IHLEFELD, JON FREDRICK. *Synthesis and Properties of Barium Titanate Solid Solution Thin Films on Copper Substrates. (Under the direction of Jon-Paul Maria.)*

Barium titanate thin films were deposited via chemical solution deposition using a hybrid-chelate chemistry directly on copper foil substrates. A process was developed to crystallize and densify the ferroelectric films at 900°C by using a reductive atmosphere containing nitrogen, hydrogen, water vapor, and oxygen impurities such that film constituents were oxidized to form barium titanate and the foil substrate remained metallic. The crystallized films are polycrystalline with equiaxed morphology and average grain diameters in excess of 100 nm. The dielectric properties exhibit permittivities in excess of 1800 at room temperature and zero bias with tunabilities of greater than 90% and high field loss tangents of less than 1%.

A series of samples was prepared with varying grain and crystallite sizes by dividing and processing a single film over a range of temperature from 700 to 900°C. This ensures that the chemical composition and film thickness is invariant for each sample. It is shown that the grain size increases with higher process temperatures and results in a concomitant increase in permittivity and tunability. These enhancements, combined with the constant paraelectric/ferroelectric phase transition temperature, indicated that a combination of film crystallinity and grain size is responsible for diminished performance.

The phase transition temperature and temperature coefficient of capacitance modified by partially substituting zirconium, hafnium, and tin for titanium. The resulting films were single phase and the phase transition shifts were consistent with bulk materials. A reduction in permittivity was observed for increasing substituent level and was attributed to a reduction
in grain size for both barium titanate zirconate and barium titanate hafnate. Processing conditions were chosen to stabilize Sn$^{2+}$ during the firing process in an attempt to flux the system and increase grain size. The barium titanate stannate films had less reduction in grain size per substituent level than either zirconium or hafnium, however a similar reduction in permittivity was observed. The diminished dielectric response was explained by a defect reaction involving divalent tin and oxygen vacancies that quenched the extrinsic domain response to the dielectric constant.

Defect equilibria were investigated with respect to processing atmosphere, stoichiometry, and dopant concentration. The solubility of excess barium and titanium was found to be greater in the films than is expected in the bulk, however it is unclear that equilibrium is achieved in the process. It was demonstrated that dopants could successfully eliminate the necessity of a reoxidation anneal to compensate for oxygen point defects resulting from the low $pO_2$ atmospheres. The dopant levels necessary and insulation resistance of pure BaTiO$_3$ were greater than expected from thermodynamic calculations. It was suggested that this is the result of a reduction in the enthalpy of reduction, stemming from an increase in grain boundary volume.

Barium borate fluxes were used to improve densification and crystallinity. Barium borate additions between 0 and 3% uniformly increased grain size and density, while levels greater than 3% resulted in anomalous grain growth. Films with exaggerated grains show tetragonal peak splitting in the X-ray diffraction patterns, consistent with bulk barium titanate. In materials without exaggerated grain growth, dielectric measurements revealed permittivities in excess of 3000 at room temperature (for average grain sizes of approximately 160 nm). This value is equivalent to the finest-prepared bulk ceramics and
substantially greater than any polycrystalline film ever reported. This has been attributed to
in improvement in film crystallinity. These two accomplishments – tetragonal crystal
symmetry and permittivities in excess of 3000 – represent dramatic breakthroughs in
ferroelectric thin film technology.
SYNTHESIS AND PROPERTIES OF BARIUM TITANATE SOLID SOLUTION THIN FILMS DEPOSITED ON COPPER SUBSTRATES

By

JON FREDRICK IHLEFELD

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

MATERIALS SCIENCE AND ENGINEERING

Raleigh

2006

APPROVED BY:

Jon-Paul Maria
Associate Professor of Materials Science and Engineering
Chair of Advisory Committee

