology in the future as natural gas and biofuels become more prevalent.

A solid oxide fuel cell is composed of three components: a cathode, an electrolyte, and an anode. A schematic of an SOFC can be seen in Figure 1, below.



Figure 1: Solid oxide fuel cell schematic

Hydrocarbon fuel is continuously fed to the anode side of the cell where the fuel is oxidized, pulling oxygen from the lattice of the anode. This reaction forms an oxygen vacancy, V_0^{**} , water, and electrons which flow through an external circuit. The oxygen vacancy migrates through the electrolyte into the cathode where it is consumed at the surface of the cathode and replaced by an oxygen ion. In Kroger-Vink notation these half-reactions look like:

Anode:

$$H_2 + O_0^X \to H_2 O + V_0^{**} + 2e'$$
 (1)

Cathode:

$$\frac{1}{2}O_{2(g)} + V_0^{**} + 2e' \to O_0^X \tag{2}$$

These surface reactions and the diffusion of charged species through a solid electrolyte require high temperatures to operate efficiently which contributes to industrial SOFCs having operating temperatures of 700-1000°C[1]. Such high operating temperatures necessitate the use of durable, expensive materials and reduce SOFC operating lifetimes. Therefore, the focus of much SOFC research is in reducing the operating temperatures in the hope of reducing cost and improving lifetime, thus gaining more industrial traction for SOFCs.

1.2 STRAIN ENGINEERING

Applying strain to functional materials has been shown to improve performance in catalysts[4-8] and semiconductors[9, 10]. Similar experiments have been performed on SOFC materials and suggest that applying strain can improve the speed of both oxygen transport through the electrolyte [11-15] and surface exchange at the cathode surface [16-21] resulting in 100°C operating temperature reductions. Such a decrease is a huge step in the right direction, but the method these studies use to apply strain renders the results inconclusive. These studies deposit thin films on different substrate materials to induce various levels of lattice-mismatch strains on the films. This technique has several drawbacks: 1) depositing on different substrates can affect the film stress and/or structure which can have an impact on performance[22], thus the reported performance improvements may not only be due to strain, 2) many of these studies perform no *in-situ* measurement of stress on performance so the reported strains due to lattice mismatch may not accurately depict the stress that the film experiences, and 3) all of these studies are done on epitaxial thin films while real world SOFCs use polycrystalline electrodes; thus the strain effects on real SOFC materials cannot be examined using this technique. For these reasons, a new method of measuring

stress *in-situ* is needed so that stress and performance of SOFC materials can be properly studied.

1.3 STRESS MEASUREMENT

Measuring the stress of a thin film can be easily accomplished by measuring sample curvature, a simple experiment that can be done *in-situ*[23-25], and using Stoney's Equation [26] to calculate film stress. However, determining stress in this fashion can only be done on circular samples with a thin film deposited on a thick substrate which drastically limits the applicability of such experiments in the real-world where films are not always thin and abnormal geometries are commonly observed.

Stress measurement using fluorescent stress-sensors is an alternative method to measuring stress that has been commonly employed in the mineral physics and geology communities since the first calibration of ruby fluorescence peak shift in 1978[27]. Since then, different materials like diamond[28], Samarium doped yttria-aluminum garnet (Sm:YAG)[29], and doped tetraborate [30, 31] have all been calibrated as fluorescent pressure sensors. Each of these materials uses the same fundamental principle to measure stress: As stress is applied, the fluorescence peak position(s) of the material changes in a reproducible way. Once the change in peak position with stress is calibrated, fluorescence spectroscopy can be used to measure the peak position, and therefore stress, during experiments.

These fluorescence sensors are typically utilized in diamond anvil cells (DACs) under hydrostatic stress. For nonhydrostatic stresses, the usual peak shift-stress calibrations are not valid and the piezospectroscopic tensor of the stress sensing material must be used. For ruby, the piezospectroscopic tensor has been evaluated up to 0.9 GPa[32] which allows stresses applied in non-hydrostatic environments to be determined from fluorescence peak shift. However, the accuracy of stress measurements from this piezospectroscopic tensor have not been evaluated so there remains a knowledge gap in measuring non-hydrostatic stress using fluorescent stress sensors.

1.4 HYPOTHESIS AND AIM OF THIS WORK

To improve SOFC performance through strain engineering, there is dire need for a way to measure non-hydrostatic film stress *in-situ* without relying on curvature measurements which are limited by the system geometry. Using ruby thin films as a fluorescent pressure sensor offers a promising option for measuring non-hydrostatic stress, but the accuracy of such measurements needs to be confirmed at stresses higher than 0.9 GPa in order to enable strain engineering experiments at higher stresses. The hypothesis of this work is: Depositing ruby thin films onto thick substrates will allow wafer curvature determined stress measurements to confirm biaxial fluorescence stress measurements; thus, validating the ruby piezospectroscopic tensor to higher stress and enabling ruby thin films to be used as a novel *in-situ* stress sensor.

Of the following chapters, Chapter 2 will outline the relevant literature of stress measurements from curvature and fluorescence, Chapter 3 will explain in detail the experimental techniques used in this work, Chapter 4 will use fluorescence and curvature measurements to study the stress of ruby thin films, and Chapter 5 will summarize the conclusions and future possibilities of this work.

CHAPTER 2 – LITERATURE REVIEW

2.1 FILM/SUBSTRATE STRESS FROM CURVATURE

2.1.1 Stoney's Equation

For a thin film deposited onto a thick circular substrate, the famous Stoney Equation can be used to determine the average film stress[26]. The equation is as follows:

$$\sigma_f = \frac{h_s^2 M_s \kappa}{6h_f} \tag{3}$$

 $\sigma_{\rm f}$ is the average film stress (GPa), h_s is the substrate thickness (m), M_s is the substrate biaxial modulus (GPa), κ is sample curvature (m⁻¹), and h_f is the film thickness (m). Stoney's equation assumes that both film and substrate exhibit linear-elastic deformation, stress in the sample plane is biaxial (i.e. stress in both x and y directions are equal) and the stress out-of-plane (denoted as z) is 0, and sample curvature is uniform. In circumstances where these assumptions are met, film stress can be easily calculated from film thickness, curvature, substrate thickness, and known substrate material properties. For discussions on film thickness and curvature measurements, see Chapters 3.1.2 and 3.2, respectively.

2.1.2 Single Crystal Material Properties

As noted above in equation 3, the substrate biaxial modulus must be known in order to determine film stress. In general, biaxial modulus is calculated as:

$$M = \frac{E}{1 - \nu} \tag{4}$$

E is the Young's Modulus (GPa) and v is the Poisson's ratio. For single crystals E and v, and therefore M, are dependent upon the direction which the stress is applied relative to the crystal orientation. This is shown in the generic form of Hooke's law:

$$\sigma_{ij} = C_{ik} \varepsilon_{ij} \tag{5}$$

 σ_{ij} is the stress acting in the j direction on the plane with normal direction i, ε_{ij} is the strain in the j direction acting on the plane with normal direction i, and C_{ik} is the elastic constant matrix. For a cubic material, like yttria-stabilized zirconia, the elastic constant matrix is:

$$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}$$

For a trigonal material, like Al_2O_3 , the matrix is:

| ΓC_{11} | C_{12} | C_{13} | C_{14} | 0 | 0 - |
|------------------------|------------------------|----------|-----------|----------|------------------|
| <i>C</i> ₁₂ | <i>C</i> ₁₁ | C_{13} | $-C_{14}$ | 0 | 0 |
| <i>C</i> ₁₃ | <i>C</i> ₁₃ | C_{33} | 0 | 0 | 0 |
| C_{14} | $-C_{14}$ | 0 | C_{44} | 0 | 0 |
| 0 | 0 | 0 | 0 | C_{44} | C_{14} |
| Lo | 0 | 0 | 0 | C_{14} | C ₆₆₋ |

In a cubic material, Young's modulus and Poisson's ratio can be determined as a function of direction using the following equations [33]:

$$\frac{1}{E_{hkl}} = S_{11} + 2(S_{11} - S_{12} - 0.5 * S_{44})(\alpha^2 \beta^2 + \alpha^2 \gamma^2 + \beta^2 \gamma^2)$$
(6)

$$\nu = \frac{2 C_{12} (h^4 + k^4 + l^4) + (C_{11} + C_{12} - 2*C_{44}) (h^2 k^2 + h^2 l^2 + k^2 l^2)}{C_{11} (h^4 + k^4 + l^4) + 2(C_{12} + 2C_{44}) (h^2 k^2 + h^2 l^2 + k^2 l^2)}$$
(7)

 S_{ij} is a compliance value (the compliance matrix is calculated as the inverse of the elastic constant matrix: $[S_{ij}]=[C_{ij}^{-1}]$), E_{hkl} is the Young's modulus in the hkl direction (indicated by the plane of the single-crystal substrate), and α , β , and γ are angles between the direction of the stress and the principle directions, x, y, and z.