Angis Kingon
Professor of Materials Science and Engineering

Zlatko Sitar
Professor of Materials Science and Engineering

Robert Nemanich
Professor of Physics

William Borland
Research Fellow, E.I. DuPont de Nemours
Biography

Jon Ihlefeld was born on March 20, 1980 to parents Dr. Gary and Jeanne Ihlefeld in Iowa City, Iowa. His stay in Iowa City was short lived, as he was quickly whisked away to the small southeast Iowa city of Muscatine where he spent his first 18 years nurturing interests in athletics, auto restoration, and assembling plumbing fittings to launch the best in Midwestern produce. He graduated from Muscatine High School in 1998 and enrolled at the Iowa State University of Science and Technology where he declared a major in Materials Science and Engineering with specializations in metallurgy and electronic properties of materials. He worked in his free time at the U.S. Department of Energy Ames Laboratory on the Iowa State campus heat treating nickel superalloys and performing flexure tests on thermal barrier coatings from steam turbines. Feeling a need to expand his knowledge further, he accepted a summer position at Northrop Grumman Life Support in Davenport, Iowa following his junior year of college where he learned from a skilled team of physicists and ceramists about ceramic oxygen conductors and advanced methods of ceramic processing. Upon returning to ISU for his senior year, Jon was awarded the Most Outstanding Senior Award from the Materials Science department and graduated with a Bachelors degree in Materials Engineering. After spending 22 years in the bitter cold winters and sweltering summers of Iowa, he decided that it was time for a change of climate and enrolled in Jon-Paul Maria’s research group at North Carolina State University with an interest in working on gate dielectrics for next generation CMOS. At the encouragement of Professor Maria however, Jon was tasked with developing materials and processes for depositing barium titanate-based films on copper foil substrates – a fortuitous event as it turned out. Jon received his Masters of Materials Science and Engineering from North Carolina State in May 2005 and his Doctor of Philosophy in August 2006. Afterwards, he pursued a career in academia by accepting a joint post-doctoral scholar position with Dr. Darrell Schlom at The Pennsylvania State University and Dr. Ramamoorthy Ramesh at the University of California-Berkeley to grow and characterize epitaxial bismuth iron oxide thin films.
Acknowledgements

First and foremost, I would like to thank my advisor, mentor, and friend Professor Jon-Paul Maria for providing me with opportunities, guidance, and support to grow and develop as a young scientist and for making these last four years at NC State an absolute pleasure. I could not have accomplished this without him and for that I am truly grateful.

I would like to express my gratitude and appreciation to my colleagues in the Electroceramic Thin Film Group and friends in the university. Special acknowledgements go to Brian Laughlin and Alisa Hunt-Lowery who worked closely with me on this project, Mark Losego who taught me more than I could ever care to know about sol-gel and ketchup, Dr. Charles Parker for teaching me the ways of the sometimes frustrating temperature dependent measurements, and Brian Boyette, Leslie Jimison, Dr. Dipankar Ghosh, Spalding Craft, Jess Jur, Seymen Aygün, Peter Lam, Erin Gross, Patrick Daniels, and Jon Pierce who have tolerated my ‘Iowa bitterness’ over the course of my studies and helped keep me balanced by going out and having a ‘few’ beers and creating some great memories, which I will cherish forever.

I would like to acknowledge those who taught and helped me with various characterization techniques including Dr. Ramòn Callazo with XPS; Dr. Brian Rodriquez, Tom Blair, and Jacquie Hanson with AFM, Dr. Dale Bachelor, Roberto Garcia, and Chuck Mooney with SEM, and Dr. Simon Lappi and Crissy Rhodes with IR.

I appreciate the time and efforts of my committee members Dr. Angus Kingon for his many informative discussions, Dr. Robert Nemanich and Dr. Zlatko Sitar for being inspirational teachers and instructors, and Dr. Bill Borland who allowed me free reign to study some fundamental aspects of ferroelectric films not originally included in the research proposal and provided invaluable insight into the field for which this work was conducted.