For a trigonal material, calculating Young's modulus and Poisson's ratio is slightly more complicated [33, 34]. The quantities are calculated as:

$$E = \frac{1}{S'_{11}}$$
 (8)

$$\nu = -\frac{S_{12}'}{S_{11}'} \tag{9}$$

In this case, S'_{11} and S'_{12} are calculated as:

$$\begin{split} S_{11}' &= a_{11}^4 S_{11} + A_{11}^2 a_{12}^2 (2S_{12} + S_{66}) + a_{13}^4 S_{33} + a_{13}^2 (1 - a_{13}^2) (2S_{13} + S_{44}) + 2a_{12} a_{13} (3a_{11}^2 - a_{12}^2) S_{14} \end{split} \tag{10}$$

$$S_{12}' &= (a_{11}^2 a_{21}^2 + a_{12}^2 a_{22}^2) S_{11} + (a_{21}^2 a_{12}^2 + a_{11}^2 a_{22}^2) S_{12} + [a_{23}^2 (a_{11}^2 + a_{12}^2) + a_{13}^2 (a_{21}^2 + a_{22}^2)] S_{13} + [2a_{21}a_{11}(a_{23}a_{12} + a_{13}a_{22}) + a_{22}a_{23}(a_{11}^2 - a_{12}^2) + a_{12}a_{13}(a_{21}^2 - a_{22}^2)] S_{14} + a_{23}^2 a_{13}^2 S_{33} + [a_{13}a_{22}(a_{12}a_{22} + a_{11}a_{21})] S_{44} + a_{21}a_{22}a_{11}a_{12}S_{66} \tag{11}$$

The values of S are again compliances and a_{ij} is a directional cosine, calculated as:

 $\begin{bmatrix} \cos(\alpha)\cos(\beta) & \sin(\alpha)\sin(\beta) & \sin(\beta) \\ -\cos(\alpha)\sin(\beta)\cos(\gamma) + \sin(\alpha)\sin(\gamma) & -\sin(\alpha)\sin(\beta)\cos(\gamma) - \cos(\alpha)\sin(\gamma) & \sin(\beta)\cos(\gamma) \\ -\cos(\alpha)\sin(\beta)\sin(\gamma) + \sin(\alpha)\cos(\gamma) & -\sin(\alpha)\sin(\beta)\sin(\gamma) + \cos(\alpha)\cos(\gamma) & \sin(\beta)\sin(\gamma) \end{bmatrix}$

 α , β , and γ have their previously defined meanings. Combining the definition of the directional cosine above with equations 10 and 11, then plugging into equations 8 and 9 will give the biaxial modulus of a trigonal crystal.

2.2 FLUORESCENT PRESSURE SENSORS

As the name implies, the operating principle of fluorescent pressure sensors relies upon the phenomenon of fluorescence. Excitation, in this case caused by an incoming laser pulse, promotes electrons into higher energy shells. When the laser is turned off, the electrons collapse back into lower energy shells which causes the emission of a photon. Different materials have different characteristic wavelengths at which the fluorescent light is emitted, which is caused by crystal field splitting of d or f electron orbitals. For d electrons there are 5 possible electron orbitals, as shown in Figure 2 [35]. When a dopant atom exists on an atomic site, like Cr on an Al site in the Al₂O₃ lattice or Sm on the Y site of YAG, the bond lengths between the central metal atom and surrounding oxygen atoms is distorted. This distortion creates some higher energy d orbitals (those that have become closer to an O atom due to distortion, and thus have higher electron-electron repulsions) and some with lower energy d orbitals (those that have become further from the neighboring O atom).



Figure 2: Diagrams of the five d-electron orbitals [36]

As stress is applied bond distances within the material change which results in a change of the energy levels of the electron shells. Thus, as stress is applied the characteristic wavelengths changes. Calibrating the change in wavelength with stress is typically done using a diamond anvil cell (DAC). Fluorescence spectra are collected as hydrostatic pressure is applied to the stress sensing material, so the change in characteristic wavelength can be observed. Within the DAC is a standard, typically a simple metal. The specific volume of the standard is measured using X-ray diffraction (XRD) and equations of state are used to determine the pressure from the specific volume. Therefore, the change in characteristic wavelength of the fluorescent sensor is measured at the same time as the stress is determined from the standard, effectively calibrating the change in wavelength with stress in the fluorescent sensor to be placed in the DAC and the stress can then be determined from the characteristic wavelength measured via fluorescence spectroscopy.

As alluded to in section 1.3, there are several different fluorescent pressure sensors that have been considered over the years. Ruby was the first fluorescent pressure sensor to be calibrated [27], followed by Sm:YAG [29], Sm doped strontium tetraborate [31, 36], Alexandrite [37] and diamond [28]. The ideal fluorescence sensor for this work must possess several desired characteristics: 1) high sensitivity of the characteristic wavelength to pressure changes, so that stresses down to 10 or 100 MPa can be resolved, 2) distinctive fluorescence peaks with high intensity so that peak fits give accurate positions, 3) the fluorescence sensor must be able to be deposited as a thin film, and 4) the sensor must have a known piezospectroscopic tensor in order to measure non-hydrostatic stresses (since a thin film sensor on a substrate will be subject to biaxial stress). A final criterion to be considered, especially for future work, is that the pressure sensor should be able to accurately measure pressure at high temperatures since future strain engineering experiments will need to be conducted at SOFC operating temperatures which can exceed 700°C.

Table 1: Summary table of pressure sensor metrics for materials considered for this work, adapted from Raju et al [38]

| Sample | λ_0 (nm) | $\mathrm{d}\lambda/\mathrm{dP}\ (\mathrm{nm/GPa})$ | ${ m d}\lambda/{ m d}T^*10^{-3}$ (nm/K) | T-Range: Room T to | Reference |
|-----------------------|------------------|----------------------------------------------------|-----------------------------------------|-----------------------|------------|
| Ruby | | | | | |
| R_1 | 694.25 | 0.348 | 7.7 | | [38] |
| R_1 | 694.28 | 0.365 | 7.3 | | [27], [39] |
| R_1 | 694.05 | | 7.0 | 600 K | [37] |
| R_2 | 694.7 | | 7.8 | 600 K | 38 |
| R_2 | 692.52 | | 7.3 | | [37] |
| $Sm^{2+}:SrB_4O_7$ | | | | | |
| S_1 | 685.38 | 0.281 | ~0 | 823 K | [38] |
| S_1 | 685.4 | 0.255 | ~0 | | 39 |
| Alexandrite | | | | | |
| A_1 | 680.47 | 0.321 | 8.9 | 823 K | [38] |
| A_1 | 680.2 | | 8.7 | 500 K | 37 |
| A_2 | 678.55 | 0.519 | 8.1 | 823 K | [38] |
| A_2 | 678.6 | | 7.8 | 500 K | 37 |
| Sm ³⁺ :YAG | | | | | |
| Y ₁ | 617.9 | 0.292 | 0.55 | 823 K | [38] |
| Y ₁ | 617.75 | | 0.17 | 823 K | 40 |
| Y_2 | 616.47 | 0.249 | -0.05 | 823 K | 38 |
| Y_2 | 616.11 | | -0.06 | 823K | [40] |

As seen in Table 1, above, doped tetraborate and Sm:YAG show low sensitivity of the characteristic wavelength to pressure, making them unideal for this work since the resolution of these sensors is not good enough to accurately measure stress in the MPa range. However, both materials show little or no change in peak position with temperature, making them possibilities for strain engineering experiments at SOFC operating temperatures. Ruby exhibits good sensitivity and Alexandrite exhibits excellent sensitivity, especially for the A_2 peak. However, taking a deeper look at the Alexandrite peaks shows that the peaks are not well resolved, even at room temperature, which indicates that Alexandrite cannot be considered as a thin-film fluorescent stress sensor. This leaves ruby as the optimal stress sensor for the work presented here.

2.2.1 Ruby Pressure Sensors

The addition of Cr on an octahedrally-coordinated Al site in an Al₂O₃ lattice structure causes the 5 *d* orbitals to split into 2 with higher energy $(d_{x^2-y^2}$ and d_{z^2} orbitals) and 3 with lower energy states $(d_{xy}, d_{xz}, and d_{yz}, for images of these orbitals see Figure 2)$ [41]. This results in two distinct fluorescence peaks: the R₁ peak located at 694.2 nm resulting from an electron relaxing from the \bar{E} shell to the ground state, ⁴A₂, and the R₂ peak located at 693.0 nm resulting from an electron relaxing from the 2Å state to the ground state [42, 43]. Pressure calibration of the R₁ and R₂ peaks under hydrostatic stress has been conducted from 0-1 GPa [44] up to 150 GPa [45]. There have also been studies of ruby under non-hydrostatic [46] or quasi-hydrostatic conditions [47] where the pressures within the DAC are so high that the conducting medium cannot support hydrostatic stresses.

While ruby remains the gold-standard fluorescent stress sensor, there are some drawbacks. At temperatures above 550K, the R_1 and R_2 peaks have merged so significantly that stress measurements are inaccurate [48]. The work of Ragan et al reports significant error in pressure measurements above 400K [49] which suggests that ruby may not be an ideal stress sensor under SOFC operating temperatures. However, for the work here that is investigating thin film stress sensors, ruby offers advantages over the other stress sensing materials, like Sm:YAG, that perform better at high temperatures. These advantages are: 1) studies have shown that the R_2 peak position doesn't change with non-hydrostatic stresses

[46], 2) under stresses normal to the c-axis, the change in R_1 and R_2 peak split is minimal which suggests that the peaks will not merge under non-hydrostatic stress [46], 3) high quality fluorescent ruby thin films have already been deposited on sapphire via PLD [50, 51], and 4) the piezospectroscopic tensor of ruby [32] has been calibrated, so non-hydrostatic stresses, like the biaxial stresses thin films on substrates are subjected to, can be correlated to changes in fluorescent peak positions, something that cannot be said for any other fluorescent stress sensing material. Therefore, while ruby does have stress-sensing limitations at high temperatures it is the optimal stress sensor to measure biaxial stresses in thin films.

2.2.2 Piezospectroscopic Stress Sensors

In general, the change in fluorescence peak frequency (the inverse of wavelength) is related to the change in stress by the following expression:

$$\Delta \nu = \Pi_{ii} \sigma_{ii} \tag{12}$$

 σ_{ij} has the same definition as in equation 5, Δv is the change in fluorescence peak frequency (cm⁻¹), and Π_{ij} is the piezospectroscopic tensor:

$$\Pi_{ij} = \begin{bmatrix} \Pi_{11} & 0 & 0 \\ 0 & \Pi_{22} & 0 \\ 0 & 0 & \Pi_{33} \end{bmatrix}$$

Here, the '11' direction is parallel to the a-axis of the Al₂O₃ lattice, the '22' direction is parallel to the m-axis, and the '33' direction is parallel to the c-axis. The values for the piezospectroscopic coefficients (Π_{11} , Π_{22} , and Π_{33}) have been calibrated at room temperature from 0-0.9 GPa [32]. The values are shown in Table 2, below.