I would like to acknowledge my good friends Shane Soboroff and Katie Brooker who challenged me everyday and have helped me see my potential. My brother Allen, sister-in-law Marie, and the Ziebell family have supported me along this journey and I thank them. Finally, and most importantly, I thank my parents, Gary and Jeanne Ihlefeld, for instilling in me a strong Midwest work ethic and for inspiring me everyday. I would have never made it this far without their continual love and encouragement and I am forever indebted.
# Table of Contents

**List of Figures** .................................................................................................................. vi
**List of Tables** .................................................................................................................................. xx

## CHAPTER 1: INTRODUCTION ................................................................................................. 1
  1.1 Outcomes .................................................................................................................................. 1

## CHAPTER 2: LITERATURE REVIEW ....................................................................................... 3
  2.1 Embedded Passives .................................................................................................................. 3
  2.2 Ferroelectric Crystals ............................................................................................................... 5
    2.2.1 Historical perspective of Ferroelectric Crystals ................................................................. 5
    2.2.2 Perovskite Crystal Structure ............................................................................................... 7
    2.2.3 The Ferroelectric Phase Transition ..................................................................................... 9
    2.2.4 Chemical Bonding in Ferroelectrics .................................................................................... 12
    2.2.5 Dielectric Properties ........................................................................................................... 14
  2.3 Scaling and Size Effects ............................................................................................................ 25
    2.3.1 True Size Effects ................................................................................................................ 26
    2.3.2 Observed Scaling Effects in Bulk Ceramics ........................................................................ 27
    2.3.3 Observed Scaling Effects in Thin Films Ferroelectrics ......................................................... 33
    2.3.4 Extrinsic Effects to Scaling ................................................................................................. 35
  2.4 Barium Titanate Based Solid Solutions ................................................................................... 40
    2.4.1 Barium Titanate-Strontium Titanate ................................................................................ 41
    2.4.3 Barium Titanate-Barium Zirconate .................................................................................... 42
    2.4.3 Barium Titanate-Barium Steannate ................................................................................... 45
    2.4.4 Barium Titanate–Barium Hafnate ..................................................................................... 47
  2.5 Chemical Solution Deposition of Thin Films .......................................................................... 48
    2.5.1 Solution Processing of Barium Titanate Thin Films .......................................................... 54
  2.6 Controlled Atmosphere Processing ......................................................................................... 56
  2.7 Defect Chemistry in Barium Titanate ...................................................................................... 61
    2.7.1 Doping in Barium Titanate ................................................................................................. 64
    2.7.2 Reoxidation of Barium Titanate .......................................................................................... 69
  2.8 Flux and Liquid Phase assisted Sintering ................................................................................. 70
    2.8.1 Binary and Ternary Fluxes and Liquid Phases ....................................................................... 71
    2.8.2 Unary Fluxes and Liquid Phases ........................................................................................... 73
    2.8.3 Fluxes and Liquid Phase Sintering in Thin Films ................................................................. 76

## CHAPTER 3: Barium Titanate Solution and Thin Film Preparation and Properties .................. 78
  3.1 Barium Titanate Solution Chemistry ....................................................................................... 78
  3.2 Barium Titanate Thin Films on Platinized Silicon Substrates ................................................ 81
  3.3 Barium Titanate Thin Films on Copper Substrates ................................................................. 84
    3.3.1 Principles of Low pO₂ Processing of Barium Titanate Thin Films ..................................... 84
    3.3.2 Phase Development of Barium Titanate Thin Films ........................................................... 87
    3.3.3 Physical Characterization of BaTiO₃ Thin Films ................................................................. 90
<table>
<thead>
<tr>
<th>3.3.4</th>
<th>Dielectric Properties of BaTiO$_3$ Thin Films on Copper</th>
<th>93</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.5</td>
<td>Material Optimization</td>
<td>96</td>
</tr>
</tbody>
</table>

**CHAPTER 4: SCALING EFFECTS IN BARIUM TITANATE THIN FILMS**

**CHAPTER 5: PHASE TRANSITION ENGINEERING**

5.1 Barium Titanate-Barium Zirconate Solid Solutions
5.2 Barium Titanate-Barium Hafnate Solid Solutions
5.3 Barium Titanate-Barium Stannate Solid Solutions