Table 2: Piezospectroscopic coefficients of ruby fluorescence peaks [32]

| Peak | Π ₁₁ | Π ₂₂ | П ₃₃ |
|----------------|-----------------|-----------------|-----------------|
| R ₁ | 2.56 | 3.50 | 1.53 |
| R_2 | 2.65 | 2.80 | 2.16 |

Equation 12 can be simplified by expanding the right-hand side:

$$\Delta \nu = \Pi_{11} \sigma_{11} + \Pi_{22} \sigma_{22} + \Pi_{33} \sigma_{33} \tag{13}$$

The change in frequency is simply the measured frequency of a sample, ν_{sample} (cm⁻¹), minus the frequency at some stress-free position (SFP), ν_{SFP} (cm⁻¹):

$$\nu_{\text{sample}} - \nu_{SFP} = \Pi_{11}\sigma_{11} + \Pi_{22}\sigma_{22} + \Pi_{33}\sigma_{33} \tag{14}$$

Applying the fact that frequency is the inverse of wavelength and converting from cm to nm, we can simplify this equation further:

$$\frac{1E7}{\lambda_{\text{sample}}} - \frac{1E7}{\lambda_{SFP}} = \Pi_{11}\sigma_{11} + \Pi_{22}\sigma_{22} + \Pi_{33}\sigma_{33}$$
(15)

 λ indicates the peak wavelength (nm) and all other variables have their previous definitions. Combining Equation 15 with the piezospectroscopic coefficients in Table 2 gives separate equations that relate the peak positions of the R₁ and R₂ peaks with the stress applied in any direction relative to the Al₂O₃ lattice:

$$\frac{1E7}{\lambda_{R1,sample}} - \frac{1E7}{\lambda_{R1,SFP}} = 2.56\sigma_{11} + 3.50\sigma_{22} + 1.53\sigma_{33}$$
(16)

$$\frac{1E7}{\lambda_{R2,sample}} - \frac{1E7}{\lambda_{R2,SFP}} = 2.65\sigma_{11} + 2.80\sigma_{22} + 2.16\sigma_{33}$$
(17)

Here, a subscript R_1 indicates the variable applies to the R_1 peak, a subscript R_2 indicates the variable applies to the R_2 peak, and all other variables have their previous definitions. Equations 16 and 17 now give R_1 and R_2 positions for stress in any direction. The effectiveness of using these piezospectroscopic stress tensor relationships has been demonstrated in literature in studies of fluorescent alumina-containing ceramic materials [52-63] and thermal barrier coatings [63-73].

CHAPTER 3 – EXPERIMENTAL TECHNIQUES

3.1 SAMPLE PREPARATION AND CHARACTERIZATION

3.1.1 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a physical vapor deposition technique used to deposit thin-films. Short pulses from a high-powered laser are focused onto a rotating polycrystalline target held in a vacuum environment. The focused laser pulses impact the target material, vaporizing it and creating a plume of particles. A substrate is suspended upside down within the plume several centimeters from the target, and particles from the plume are subsequently deposited onto the substrate[74, 75].

Two separate PLD targets were created from ruby powder with 0.05% Cr. The powder was synthesized by mixing high purity Al₂O₃ powder (Sumitomo Chemical, Tokyo, Japan) with 99.99% Chromium Nitrate (Alfa Aesar, Haverhill, MD, USA) and water. This mixture was dried while stirring in a polyethylene beaker. After the powder dried, half the powder was calcined at 1000°C for 6 hours to calcine it. Both calcined and uncalcined powders were separately ground in a high purity alumina mortar and pestle, filtered through a 45-micron stainless steel mesh (to homogenize particle size), and pressed into a target using a uniaxial press. One PLD target was created from the calcined powder and another was created from the uncalcined powder. After pressing, both targets were fired at 1400°C for 24 hours and then 1700°C for 2 hours[50]. The density of the calcined target was 72.8% while the uncalcined target was 93.1% dense, both numbers were determined geometrically.

To produce ruby films under different stress states two substrate materials were chosen. One substrate material is α -Al₂O₃, hitherto referred to as sapphire, and the other is yttria stabilized zirconia (YSZ). Depositing ruby on sapphire will produce thin films with low stress since ruby and sapphire are so chemically similar (the only difference being the nominal 0.05% Cr present in the ruby) that stresses generated from mismatch in lattice parameter and coefficient of thermal expansion (CTE) will be minimal. YSZ and ruby have a larger mismatch in lattice parameter and CTE, therefore depositing ruby on YSZ will generate films under higher stresses. One-inch diameter single crystal (0001) Al₂O₃, (MTI Corporation, Richmond, CA, USA) and single crystal (100) 9.5% YSZ (Crystec, Berlin, Germany) substrates were used in this work. The YSZ substrates were annealed at 1450°C for 20 hours while the sapphire substrates were annealed at 1400°C for 20 hours since sapphire has a slightly lower melting point than YSZ. Annealed wafers were then placed in the PLD vacuum chamber. During the thin film deposition, the vacuum chamber was injected with high purity oxygen to achieve an oxygen partial pressure, P_{02} , of 1.5-1.6*10⁻⁵ bar. A 248nm excimer laser with a rep rate of 10 Hz and laser fluence of 12-17 J/cm² was used to deposit the films. The target-substrate distance was 2.12 inches and the substrate temperature was approximately 650°C. The as-deposited films were amorphous, so after deposition the samples were crystallized in air at 1400°C for 2 hours. A picture of the PLD setup is seen in Figure 3, below.



Figure 3: Labeled image of PLD chamber

3.1.2 Scanning Electron Microscopy (SEM)

In SEM, high energy electrons are focused onto a sample causing secondary electrons and backscattered electrons to be emitted. These emitted electrons are collected by various detectors and used to image the sample. In this work, a Mira3 SEM (Tescan, Brno, Czech Republic) with back-scatter and secondary electron detectors was used on cross-sections of thin film/substrate samples to determine the thickness of the thin films in the ruby on YSZ samples. Secondary electron imaging was used to investigate topographical features of the cross-sections while backscattered imaging was used to emphasize the contrast between film and substrate, enabling film thickness determination. For the ruby on sapphire samples, there is little contrast difference between the materials since they are so chemically similar, so SEM cannot be used to determine the thickness of these samples.

3.1.3 Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

ToF-SIMS is a technique where an ion beam is focused on the sample surface causing ions to be emitted. The ions pass through a detector where the chemical identity is determined from the mass of the ions. By using ToF-SIMS while slowly milling through a surface a depth profile can be determined which shows the concentration of an ion as a function of depth through the sample.

In this work, ToF-SIMS was used to obtain the depth profile of Cr^+ ions in the RS samples in order to determine the thickness of the ruby films deposited on the two sapphire substrates. The film thickness was determined from the depth profile by measuring the depth at which the concentration of Cr^+ ions started to decrease significantly as this drop in concentration would be located at the interface between the ruby film, which nominally has 0.05 weight % of Cr, and the sapphire substrate, which is Cr free.

3.1.4 X-Ray Diffraction (XRD)

XRD was used to analyze the crystal structure of film/substrate bilayer samples; a necessary analysis step since the film orientation must be known to use the piezospectroscopic tensor equations (Equations 16 and 17) to obtain film stress. In XRD, electrons emitted from a tungsten filament hit a metal target (typically Copper) which causes electrons in the target to excite. As the electrons relax back into their ground state, an X-ray is emitted. The X-rays from the target are directed onto the sample. As the X- rays reflect off planes of atoms in the sample, the reflected waves constructively and destructively interfere. This brings about the relationship known as Bragg's Law:

$$n\lambda = 2d\sin(\theta) \tag{18}$$

Bragg's Law relates the X-ray wavelength, λ (nm), to the spacing between planes of atoms, d (nm), and the angle between the incident X-ray and the X-rays reflected off the sample, θ (degrees), [76]. In the work presented, a D2 Phaser (Bruker, Billerica, MA, USA) was used to investigate film orientation by scanning from 20-80° 2 θ at 0.02° intervals.

3.2 STRESS DETERMINATION FROM FLUORESCENCE

An Optiprexx PLS (Almax easyLab Inc, Cambridge, MA, USA) table-top spectrometer was used to collect fluorescence spectra across the surface of the film/substrate



Figure 4: Labeled image of automated fluorescence test rig

samples. A custom test rig, seen in Figure 4, was designed and built so that the sample was automatically moved to specified positions and the spectrometer was triggered to collect a spectrum at each position. This test rig was composed of two motorized 2-inch linear translation stages (Thorlabs, Newton, NJ, USA) to automatically adjust where the fluorescence laser hit the sample, a single 1/2-inch manual translation stage (Thorlabs, Newton, NJ, USA) to make sure the laser was focused on the sample, custom spacers to ensure the sample was at the proper height and that the whole rig was screwed into the spectrometer baseplate, a rotation stage (not shown in Figure 4) to keep the entire sample perpendicular to the laser, and a right-angle piece to hold one automated stage at 90° so the sample was held perpendicular to the laser. A custom-made LabView program was used to control the sample movement and fluorescence spectra collection parameters and to record the coordinates where each spectrum was collected.

Fluorescence spectra peak positions for R_1 and R_2 were determined using Origin Pro 8.1 (OriginLab Corporation, Northampton, MA, USA). A batch processing template was created in Origin Pro that was used to analyze many spectra at once. The template utilized the following steps:

- Spectral data in a single spectrum from 690-700 nm (an appropriate range to include both R₁ and R₂ peaks without including the excess noise present from 680-690nm and 700-775nm) were imported.
- 2. Each spectrum was fit to a Voigt peak shape (a combination of Gaussian and Lorentzian peaks) using no baseline treatment, identifying two peaks by analyzing 5 local points, 500 max iterations, and a tolerance of 1E-15.
- 3. A summary of key statistics for each spectrum was output to a spreadsheet. The statistics were the R₁ and R₂ peak positions (nm), error on the peak positions (nm), peak heights (counts), and R² value of the peak fit.

Once all the spectra for a sample were analyzed in Origin, crystallographic data from XRD was used with the piezospectroscopic tensor (see Equations 16 and 17, for full details see Chapter 4.2.3) to determine the film stress at each position across the sample surface. Finally, MATLAB was used to plot contour plots of stress vs. horizontal and vertical position for all points with a peak fit R^2 of 0.85 or greater. This cutoff R^2 was chosen to maximize the number of data points across the sample surface while removing points with lower R^2 values, which indicate poor fits and would result in anomalous stress values.

3.3 STRESS DETERMINATION FROM CURVATURE

One of the primary aims of this work is to calibrate the piezospectroscopic coefficients of ruby to pressures higher than 0.9 GPa, so a second method for measuring stress is needed to confirm the fluorescence-determined stress values and thus the piezospectroscopic coefficients. Curvature-determined stress is the second method which will be used validate the accuracy of ruby thin-film stress measurements. As indicated in section 2.1.1 and 2.1.2, curvature and biaxial modulus must be known in order to determine stress using Stoney's equation. To determine biaxial modulus of YSZ, literature values for the elastic constants as a function of temperature of YSZ [77] were converted to compliances and plugged into equations 6 and 7 before calculating biaxial modulus from equation 4. The result was an equation for single crystal biaxial modulus, in GPa, for (100) YSZ:

$$M_{YSZ} = -0.0591 * T + 442.32 \tag{19}$$

T is the temperature (°C). Similarly, the compliances for Al_2O_3 [78] were plugged into Equations 10 and 11, then 8 and 9 before calculating the biaxial modulus:

$$M_{Al_2O_3} = -0.0518 * T + 561.16 \tag{20}$$

The following subsections outline two separate experimental techniques that were used to measure sample curvature.

3.3.1 Multi-beam Optical Stress Sensor

One way to measure sample curvature is by using a multi-beam optical stress sensor (MOSS). MOSS has been used in literature many times to determine film stress of a thin film on a thick circular substrate [23-25, 79-81]. In this technique, a 3x3 grid of laser dots is deflected off the sample and back into a CCD camera where the spacing between dots in the laser array is measured. A simple geometric relationship between the angle of reflection, θ , the sample-detector distance, L (m), the original inter-dot spacing, d_0 , and the inter-dot spacing after the grid reflects off the sample, d, gives the curvature, $\kappa(m)$:

$$\kappa = \left(\frac{\cos(\theta)}{2L}\right) \left(1 - \frac{d}{d_0}\right) \tag{21}$$

. A schematic of the MOSS setup can be seen in Figure 5.



Figure 5: Schematic of multi-beam optical stress sensor. Adapted from [23].

3.3.2 Profilometry

Along with MOSS measurements, profilometry was used to measure curvature. Profilometry is a technique where the displacement (aka height) of a sample is measured across the sample surface. In this work, a NanoMap-500LS stylus contact surface profilometer (AEP Technology, Santa Clara, CA, USA) was used. In stylus profilometers, a needle, known as a stylus, is dragged across the sample surface while a constant force is applied. As the sample height changes due to the displacement of the sample, the profilometer determines the height from Hooke's Law.

Displacement profiles across the sample surface were taken in two perpendicular directions. Each profile was fit with a second order polynomial using least-squares regression, and curvature was determined by taking the second derivative of displacement.

CHAPTER 4- EVALUATION OF RUBY THIN FILM PRESSURE SENSORS 4.1 INTRODUCTION

As outlined in Chapter 1, there is a need for a non-hydrostatic fluorescence stress sensor in order to use strain engineering to improve SOFC performance. In this chapter, ruby thin films will be investigated to fill that need. Thin film data of ruby deposited on sapphire and YSZ substrates is presented. Fluorescence-determined stress will be compared to curvature-determined stress values to see how accurately ruby thin films can measure stress at two different stress states (a lower stress state with the ruby/sapphire samples and a higher stress state with ruby/YSZ samples). Sample manufacturing, characterization, and stress analysis are discussed in detail.

The piezospectroscopic stress sensor of ruby has been evaluated from 0-0.9 GPa which has enabled non-hydrostatic stress measurement using the fluorescence techniques that have long been used in geology and mineral physics [32]. This has allowed non-hydrostatic stress to be determined in ceramic materials as explained in section 2.2.2. However, all these studies investigate stress in ceramic materials which are fluorescent, and none of the studies confirm the accuracy of determining non-hydrostatic stress using the piezospectroscopic tensor relationship. By comparing the fluorescence-determined stress of ruby thin films to the curvature-determined stress from Stoney's equation, the accuracy of determining stress from the piezospectroscopic tensor will be evaluated for the first time and the piezospectroscopic coefficients will be calibrated beyond 0.9 GPa.

4.2 EXPERIMENTAL METHODS

4.2.1 Ruby thin film sample preparation

Ruby thin films were produced using PLD using the procedure in Chapter 3.1.1. Two samples, denoted RS1 and RS2, were deposited onto sapphire while three samples, denoted RY1, RY2, and RY3, were deposited onto YSZ substrates. The PLD parameters that differed between samples are shown in Table 3 [82], below. All other parameters are listed in Chapter 3.1.1. After deposition the ruby films were heated to 1400°C for 2 hours to produce crystalline films.

| Sample | PLD Target | Laser Fluence (J/m^2) | PLD Duration (min) | P_{O2} (bar) |
|--------|------------|-------------------------|--------------------|----------------|
| RS1 | Calcined | 17.0 | 30 | 1.49 *10-5 |
| RS2 | Uncalcined | 12.2 | 45 | 1.59 *10-5 |
| RY1 | Calcined | 17.4 | 30 | 1.54 *10-5 |
| RY2 | Calcined | 17.0 | 30 | 1.55 *10-5 |
| RY3 | Uncalcined | 12.2 | 45 | 1.55 *10-5 |

Table 3: Separate PLD conditions for the 5 ruby thin film samples [82]

4.2.3 Stress measurements from fluorescence

Equations 16 and 17 show the relationship between stress and R_1 and R_2 peak position. These equations are dependent upon the direction, relative to the crystal structure, that the stress is applied. From the XRD results shown in Chapter 4.3.1, the ruby films in each of the 5 samples were preferentially oriented in the (001) plane. This plane is parallel to the c-axis in ruby. Since the film is oriented parallel to the c-axis and we have a circular sample, the film is under a biaxial stress. Biaxial stress signifies that the stress in x and y directions, which are in the plane of the sample, are equal in magnitude while the stress in the z-direction, which is out of the plane of the sample, is 0:

$$\sigma_x = \sigma_y \tag{22}$$

$$\sigma_z = 0 \tag{23}$$

Since we have (001) oriented films this means that the out-of-plane direction (the zdirection) is the (001) direction. This is the same direction as the '33' direction denoted in the piezospectroscopic tensor while the '11' and '22' directions are the two perpendicular inplane directions. Applying this fact to equations 22 and 23 gives:

$$\sigma_{11} = \sigma_{22} = \sigma \tag{24}$$

$$\sigma_{33} = 0 \tag{25}$$

We can plug equations 24 and 25 into equations 16 and 17, with some algebraic manipulation, to obtain:

$$\frac{1E7}{\lambda_{R1,sample}} - \frac{1E7}{\lambda_{R1,SFP}} = (2.56 + 3.50)\sigma$$
(26)

$$\frac{1E7}{\lambda_{R2,sample}} - \frac{1E7}{\lambda_{R2,SFP}} = (2.65 + 2.80)\sigma$$
(27)

Rearranging, we can solve for the biaxial stress, σ , in terms of the peak wavelengths:

$$\sigma_{R1} = \frac{\left(\frac{1E7}{\lambda_{R1,sample}} - \frac{1E7}{\lambda_{R1,SFP}}\right)}{2.56 + 3.5}$$
(28)

$$\sigma_{R2} = \frac{\left(\frac{1E7}{\lambda_{R2,sample}} - \frac{1E7}{\lambda_{R2,SFP}}\right)}{(2.65 + 2.80)}$$
(29)

Here, σ_{R1} is the biaxial stress (GPa) determined from R_1 peak shift, σ_{R2} is the biaxial stress (GPa) determined from R_2 peak shift, and all other variables have their previous definitions. Measuring a stress-free ruby grain with a calibrated spectrometer gave the stress-free positions of 694.335 and 693.912nm which are nearly identical to literature room temperature SFPs [32, 64]. The fluorescence spectra collection and analysis procedure outlined in Chapter 3.2 was used along with Equations 28 and 29 to get the fluorescencedetermined stress of the ruby thin films. The error analysis procedure for propagating the uncertainty in peak positions through to the average stress values is outlined in the Appendix.

4.2.3 Stress measurements from curvature

Curvature values in two perpendicular directions across each sample were determined from both profilometry and MOSS. These curvature measurements were done on the bare, annealed wafers and then on the samples after crystallizing the ruby film. The difference in curvature between the film/substrate sample and bare wafer was then used in Stoney's Equation, Equation 3, to determine film stress. The error analysis procedure for propagating the uncertainty in curvature and film thickness through to the average film stress is outlined in the Appendix.

4.2.4 Microstructural characterization

XRD was used to determine orientation and phase-purity of ruby thin films and substrates, as outlined in Chapter 3.1.3. SEM was used to determine film thickness for the RY samples as outlined in Chapter 3.1.2. Images were taken at 5 different locations across the sample surface: at both edges, in the middle of the sample, and in between each edge and the middle. The ruler tool in Adobe Illustrator was used to measure the film thickness at 3 different locations in each image. ToF-SIMS performed by EAG Labs (East Windsor, NJ, USA) was used to determine the film thickness of the RS1 sample.