**CHAPTER 6: DEFECT EQUILIBRIA**

6.1 Intrinsic Equilibria
6.2 Extrinsic Equilibria
6.3 Reduction and Compensation

**CHAPTER 7: LIQUID PHASE SINTERING OF BaTiO$_3$ THIN FILMS**

7.1 Barium-Borate Flux Modified Barium Titanate
7.1.1 Boron Oxide Flux Modified Barium Titanate
7.1.2 Barium Oxide Modified Barium Titanate
7.1.3 Barium Borate Flux Modified Barium Titanate
7.1.4 Dielectric Properties of Barium Borate Fluxed BaTiO$_3$
7.1 Barium-Phosphate Flux Modified Barium Titanate

**CHAPTER 8: CONCLUSIONS AND FUTURE WORK**

8.1 Conclusions
8.2 Future Work

**CHAPTER 9: BIBLIOGRAPHY**

**CHAPTER 10: APPENDIX**

10.1 Defect Density Calculation for Barium Titanate
10.2 Conductivity of Pure Barium Titanate
10.3 Temperature Dependent Measurements
List of Figures

Figure 2.1: Schematic of embedded decoupling capacitors within the layers of a printed wiring board.................................................................4

Figure 2.2: Prototypical perovskite unit cell. ............................................................... 8

Figure 2.3: Perovskite unit cells in a) cubic phase and b) with a tetragonal distortion ...... 9

Figure 2.4: Temperature dependence of relative permittivity for a ferroelectric with a first order phase transition displaying Curie-Weiss behavior ..................10

Figure 2.5: Schematic showing the condensation of the transverse optic mode with decreasing temperature in a ferroelectric ........................................11

Figure 2.6: Distorted octahedra in a ferroelectric perovskite with the B-site ion shifted toward one face. ...........................................................................13

Figure 2.7: Frequency dependence of permittivity and loss tangent for a material containing space charge, dipole, ionic, and electronic relaxations ...........15

Figure 2.8: Schematic of the real versus imaginary components of permittivity separated by a phase angle δ.................................................................16

Figure 2.9: Polarization compensation mechanisms: a) surface charge, b) electrical conduction, c) polarization gradients, and d) 180° domain wall formation.................................................................18

Figure 2.10: Schematic of a 90° domain wall in a tetragonal ferroelectric crystal. ..........19

Figure 2.12: Polarization hysteresis loops for a ferroelectric under a) switching and b) subswitching fields ........................................................................19

Figure 2.12: Potential energy versus distance schematic showing a random distribution of pinning sites in a lattice..........................................................21

Figure 2.13: Piezoelectric hysteresis with applied stress under sub-switching conditions .22

Figure 2.14: Polarization hysteresis loop with applied field under a sub-switching bias. ..24

Figure 2.15: Sub-switching field dependence of the real and imaginary components to permittivity for a ferroelectric with a degree of domain wall pinning. The dashed line represents the region where the Rayleigh Law holds. ...............24
Figure 2.16: Room temperature relative permittivity as a function of average grain diameter for barium titanate ceramics .................................................................28

Figure 2.17: Temperature dependence of permittivity for a grain size series of pure barium titanate bulk ceramics.................................................................30

Figure 2.18: Temperature dependence of permittivity for a barium titanate glass-ceramic of varying grain size.................................................................32

Figure 2.19: Dependence of barium titanate phase transition temperatures on the level of substituent atoms.................................................................41

Figure 2.20: Schematic of three ferroelectric phase transitions a) normal, b) diffuse, and c) relaxor. .................................................................44

Figure 2.21: Oxygen pressure versus temperature phase diagram for the equilibrium metals, oxygen, and metal oxides. Figure b) shows the equilibrium processing space where the oxides of barium and titanium are stable with metallic nickel and copper and oxygen.................................................................58

Figure 2.22: Equilibrium phase diagram for system BaO-CuO ........................................................................59

Figure 2.23: Field dependence of permittivity for PZT deposited on stainless steel ........60

Figure 2.24: Conduction and valence bands of barium titanate with quenched in oxygen vacancies at a) 0K and b) a finite temperature. .........................63

Figure 2.25: Band diagram showing annihilation of charge carriers associated with oxygen vacancies by acceptor states. .............................................65

Figure 3.1: Solution preparation procedure for a) methanol-diluted and b) acetic acid diluted barium titanate solutions................................................61