4.3 RESULTS AND DISCUSSION

4.3.1 Microstructural characterization

Figure 6 [82], below, shows the XRD for the five ruby thin film samples and representative scans of bare, annealed YSZ and sapphire wafers. In Figure 6a, the bare sapphire wafer has some impurities at approximately 20, 57, and 64° which also appear in the crystallized thin films, RS1 and RS2. This impurity is likely from the manufacturing process of the wafers and since it is present in the bare wafer it will likely have no impact on stress measurements. Sample RS1 shows some apparent silicon contamination as indicated by the sillimanite (Al_2SiO_5) phases shown in Figure 6a. This silicon contamination occurs during the deposition and could be from the chamber, or the calcined PLD target. The same sillimanite contamination is not seen in RS2, however, as that sample shows no other impurity peaks other than those present in the sapphire wafer. RS1 was deposited after RS2 so it's possible that silicon contamination within the chamber increased during the 4 months between these depositions, causing Si impurities to only be present in RS1. It's also possible that an impurity formed in the calcined powder during formation or use of the calcined target. The sillimanite phase shown in RY1 and RY2 (which were also deposited with the calcined target) in Figure 6b suggest this is a possibility, but the RY1 and RY2 were deposited shortly after RS1 which means that Si contamination in the chamber could also be the cause of these impurities. The impact of these impurities on fluorescence results will be discussed in Chapter 4.3.2.



Figure 6: XRD data for ruby on a) sapphire substrate samples, and b) YSZ substrate samples $A=\alpha-Al_2O_3$. Y=YSZ peak. AS=Sillimanite (Al_2SiO_5) Peaks indexed for $\alpha-Al_2O_3$, YSZ, and Sillimanite using JCPDS card numbers 74-582, 70-4436, and 70-7052, respectively. Asterisks in 6a denote impurity phases present in the bare wafer [82]

Figure 6b shows that the bare YSZ wafer has only the (100) family of YSZ peaks indicating a phase-pure, single crystal wafer. As mentioned above, both RY1 and RY2 show

a small sillimanite peak at ~26°, but they also show the α -Al₂O₃ (006) peak indicating that there is a crystalline ruby film present. The RY2 sample also shows a very small (116) alumina peak at ~54°, which is also visible in RY1. From the ratio of peak heights in the JCPDS reference, it was calculated that the (006) ruby phase makes up more than 95% of the ruby film, by volume. This means that while there is a small amount of a second ruby phase, it is unlikely to significantly affect the stress calculated from Equations 28 and 29



Figure 7: Representative backscatter SEM image of ruby on YSZ [82]

which assume the film is (001) oriented.

Figure 7 shows a representative SEM image of a ruby/YSZ sample. With the backscatter detector, it is easy to see the interface between the dark gray ruby film and the lighter YSZ substrate. The film shows some waviness at the film surface, though this could be due to the titanium conductive coating that was applied to reduce charging. Some dark shading in the YSZ substrate is visible which is likely from fracturing the sample to expose the cross section.



Figure 8: Sample film thickness distributions, from SEM analysis [82]

As seen in Figure 8 [82], the film thickness for the RY samples is relatively consistent across the surface of each of the samples. The average film thicknesses, in nm, are as follows: 331 ± 14 for RY1, 348 ± 31 for RY2, and 356 ± 38 for RY3. It should be noted that, statistically speaking, the average film thickness of all the samples is identical. There are two data points that appear as outliers in Figure 8: The middle of RY3, which is noticeably higher than the other measurements in that sample and the measurement at 11 mm in RY2, which is significantly lower than the other measurements. Figure 9 shows those two SEM cross sections. In Figure 9a there is an anomalous darker layer that is too dark to be part of the film and isn't in the other images for RY2. Again, it is possible that this layer is part of the conducting layer, though the deposited conducting layer should be on the order of a few nanometers thick, not close to 200nm. It is also obvious that the RY2 film is noticeably thinner in this image which may indicate that there are some areas of the sample that weren't coated evenly. This appears to be the case in Figure 9b as well. Again, there is a darker layer on top of the ruby film, but the film itself appears thicker than in the other images for sample RY3. These variations in film thickness have been considered in the error bars for the curvature stress calculations. For full details on how the error was propagated, see the Appendix.



Figure 9: SEM cross-sections of a) RY2 and b) RY3 film thickness abnormalities

The thickness of the ruby on sapphire samples was measured to be 310.0 nm from the ToF-SIMS depth profile of Cr^+ ions seen in Figure 10. The Cr^+ concentration increases abruptly at the start of the profile as surface contamination is milled away and the ions from the film are measured in the spectrometer, therefore the film itself starts at a depth of approximately 10 nm. The concentration then increases from 0.02 to 0.0326 before decreasing. This suggests that the concentration of Cr^+ ions is not constant through the film. Since the sapphire initially has no Cr^+ ions, diffusion of the ions from the film/substrate interface into the sapphire lattice would be expected to show an exponential decay in concentration. Beginning at a depth of ~310 nm is the expected diffusion profile of the Cr^+ ions meaning that the film/substrate interface is located at a depth of approximately 320 nm, as indicated by the rightmost black bar in Figure 10. This results in a measured film thickness of 310 nm for RS1 and RS2.



Figure 10: ToF-SIMS depth profile of Cr through sample RS1 [82]

4.3.2 Fluorescence-determined stress

The contour plots for all 5 samples, seen in Figure 11 [82], show that each sample has a consistent stress value across the sample surface, as expected [83], except for RY3 which shows some area of lower stress in the middle of the sample. The RS1 and RS2 samples have similar contour plots with most of the surface appearing to be around 50 MPa with only sparse isolated data values of darker blue signifying lower stress values. These are likely due to variations, such as a piece of dust or a small film defect on the surface, which manifest in abnormal peak intensity and thus decreasing the quality of the fit. For the RY samples, we see similar contour plots with most stress values around 1800 MPa. Again, there are some points, especially in RY3, that exhibit some lower stress values. RY3 showed a higher film thickness towards the middle of the sample, as seen in Figures 8 and 9, which would suggest from Stoney's Equation that the film stress would be lower in the center. Given the high density of low stress values in the center of Figure 11e, this is further evidence that there are indeed some film thickness variations across RY3.



Figure 11: R₁ Stress contour plots for a) RS1, b) RS2, c) RY1, d) RY2, and e) RY3. All stress values are in MPa. Compressive stress is positive

The average stress values shown in Table 4 demonstrate that the fluorescencedetermined stress values in the sapphire samples agree, as do those of the YSZ samples. The standard deviations for the R_1 stress in the RY samples are less than 10% which is an impressive result. For the R_1 stress in the RS samples, the standard deviations of the stress contour plots were smaller than the manufacturer reported error for the spectrometer (which was 100 MPa). It was expected that the R_2 stress values would have higher errors since the R_2 peak height is lower, thus the signal to noise ratio isn't as good, and the peak fits are less precise. Still, the R_1 and R_2 stress values overlap when the errors are considered. This indicates that either peak can be used to determine stress, but the R_1 peak gives more accurate stress measurements.

Table 4: Average and standard deviation of contour plots. Positive stress is compressive. Error bars are standard deviation of the stress contour plot or the manufacturer reported error the spectrometer used in this work, whichever number was greater.

| Sample | $R_1 Stress (MPa)$ | $ m R_2 \ Stress \ (MPa)$ |
|--------|--------------------|---------------------------|
| RS1 | 58 ± 100 | 263 ± 461 |
| RS2 | 27 ± 100 | 197 ± 425 |
| RY1 | 1899 ± 117 | 2128 ± 389 |
| RY2 | 1878 ± 109 | 2109 ± 369 |
| RY3 | 1710 ± 133 | 1696 ± 135 |

Upon peak fitting, each reported peak center also had a reported uncertainty. The error propagation of the peak position uncertainty gave errors of at most 33 MPa which is insignificant considering the manufacture reported uncertainty for the Optiprexx PLS spectrometer is 100 MPa (see the Appendix for details on error propagation). Therefore, the error in peak fitting is less significant than the resolution limit of the spectrometer and the deviation in stress across the sample surface.

4.3.3 Curvature-determined stress

As seen in Figure 12 [82], which shows representative profilometry results for each sample, the ruby on sapphire samples had much less displacement (and therefore curvature) than the YSZ samples, which is logical since there is less thermal expansion or lattice mismatch between ruby and sapphire than between ruby and YSZ. All profiles are the expected parabolic shape except for the bare YSZ wafers which showed areas of higher displacement at the wafer edges. This is likely a result of the crystal polishing from the substrate manufacturer, but it signifies that not all residual stress was removed during annealing. However, upon deposition and crystallization of the ruby film the YSZ samples had the normal parabolic shape.



Figure 12: Representative profilometry of bare wafers and film/substrate samples for a) ruby/sapphire and b) ruby/YSZ samples

Table 5 shows a summary of the curvature change between the bare wafers and the film/substrate samples measured using MOSS and profilometry. As expected, the curvature changes of the sapphire samples are much smaller than the curvature changes of the YSZ samples. The MOSS measured curvature changes and profilometry measured curvature changes are within the error bars of each other for all samples. The error bars in each measurement come from the fact that each curvature measurement (on bare wafer and film/substrate sample) was done in two different directions perpendicular to each other, therefore the reported value is an average and the error is the standard deviation of two measurements.

| Sample | MOSS Curvature (m ⁻¹) | Profilometry Curvature (m ⁻¹) |
|--------|-----------------------------------|-------------------------------------------|
| RS1 | 0.0138 ± 0.0069 | 0.0128 ± 0.0054 |
| RS2 | 0.0014 ± 0.0026 | -0.0013 ± 0.0065 |
| RY1 | 0.2906 ± 0.0189 | 0.2927 ± 0.0193 |
| RY2 | 0.2695 ± 0.0173 | 0.2660 ± 0.0197 |
| RY3 | 0.2771 ± 0.0112 | 0.2725 ± 0.0205 |

Table 5: Average curvature values for all samples. Error is standard deviation of the curvature measurements

Taking the values in Table 5, the film thicknesses from Figures 8 and 10, and the room temperature material properties calculated from Equations 19 and 20 and plugging into Stoney's Equation (Equation 3) gives the curvature-determined stress values in Table 6. The error bars are from propagation of uncertainty in the film thickness and curvature measurements. The procedure for this error analysis is outlined in the Appendix. Table 6 shows that there is very good agreement between the MOSS-determined stress and the profilometry-determined stress values for all samples. The stress values of the ruby on YSZ samples are statistically similar as the error bars of the 3 samples overlap. Interestingly, the ruby on sapphire samples have statistically different stress values. This is likely due to

the fact that slight differences in curvature or film thickness have larger effects on stress when the magnitude of the stress is low, as is the case for the ruby/sapphire samples. The error in stress for RS1 and RS2 is also lower since the error is proportional to the magnitude of the stress, as seen in Equation A13. Also, the film thickness of sample RS2 was not measured by ToF-SIMS but was assumed to be identical to RS1 since the samples had identical deposition conditions. Therefore, a slight difference in film thickness between the RS samples could be the cause of the different stress values.

| Sample | MOSS Stress (MPa) | Profilometry Stress (MPa) |
|--------|-------------------|---------------------------|
| RS1 | 346 ± 141 | 201 ± 87 |
| RS2 | 72 ± 48 | -24 ± 117 |
| RY1 | 1802 ± 174 | 1848 ± 143 |
| RY2 | 1534 ± 156 | 1476 ± 170 |
| RY3 | 1711 ± 196 | 1616 ± 213 |

Table 6: Curvature-determined stress values (MPa) for all samples. Error is from propagation of uncertainty in film thickness and curvature measurements

4.3.4 Comparison of fluorescence and curvature-determined stress

The stress values of Table 6 and Table 4 are compared in Figure 13, below [82], and the results show good precision for the stress measurements in samples of the same substrate. Since the MOSS and profilometry-determined stress values were statistically similar, Figures 13a and 13b are essentially identical as are Figures 13c and 13d. In this plot, a data point that overlaps the 45° line would represent perfect agreement between the curvaturedetermined stress and the fluorescence-determined stress. For R₁ fluorescence-determined stress: Samples RY1 and RY3 show agreement between fluorescence and curvaturedetermined stresses while RY2 is slightly off, and sample RS2 has perfect agreement while RS1 is slightly off the line. For the R₂ fluorescence-determined stress, all samples perfectly agree except for RY2 which is again slightly off the line. While there are the slight differences in stress measured with the two different methods (which likely stems from the sillimanite phase impurities and/or the small fraction of (116) oriented ruby film), the small spread between samples deposited on the same substrate and the effectiveness with which the stress is measured from 50-1900 MPa renders this work a success. It is clear that ruby thin films can be used to measure biaxial stress and the piezospectroscopic coefficients are valid up to 1.9 GPa of compressive stress.



Figure 13: Comparison plot of a) R1 fluorescence-determined stress with MOSSdetermined stress b) R1 fluorescence stress with profilometry determined stress c) R2 fluorescence-determined stress with MOSS stress and d) R2 fluorescencedetermined stress with profilometry stress. The dashed 45-degree line is added to aid the eye [82]

4.4 CONCLUSIONS

Oriented, crystalline ruby thin films deposited via PLD onto sapphire and YSZ substrates have been used as fluorescent stress sensors for the first time. These thin film sensors show incredibly high spatial resolution as they were used to determine differences in stress on areas of 0.01 mm². The accuracy of the piezospectroscopic coefficients of ruby was confirmed by measuring thin film biaxial stress using both fluorescence and wafer curvature measurements. The curvature-determined stress values confirmed that at stress values up to 1.9 GPa, these novel thin film stress sensors provide accurate fluorescence-determined stress measurements indicating that the piezospectroscopic tensor of ruby is accurate up to 1.9 GPa (more than double the previous calibration). These novel PLD thin film sensors can now be used to measure film stress in real devices which can help to improve performance.

CHAPTER 5- CONCLUSIONS

Reducing solid oxide fuel cell (SOFC) operating temperatures is of the utmost importance as it would reduce the cost of the technology. Making SOFCs more widespread is critical since SOFCs offer energy density, energy efficiency, and fuel flexibility that other energy technologies cannot match. Strain engineering has been proposed to help improve SOFC performance, and thus reduce operating temperatures, but few studies have been able to measure stress and performance *in-situ* or isolate the effect of stress and strain on performance. A thin-film stress sensor that works under non-hydrostatic stress is sorely needed to make strain engineering experiments possible.

The work presented here has demonstrated the use of ruby as a thin film fluorescent stress sensor for biaxial stress. These thin films were deposited onto sapphire and YSZ substrates where the measured fluorescence stresses were approximately 0.05 and 1.9 GPa, respectively. The accuracy of fluorescence stress measurements was confirmed by determining stress from curvature using Stoney's Equation with curvature measured using a multi-beam optical stress sensor and a profilometer. The curvature stress measurements confirmed that the samples reproducibly and accurately measure stress, even with multiple phases and impurities present. Therefore, at ~2 GPa these novel sensors are robust enough to accurately measure stress and the piezospectroscopic coefficients of ruby have been calibrated to more than double the previous stress calibrations. All this work establishes PLD ruby thin films as a novel technology that is ready to be implemented to study nonhydrostatic stress effects on thin film performance in real world devices like SOFCs. APPENDIX

Fluorescence-Determined Stress Error Analysis

As described in the main article, R_1 and R_2 stress of (001) ruby films on substrate can be determined from fluorescence peak position using the piezospectroscopic equations that simplified down to equations 6-8. Equation 6, the general form of equations 7 and 8 is rewritten below

$$\sigma = \frac{\frac{1}{\lambda_{\text{sample}}} - \frac{1}{\lambda_{SFP}}}{(\Pi_{11} + \Pi_{22})} \tag{A1}$$

 σ denotes stress (GPa), λ_{SFP} denotes the wavelength of the stress-free fluorescence peak position (nm), and λ_{sample} denotes the wavelength of the sample fluorescence peak position (nm). This equation, which can be applied for both R₁ and R₂ peaks, is dependent on a single independent variable, the peak position, therefore only the error propagation of the peak position measurements needs to be considered when determining the error in the stress value. For a single variable equation, calculating the propagated error is done with the following equation[84]:

$$\alpha_Z = f(\bar{A} + \alpha_A) - f(\bar{A}) \tag{A2}$$

Where Z is a function of A, \overline{A} is the mean of A, and α is the error of the variable denoted by the subscript. Applying this error propagation to equation 1 above, we get:

$$\alpha_{\sigma_i} = \frac{\frac{1}{\bar{\lambda}_{sample} + \alpha_{\lambda}} - \frac{1}{\bar{\lambda}_{SFP}}}{(\Pi_{11} + \Pi_{22})} - \frac{\frac{1}{\bar{\lambda}_{sample}} - \frac{1}{\bar{\lambda}_{SFP}}}{(\Pi_{11} + \Pi_{22})}$$
(A3)

where α_{σ_i} is the error in an individual stress measurement, $\bar{\lambda}_{sample}$ is the recorded peak position, and α_{λ} is the error in the recorded peak position, which is reported by Origin during the peak fitting process. Of course, this error applies to every point on the sample where a fluorescence spectrum was recorded so those errors must be propagated to determine the error in the average stress that is reported. The average stress is calculated as:

$$\bar{\sigma} = \frac{\sum_{i=1}^{n} \sigma_i}{n} \tag{A4}$$

This equation is dependent upon n variables, the number of fluorescence spectra. To calculate the error for a multi-variable function, the following equation is used[84]:

$$(\alpha_Z)^2 = (\alpha_Z^A)^2 + (\alpha_Z^B)^2 + (\alpha_Z^C)^2 + \cdots$$
 (A5)

Where Z is a function of A, B, and C and α_Z^A, α_Z^B and α_Z^C are the change in Z when A, B, and C, respectively, are varied but the other variables are held constant. These are calculated as:

$$\alpha_Z^A = f(\bar{A} + \alpha_A, \bar{B}, \bar{C}) - f(\bar{A}, \bar{B}, \bar{C})$$
(A6)

$$\alpha_Z^B = f(\bar{A}, \bar{B} + \alpha_B, \bar{C}) - f(\bar{A}, \bar{B}, \bar{C})$$
(A7)

$$\alpha_Z^C = f(\bar{A}, \bar{B}, \bar{C} + \alpha_C) - f(\bar{A}, \bar{B}, \bar{C})$$
(A8)

Applying equation 5 to equation 4 gives:

$$(\alpha_{\overline{\sigma}})^2 = \left(\alpha_{\overline{\sigma}}^{\sigma_1}\right)^2 + \left(\alpha_{\overline{\sigma}}^{\sigma_2}\right)^2 + \left(\alpha_{\overline{\sigma}}^{\sigma_3}\right)^2 + \cdots \left(\alpha_{\overline{\sigma}}^{\sigma_n}\right)^2 \tag{A9}$$

Combining equations 4 and 6 gives the error in average stress due to the variance of a single measurement:

$$\alpha_{\overline{\sigma}}^{\sigma_1} = \frac{(\sigma_1 + \alpha_{\sigma_1}) + \sum_{i=2}^n \sigma_i}{n} - \frac{\sum_{i=1}^n \sigma_i}{n}$$
(A10)

In the work presented, equation 3 was used to calculate the error in every individual measurement, then equations 9 and 10 were used to determine the error in the average stress value.