Figure 3.2: X-ray diffraction patterns for barium titanate thin films on platinized silicon substrates processed in air in a temperature range of 350 to 750°C....82

Figure 3.3: Capacitance density versus a) applied bias and b) capacitance density versus frequency for a BaTiO₃ thin film on platinized silicon...............83

Figure 3.4: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides. The shaded region represents the conditions where barium and titanium oxidize and copper is reduced. ..........................85

Figure 3.5: Process flow of the formation of barium titanate thin films on copper Substrates ........................................................................87
Figure 3.6: X-ray diffraction patterns for barium titanate thin films on copper substrates processed in reducing atmospheres in a temperature range of 300 to 900°C .................................................................88

Figure 3.7: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides with the actual firing conditions plotted ...............89

Figure 3.8: Oxygen pressure-temperature phase diagram for the reaction of copper and oxygen to form copper oxide and the reaction of carbon monoxide with oxygen to form carbon dioxide.................................................................90

Figure 3.9: X-ray diffraction pattern for a solution deposited barium titanate thin film on a copper substrate processed under reducing conditions.........................91

Figure 3.10: 5µm x 5µm topographical AFM scan of a barium titanate thin film on a copper substrate. .................................................................92

Figure 3.11: Bright field TEM image of a barium titanate thin film on copper. .................92

Figure 3.12: XPS spectrum for a barium titanate thin film on copper.................................93

Figure 3.13: Field dependence of permittivity and loss tangent for a 450 nm thick, 180 nm grain-sized barium titanate thin film on copper .................................95

Figure 3.14: Temperature dependence of permittivity and loss tangent for a 450 nm thick, 180 nm grain-sized barium titanate thin film on copper.................................96

Figure 3.15: SEM micrographs of barium titanate thin films dried from a) 200°C to d) 275°C for 5 minutes.................................................................................97

Figure 3.16: SEM micrographs of barium titanate thin films dried at 250°C for a) 2:30 to d) 10:00 minutes.................................................................................98

Figure 3.17: Solution preparation procedure for a) methanol-diluted and b) acetic acid diluted barium titanate solutions.................................................................99

Figure 3.17: SEM micrographs barium titanate thin films with thickness ranging from a) 3-layers to c) 5-layers for films derived from solutions containing DEA.............................................................................100

Figure 3.18: X-ray diffraction patterns for a pure barium titanate thin film after firing. The lower pattern is an as-fired film. The top pattern is a film reoxidized at 450°C and 10⁻⁴ Torr O₂ .............................................................................102

Figure 3.19: Loss tangent distributions for barium titanate films reoxidized under varying conditions .............................................................................103
Figure 3.20: Field dependence of permittivity and loss tangent for a 580 nm thick, 140 nm grain-sized barium titanate thin film on copper. ........................................ 103

Figure 3.21: Temperature dependence of permittivity and loss tangent for a 580 nm thick, 140 nm grain-sized barium titanate thin film on copper. ............................... 104

Figure 3.22: Frequency dependence of permittivity (closed circles) and loss tangent (open circles) for a barium titanate thin film at 0 bias (red) and 8V bias (140 kV/cm) (blue). ........................................................................................................ 104

Figure 3.23: Polarization versus field for barium titanate on copper. ................................. 105

Figure 3.24: Field dependence of permittivity and loss tangent for a 780 nm thick, 161 nm grain-sized barium titanate thin film on copper. .................................................... 106

Figure 3.25: Temperature dependence of permittivity and loss tangent for a 780 nm thick, 161 nm grain-sized barium titanate thin film on copper. ............................... 107

Figure 3.26: Field dependence of permittivity for barium titanate thin films deposited on copper substrates (blue) and platinized silicon (red). ............................................. 107

Figure 3.27: Permittivity versus temperature plots for fine-grained bulk ceramics, thin films on platinized silicon, and a film on copper ...................................................... 108

Figure 4.1: X-ray diffraction patterns for barium titanate thin films processed between 700°C and 900°C on copper. ............................................................................. 111