Curvature-Determined Stress Error Analysis

Stoney's equation was used to determine stress from curvature measurements:

$$\sigma_f = \frac{h_s^2 M_s \kappa}{6h_f} \tag{A11}$$

Where σ is stress (GPa), h is layer thickness (m), κ is sample curvature (m⁻¹), subscript 's' indicates a substrate property, a subscript 'f' indicates a film property, and M is Biaxial Modulus (GPa). The substrate thickness is a constant, as is the biaxial modulus for

measurements taken at constant temperature, so this equation is dependent upon two variables with error: sample curvature and film thickness. For a two variable equation of the form $Z=k^*A/B$, where k is a constant and A and B are variables, the following equation gives the error in Z[84]:

$$\frac{\alpha_Z}{Z} = \sqrt{\left(\frac{\alpha_A}{A}\right)^2 + \left(\frac{\alpha_B}{B}\right)^2} \tag{A12}$$

Applying equation 12 to equation 11 gives:

$$\alpha_{\sigma} = \sigma_{\sqrt{\left(\frac{\alpha_{\kappa}}{\bar{\kappa}}\right)^2 + \left(\frac{\alpha_{h_f}}{\bar{h_f}}\right)^2}}$$
(A13)

Where the errors in κ and h_f are simply the standard deviations in the measurements, $\bar{\kappa}$ is average curvature, and $\overline{h_f}$ is the average film thickness.

BIBLIOGRAPHY

BIBLIOGRAPHY

- 1. Wachsman, E.D. and K.T. Lee, *Lowering the Temperature of Solid Oxide Fuel Cells.* Science, 2011. **334**(6058): p. 935-939.
- 2. Nicholas, J.D., *Highlights from the 2013 National Science Foundation Solid Oxide Fuel Cell Promise, Progress, and Priorities (SOFC-PPP) Workshop.* Electrochemical Society Interface, 2013. **22**: p. 49-54.
- 3. Steele, B.C.H. and A. Heinzel, *Materials for fuel-cell technologies*. Nature, 2001. **414**(6861): p. 345-352.
- 4. Yan, K., et al., *The Influence of Elastic Strain on Catalytic Activity in the Hydrogen Evolution Reaction.* Angewandte Chemie International Edition, 2016. **55**(21): p. 6175-6181.
- Yang, J., et al., Core-Shell CdSe@ Pt Nanocomposites with Superior Electrocatalytic Activity Enhanced by Lateral Strain Effect. Journal of Materials Chemistry, 2011. 21(25): p. 9088-9094.
- 6. Wu, J., et al., Surface Lattice-Engineered Bimetallic Nanoparticles and their Catalytic Properties. Chemical Society Reviews, 2012. **41**(24): p. 8066-8074.
- 7. Bissett, M.A., et al., Enhanced Chemical Reactivity of Graphene Induced by Mechanical Strain. ACS Nano, 2013. 7(11): p. 10335-10343.
- 8. Mavrikakis, M., B. Hammer, and J.K. Nørskov, *Effect of Strain on the Reactivity of Metal Surfaces.* Physical Review Letters, 1998. **81**(13): p. 2819-2822.
- 9. Rim, K., J.L. Hoyt, and J.F. Gibbons, *Fabrication and Analysis of Deep Submicron* Strained-Si n-MOSFET's. IEEE Transactions on Electron Devices, 2000. **47**(7): p. 1406-1415.
- 10. Lee, M.L., et al., Strained Si, SiGe, and GeCchannels for High-Mobility Metal-Oxide-Semiconductor Field-Effect Transistors. Journal of Applied Physics, 2005. 97(1): p. 011101.
- 11. De Souza, R.A., A. Ramadan, and S. Horner, *Modifying the Barriers for Oxygen-Vacancy Migration in Fluorite-Structured CeO2 Electrolytes Through Strain: A Computer Simulation Study.* Energy & Environmental Science, 2012. **5**(1): p. 5445-5453.
- 12. Fluri, A., et al., In Situ Stress Observation in Oxide Films and How Tensile Stress Influences Oxygen Ion Conduction. Nature communications, 2016. 7.
- 13. Mayeshiba, T. and D. Morgan, *Strain Effects on Oxygen Migration in Perovskites.* Physical Chemistry Chemical Physics, 2015. **17**(4): p. 2715-2721.
- 14. Schweiger, S., et al., A Microdot Multilayer Oxide Device: Let Us Tune the Strain-Ionic Transport Interaction. ACS Nano, 2014. 8(5): p. 5032-5048.

- 15. Shi, Y., et al., The Effect of Mechanical Twisting on Oxygen Ionic Transport in Solid-State Energy Conversion Membranes. Nature materials, 2015. 14(7): p. 721.
- 16. Han, J.W. and B. Yildiz, *Enhanced One Dimensional Mobility of Oxygen on Strained LaCoO3(001) Surface*. Journal of Materials Chemistry, 2011. **21**(47): p. 18983.
- 17. Jalili, H., et al., New Insights into the Strain Coupling to Surface Chemistry, Electronic Structure, and Reactivity of La0.7Sr0.3MnO3. The Journal of Physical Chemistry Letters, 2011. 2(7): p. 801-807.
- Kubicek, M., et al., Tensile Lattice Strain Accelerates Oxygen Surface Exchange and Diffusion in La1-xSrxCoO3- δ Thin Films. ACS Nano, 2013. 7(4): p. 3276-3286.
- 19. Kushima, A., S. Yip, and B. Yildiz, *Competing Strain Effects in Reactivity* of *LaCoO3with Oxygen.* Physical Review B, 2010. **82**(11): p. 115435.
- 20. Tsvetkov, N., et al., Accelerated Oxygen Exchange Kinetics on Nd2NiO4+ δ Thin Films with Tensile Strain along c-Axis. ACS Nano, 2015. **9**(2): p. 1613-1621.
- 21. Yildiz, B., "Stretching" the Energy Landscape of Oxides—Effects on Electrocatalysis and Diffusion. MRS Bulletin, 2014. **39**(02): p. 147-156.
- Kerman, K., C. Ko, and S. Ramanathan, Orientation Dependent Oxygen Exchange Kinetics on Single Crystal SrTiO3 Surfaces. Physical Chemistry Chemical Physics, 2012. 14(34): p. 11953-11960.
- 23. Nicholas, J., *Practical considerations for reliable stress and oxygen surface exchange coefficients from bilayer curvature relaxation measurements.* 2016.
- 24. Yang, Q., Development and Use of a New Curvature Relaxation Technique to Measure the In Situ Oxygen Surface Exchange Coefficients and Stress of Lanthanum Strontium Ferrite Films, in Materials Science and Engineering. 2014, Michigan State University: East Lansing.
- 25. Yang, Q., et al., In situ Oxygen Surface Exchange Coefficient Measurements on Lanthanum Strontium Ferrite Thin Films Via the Curvature Relaxation Method. Solid State Ionics, 2013. 249: p. 123-128.
- 26. Stoney, G.G., *The Tension of Metallic Films Deposited by Electrolysis.* Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, 1909. **82**(553): p. 172-175.
- 27. Mao, H.K., et al., Specific Volume Measurements of Cu, Mo, Pd, and Ag and Calibration of the Ruby R1 Fluorescence Pressure Gauge from 0.06 to 1 Mbar. Journal of Applied Physics, 1978. **49**(6): p. 3276-3283.
- 28. Grasset, O., E. Amiguet, and M. Choukroun, *Pressure Measurements Within Optical Cells Using Diamond Sensors: Accuracy of the Method Below 1 GPa.* High Pressure Research, 2005. **25**(4): p. 255-265.

- 29. Hess, N.J. and G.J. Exarhos, *Temperature and Pressure Dependence of Laser Induced Fluorescence in Sm:YAG—A New Pressure Calibrant.* High Pressure Research, 1989. **2**(1): p. 57-64.
- Rashchenko, S.V., et al., Revised Calibration of the Sm:SrB4O7 Pressure Sensor Using the Sm-Doped Yttrium-Aluminum Garnet Primary Pressure Scale. Journal of Applied Physics, 2015. 117(14): p. 145902.
- 31. Lacam, A. and C. Chateau, *High-Pressure Measurements at Moderate Temperatures* in a Diamond Anvil Cell with a New Optical Sensor: SrB4O7:Sm2+. Journal of Applied Physics, 1989. **66**(1): p. 366-372.
- He, J. and D.R. Clarke, Determination of the Piezospectroscopic Coefficients for Chromium-Doped Sapphire. Journal of the American Ceramic Society, 1995. 78(5): p. 1347-1353.
- 33. Nye, J.F., *Physical Properties of Crystals: Their Representation by Tensors and Matrices.* 1985: Oxford university press.
- 34. Gunton, D. and G. Saunders, *The Young's Modulus and Poisson's Ratio of Arsenic, Antimony and Bismuth.* Journal of Materials Science, 1972. **7**(9): p. 1061-1068.
- 35. Rogers, E., et al. *Fundamentals of Chemistry*. 2000; Available from: <u>http://www.chem.uiuc.edu/rogers/text5/Tx53/tx53.html</u>.
- 36. Leger, J.M., C. Chateau, and A. Lacam, *SrB4O7:Sm2+ Pressure Optical Sensor: Investigations in the Megabar Range.* Journal of Applied Physics, 1990. **68**(5): p. 2351-2354.
- 37. Jahren, A.H., M.B. Kruger, and R. Jeanloz, *Alexandrite as a High-Temperature Pressure Calibrant, and Implications for the Ruby-Fluorescence Scale.* Journal of Applied Physics, 1992. **71**(4): p. 1579-1582.
- Raju, S.V., et al., Determination of the Variation of the Fluorescence Line Positions of Ruby, Strontium Tetraborate, Alexandrite, and Samarium-Doped Yttrium Aluminum Garnet with Pressure and Temperature. Journal of Applied Physics, 2011. 110(2): p. 023521.
- 39. Datchi, F., R. LeToullec, and P. Loubeyre, *Improved Calibration of the* SrB4O7:Sm2+ Optical Pressure Gauge: Advantages at Very High Pressures and High Temperatures. Journal of Applied Physics, 1997. **81**(8): p. 3333-3339.
- 40. Zhao, Y., et al., *Pressure Measurement at High Temperature Using Ten Sm: YAG Fluorescence Peaks.* Journal of Applied Physics, 1998. **84**(8): p. 4049-4059.
- 41. Barsoum, M. and M.W. Barsoum, *Fundamentals of Ceramics*. 2002: CRC Press.
- 42. Syassen, K., Ruby Under Pressure. High Pressure Research, 2008. 28(2): p. 75-126.
- 43. Eggert, J.H., K.A. Goettel, and I.F. Silvera, *Ruby at High Pressure. I. Optical Line Shifts to 156 GPa.* Physical Review B, 1989. **40**(8): p. 5724-5732.