Figure 4.2: 3µm x 3µm topographical AFM scans of barium titanate processed at a) 700°C, b) 800°C, and c) 900°C. .................................................................................. 112

Figure 4.3: Secondary electron images of cross-sections of barium titanate thin films processed at a) 700°C, b) 800°C, and c) 900°C. ................................................................. 112

Figure 4.4: Average grain size as a function process temperature for a series of barium titanate thin films on copper. ................................................................. 113

Figure 4.5: Temperature dependence of permittivity and loss tangent for a grain size series of barium titanate thin films on copper substrates. ................................. 113

Figure 4.6: Dependence of the average grain size on the Curie point of barium titanate thin films. ........................................................................................................ 114

Figure 4.7: FT-IR absorbance spectra of barium titanate thin films processed between 700°C and 900°C. .................................................................................. 115
Figure 4.8: Field dependence of permittivity and loss tangent of a series of barium titanate thin films with varying grain size. ................................................................. 117

Figure 4.9: Relative permittivity at 20°C as a function of average grain size from several barium titanate scaling effects studies ................................................................. 118

Figure 4.10: X-ray diffraction patterns of a) as-deposited and b) as-fired barium titanate thin films on copper. The discontinuous copper diffraction arc in the as-fired sample suggests large-scale grain growth. ........................................... 120

Figure 5.1: Temperature dependence of permittivity for pure barium titanate on copper. The shaded region represents the X7R EIA specification for capacitance stability ........................................................................................................ 121

Figure 5.2: Solution preparation procedure for a barium titanate zirconate hybrid-chelate solution chemistry ........................................................................................................ 122

Figure 5.3: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides. The shaded region represents the conditions where barium titanium and zirconium oxidize and copper is reduced ........... 123

Figure 5.4: X-ray diffraction patterns for Ba(Ti$_{1-x}$Zr$_x$)O$_3$ thin films processed at 900°C on copper ........................................................................................................ 123

Figure 5.5: Measured lattice parameter and lattice parameter calculated from Vegard’s Law for barium titanate zirconate thin films ........................................................................................................ 124

Figure 5.6: Temperature dependence of permittivity and loss tangent for Ba(Ti$_{1-x}$Zr$_x$)O$_3$ thin films on copper substrates ........................................................................................................ 125

Figure 5.7: Phase transition temperature versus composition of barium titanate zirconate thin films and bulk ceramics. ........................................................................................................ 126

Figure 5.8: Permittivity at $T_{\text{max}}$ versus composition for barium titanate zirconate thin films ........................................................................................................ 126

Figure 5.9: 3µm x 3µm topographical AFM scans of a series of barium titanate zirconate thin films with compositions of a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Zr$_{0.05}$)O$_3$, c) Ba(Ti$_{0.80}$Zr$_{0.10}$)O$_3$, d) Ba(Ti$_{0.75}$Zr$_{0.25}$)O$_3$. ........................................................................................................ 127

Figure 5.10: Average grain size versus composition for barium titanate zirconate thin films ........................................................................................................ 127

Figure 5.11: Temperature dependence of permittivity for a reference set of pure barium titanate thin films of varying grain size ........................................................................................................ 128
Figure 5.12: Grain size dependence of permittivity at $T_{\text{max}}$ for barium titanate zirconate and barium titanate thin films. ................................................................. 128

Figure 5.13: Field dependence of permittivity and loss tangent for a composition series of barium titanate zirconate thin films at room temperature .......... 129

Figure 5.14: Field dependence of permittivity and loss tangent for a composition series of barium titanate zirconate thin films at each composition’s respective $T_{\text{max}}$ ............................................................ 130

Figure 5.15: Tunability as a function of temperature for a field strength of 130 kV/cm for Ba(Ti$_{1-x}$Zr$_x$)O$_3$ thin films ................................................................................................................................. 131

Figure 5.16: Temperature dependence of permittivity at 1, 10, and 100 kHz for a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Zr$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Zr$_{0.10}$)O$_3$, and d) Ba(Ti$_{0.75}$Zr$_{0.25}$)O$_3$ thin films ......................................................................................................................... 132

Figure 5.17: Temperature dependence of permittivity with EIA specification X7R regions mapped for a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Zr$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Zr$_{0.10}$)O$_3$ and d) Ba(Ti$_{0.75}$Zr$_{0.25}$)O$_3$ thin films ......................................................................................................................... 133

Figure 5.18: Solution preparation procedure for a barium titanate hafnate hybrid-chelate solution chemistry. ................................................................. 134

Figure 5.19: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides. The shaded region represents the conditions where barium titanium and zirconium oxidize and copper is reduced ......................................................................................................................... 135

Figure 5.20: X-ray diffraction patterns for Ba(Ti$_{1-x}$Hf$_x$)O$_3$ thin films processed at 900°C on copper. ................................................................................ 136

Figure 5.21: Measured lattice parameter and lattice parameter calculated from Vegard’s Law for barium titanate hafnate thin films. ................................................................. 137

Figure 5.22: Temperature dependence of permittivity and loss tangent for Ba(Ti$_{1-x}$Hf$_x$)O$_3$ thin films on copper substrates ................................................................. 138

Figure 5.23: Phase transition temperature versus composition of barium titanate hafnate thin films and bulk ceramics ................................................................. 138

Figure 5.24: Permittivity at $T_{\text{max}}$ versus composition for barium titanate hafnate thin films ........................................................................................................ 139
Figure 5.25: 3µm x 3µm topographical AFM scans of a series of barium titanate hafnate thin films with compositions of a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Hf$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Hf$_{0.10}$)O$_3$, d) Ba(Ti$_{0.75}$Hf$_{0.25}$)O$_3$.

Figure 5.26: Average grain size versus composition for barium titanate hafnate thin films.

Figure 5.27: Grain size dependence of permittivity at $T_{\text{max}}$ for barium titanate hafnate and barium titanate thin films.

Figure 5.28: Field dependence of permittivity and loss tangent for a composition series of barium titanate hafnate thin films at room temperature.

Figure 5.29: Temperature dependence of permittivity at 1, 10, and 100 kHz for a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Hf$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Hf$_{0.10}$)O$_3$, and d) Ba(Ti$_{0.75}$Hf$_{0.25}$)O$_3$ thin films.

Figure 5.30: Temperature dependence of permittivity with EIA specification X7R regions mapped for a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Hf$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Hf$_{0.10}$)O$_3$, and d) Ba(Ti$_{0.75}$Hf$_{0.25}$)O$_3$ thin films.

Figure 5.31: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides. The shaded region represents the conditions where barium, titanium, and tin oxidize and copper is reduced.

Figure 5.32: Solution preparation procedure for a barium titanate stannate hybrid-chelate solution chemistry.

Figure 5.33: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides with the actual firing conditions plotted.

Figure 5.34: X-ray diffraction patterns for Ba(Ti$_{1-x}$Sn$_x$)O$_3$ thin films processed at 900°C on copper.

Figure 5.35: Measured lattice parameter and lattice parameter calculated from Vegard’s Law for barium titanate stannate thin films.

Figure 5.36: Temperature dependence of permittivity and loss tangent for Ba(Ti$_{1-x}$Sn$_x$)O$_3$ thin films processed at 900°C on copper.

Figure 5.37: Phase transition temperature versus composition of barium titanate stannate thin films and bulk ceramics.

Figure 5.38: Permittivity at $T_{\text{max}}$ versus composition for barium titanate stannate thin films.
Figure 5.39: 3µm x 3µm topographical AFM scans of a series of barium titanate stannate thin films with compositions of a) BaTiO₃, b) Ba(Ti₀.₉₅Sn₀.₀₅)O₃, c) Ba(Ti₀.₉₀Sn₀.₁₀)O₃, d) Ba(Ti₀.₇₅Sn₀.₂₅)O₃.

Figure 5.40: Average grain size versus composition for barium titanate stannate thin films.

Figure 5.41: Grain size dependence of permittivity at T_max for barium titanate stannate and barium titanate thin films.

Figure 5.42: Field dependence of permittivity and loss tangent for a composition series of barium titanate stannate thin films at room temperature.