- 44. Grasset, O., Calibration of the R Ruby Fluorescence Lines in the Pressure Range [0-1 GPa] and the Temperature Range [250-300 K]. High Pressure Research, 2001. 21(3-4): p. 139-157.
- 45. Silvera, I.F., et al., *Calibration of the Ruby Pressure Scale to 150 GPa.* physica status solidi (b), 2007. **244**(1): p. 460-467.
- 46. Chai, M. and J. Michael Brown, *Effects of Static Non-Hydrostatic Stress on the R* Lines of Ruby Single Crystals. Geophysical Research Letters, 1996. **23**(24): p. 3539-3542.
- 47. Mao, H.K., J. Xu, and P.M. Bell, *Calibration of the Ruby Pressure Gauge to 800 kbar Under Quasi-Hydrostatic Conditions.* Journal of Geophysical Research: Solid Earth, 1986. **91**(B5): p. 4673-4676.
- 48. Datchi, F., et al., *Optical Pressure Sensors for High-Pressure–High-Temperature Studies in a Diamond Anvil Cell.* High Pressure Research, 2007. **27**(4): p. 447-463.
- 49. Ragan, D.D., R. Gustavsen, and D. Schiferl, *Calibration of the Ruby R1 and R2 Fluorescence Shifts as a Function of Temperature from 0 to 600 K.* Journal of Applied Physics, 1992. **72**(12): p. 5539-5544.
- 50. Kumari, S. and A. Khare, *Note: Epitaxial Ruby Thin Film Based Photonic Sensor* for Temperature Measurement. Review of Scientific Instruments, 2011. **82**(6): p. 066106.
- 51. Kumari, S. and A. Khare, *Langmuir Probe Studies of Laser Ablated Ruby Plasma and Correlation with Pulsed Laser Deposited Ruby Thin Film Properties.* Laser and Particle Beams, 2014. **32**(03): p. 359-367.
- 52. Ma, Q. and D.R. Clarke, *Optical Fluorescence from Chromium Ions in Sapphire: A Probe of the Image Stress.* Acta Metallurgica et Materialia, 1993. **41**(6): p. 1811-1816.
- 53. Ma, Q. and D.R. Clarke, *Stress Measurement in Single-Crystal and Polycrystalline Ceramics Using Their Optical Fluorescence.* Journal of the American Ceramic Society, 1993. **76**(6): p. 1433-1440.
- 54. Ma, Q. and D.R. Clarke, *Measurement of Residual Stresses in Sapphire Fiber Composites Using Optical Fluorescence.* Acta Metallurgica et Materialia, 1993. **41**(6): p. 1817-1823.
- 55. Ma, Q. and D.R. Clarke, *Piezospectroscopic Determination of Residual Stresses in Polycrystalline Alumina.* Journal of the American Ceramic Society, 1994. **77**(2): p. 298-302.
- 56. Asmus, S.M.F. and G. Pezzotti, *Analysis of Microstresses in Cement Paste by Fluorescence Piezospectroscopy.* Physical Review E, 2002. **66**(5): p. 052301.
- Guo, S., A. Limpichaipanit, and R.I. Todd, *High Resolution Optical Microprobe Investigation of Surface Grinding Stresses in Al2O3 and Al2O3/SiC Nanocomposites.* Journal of the European Ceramic Society, 2011. **31**(1-2): p. 97-109.

- Guo, S. and R.I. Todd, Quantitative Optical Fluorescence Microprobe Measurements of Stresses Around Indentations in Al2O3 and Al2O3/SiC Nanocomposites: The Influence of Depth Resolution and Specimen Translucency. Acta Materialia, 2011. 59(7): p. 2637-2647.
- 59. Hanhan, I., et al., Portable Piezospectroscopy System: Non-Contact In-Situ Stress Sensing Through High Resolution Photo-Luminescent Mapping. Journal of Instrumentation, 2014. 9(11): p. P11005.
- 60. Hough, H., et al., Luminescence Sensing of Stress in Ti/Al2O3 Fiber Reinforced Composites. Acta Metallurgica et Materialia, 1995. **43**(2): p. 821-834.
- 61. Munisso, M.C., et al., Spatially Resolved Piezo-Spectroscopic Characterizations for the Validation of Theoretical Models of Notch-Root Stress Fields in Ceramic Materials. Continuum Mechanics and Thermodynamics, 2008. **20**(3): p. 123-132.
- 62. Myers, G.A., C.A. Michaels, and R.F. Cook, *Quantitative Mapping of Stress Heterogeneity in Polycrystalline Alumina Using Hyperspectral Fluorescence Microscopy.* Acta Materialia, 2016. **106**: p. 272-282.
- 63. Schlichting, K.W., et al., Application of Cr3+ Photoluminescence Piezo-Spectroscopy to Plasma-Sprayed Thermal Barrier Coatings for Residual Stress Measurement. Materials Science and Engineering: A, 2000. **291**(1-2): p. 68-77.
- 64. Nychka, J.A. and D.R. Clarke, *Damage quantification in TBCs by photo-stimulated luminescence spectroscopy*. Surface and Coatings Technology, 2001. **146-147**: p. 110-116.
- 65. Gong, X.-Y. and D.R. Clarke, On the Measurement of Strain in Coatings Formed on a Wrinkled Elastic Substrate. Oxidation of Metals, 1998. **50**(5): p. 355-376.
- 66. Christensen, R.J., D.M. Lipkin, and D.R. Clarke, Nondestructive Evaluation of the Oxidation Stresses Through Thermal Barrier Coatings Using Cr3+ Piezospectroscopy. Applied Physics Letters, 1996. **69**(24): p. 3754-3756.
- 67. Gell, M., et al., *Photoluminescence Piezospectroscopy: A Multi-Purpose Quality Control and NDI Technique for Thermal Barrier Coatings.* International Journal of Applied Ceramic Technology, 2004. 1(4): p. 316-329.
- 68. Lipkin, D., et al., Stress development in alumina scales formed upon oxidation of (111) NiAl single crystals. Corrosion Science, 1997. **39**(2): p. 231-242.
- 69. Lipkin, D.M. and D.R. Clarke, Sample-probe interactions in spectroscopy: Sampling microscopic property gradients. Journal of Applied Physics, 1995. **77**(5): p. 1855-1863.
- 70. Lipkin, D.M. and D.R. Clarke, *Measurement of the stress in oxide scales formed by* oxidation of alumina-forming alloys. Oxidation of Metals, 1996. **45**(3): p. 267-280.
- 71. Sridharan, S., et al., Stress variation with thermal cycling in the thermally grown oxide of an EB-PVD thermal barrier coating. Surface and Coatings Technology, 2004. **179**(2): p. 286-296.

- Tolpygo, V.K. and D.R. Clarke, Wrinkling of α-Alumina Films Grown by Thermal Oxidation—I. Quantitative Studies on Single Crystals of Fe-Cr-Al alloy. Acta Materialia, 1998. 46(14): p. 5153-5166.
- 73. Tolpygo, V.K., J.R. Dryden, and D.R. Clarke, Determination of the Growth Stress and Strain in α-Al2O3 Scales During the Oxidation of Fe-22Cr-4.8AI-0.3Y Alloy. Acta Materialia, 1998. 46(3): p. 927-937.
- 74. Lowndes, D.H., et al., Synthesis of novel thin-film materials by pulsed laser deposition. Science, 1996. **273**(5277): p. 898-903.
- 75. Eason, R., *Pulsed laser deposition of thin films: applications-led growth of functional materials.* 2007: John Wiley & Sons.
- 76. Cullity, B.D., *Elements of XRD.* USA Edison-Wesley P Inc, 1978.
- 77. Botha, P.J., et al., *Behavior of Elastic Constants, Refractive Index, and Lattice Parameter of Cubic Zirconia at High Temperatures.* Journal of Applied Physics, 1993. **73**(11): p. 7268-7274.
- 78. Tefft, W.E., *Elastic Constants of Synthetic Single Crystal Corundum.* Elastic, 1966. **70**(4): p. 277-280.
- 79. Nicholas, J.D., In situ Wafer Curvature Relaxation Measurements to Determine Surface Exchange Coefficients and Thermo-Chemically Induced Stresses, in Electro-Chemo-Mechanics of Solids. 2016, Springer: Ney York.
- Yang, Q., R.R. Lunt, and J.D. Nicholas, Low Temperature Lanthanum Strontium Ferrite Thin Film Stress and Oxygen Surface Exchange Coefficient Measurements. High Temperature Experimental Techniques and Measurements, 2013. 58(3): p. 37-46.
- 81. Yang, Q. and J.D. Nicholas, *Porous Thick Film Lanthanum Strontium Ferrite Stress and Oxygen Surface Exchange Bilayer Curvature Relaxation Measurements.* Journal of the Electrochemical Society, 2014. **161**(11): p. F3025-F3031.
- 82. Straley, E.M., Dorfman, Susannah M., Nicholas, Jason D, *Pulsed-Laser Deposited Ruby Thin Films for Piezospectroscopic Biaxial Stress Sensing.* In Preparation, 2018.
- 83. Freund, L.B. and S. Suresh, *Thin Film Materials*. 2003.
- 84. Hughes, I. and T. Hase, *Measurements and Their Uncertainties : A Practical Guide to Modern Error Analysis.* 2010, Oxford, UNITED KINGDOM: Oxford University Press USA OSO.