Figure 5.43: Temperature dependence of permittivity at 1, 10, and 100 kHz for a) BaTiO₃, b) Ba(Ti₀.₉₅Sn₀.₀₅)O₃, c) Ba(Ti₀.₉₀Sn₀.₁₀)O₃, and d) Ba(Ti₀.₇₅Sn₀.₂₅)O₃ thin films.

Figure 5.44: Temperature dependence of permittivity with EIA specification X7R regions mapped for a) BaTiO₃, b) Ba(Ti₀.₉₅Sn₀.₀₅)O₃, c) Ba(Ti₀.₉₀Sn₀.₁₀)O₃, and d) Ba(Ti₀.₇₅Sn₀.₂₅)O₃ thin films.

Figure 6.1: Equilibrium phase diagrams for the BaO-TiO₂ system.

Figure 6.2: X-ray diffraction patterns of Ba₁₋ₓTiO₃ thin films with x ranging from 0 to 0.05 fired at 900°C for 30 minutes.

Figure 6.3: X-ray diffraction patterns of BaTi₁₋ₓO₃ thin films with x ranging from 0 to 0.05 fired for 30 minutes at 900°C.

Figure 6.4: X-ray diffraction patterns of Ba₁₋ₓTiO₃ thin films with x ranging from 0 to 0.05 fired at 900°C for 14 hours.

Figure 6.5: X-ray diffraction patterns of BaTi₁₋ₓO₃ thin films with x ranging from 0 to 0.05 fired at 900°C for 14 hours.

Figure 6.6: Field dependence of permittivity and loss tangent for a 680 nm thick, 140 nm grain-sized barium titanate thin film on copper fired at 900°C and 10⁻¹³ atm O₂ without reoxidation.

Figure 6.7: X-ray diffraction patterns for pure and Mn-doped barium titanate thin films on copper. Film stoichiometry is BaTi₁₋ₓMnₓO₃, where the levels indicated represent x.

Figure 6.8: X-ray diffraction patterns for pure and Mg-doped barium titanate thin films on copper. Film stoichiometry is BaTi₁₋ₓMgₓO₃, where the levels indicated represent x.
**Figure 6.9:** X-ray diffraction patterns for pure and Ca-doped barium titanate thin films on copper. Film stoichiometry is $\text{BaTi}_{1-x}\text{Ca}_x\text{O}_3$ where the levels indicated represent $x$. .................................................................166

**Figure 6.10:** SEM secondary electron topographical images of manganese-doped barium titanate ($\text{BaTi}_{1-x}\text{Mn}_x\text{O}_3$) thin films with compositions of a) pure $\text{BaTiO}_3$, b) 100 ppm Mn, c) 1000 ppm Mn, and d) 1 mol% Mn ......................167

**Figure 6.11:** SEM secondary electron topographical images of magnesium-doped barium titanate ($\text{BaTi}_{1-x}\text{Mg}_x\text{O}_3$) thin films with compositions of a) pure $\text{BaTiO}_3$, b) 100 ppm Mg, c) 1000 ppm Mg, and d) 1 mol% Mg .................168

**Figure 6.12:** SEM secondary electron topographical images of calcium-doped barium titanate ($\text{BaTi}_{1-x}\text{Ca}_x\text{O}_3$) thin films with compositions of a) pure $\text{BaTiO}_3$, b) 100 ppm Ca, c) 1000 ppm Ca, and d) 1 mol% Ca. ..................169

**Figure 6.13:** Average grain diameter plotted versus dopant level of manganese-doped barium titanate ($\text{BaTi}_{1-x}\text{Mn}_x\text{O}_3$). Error bars indicate a 95% confidence interval for each composition .................................................................168

**Figure 6.14:** Average grain diameter plotted versus dopant level of magnesium-doped barium titanate ($\text{BaTi}_{1-x}\text{Mg}_x\text{O}_3$). Error bars indicate a 95% confidence interval for each composition .................................................................169

**Figure 6.15:** Average grain diameter plotted versus dopant level of calcium-doped barium titanate ($\text{BaTi}_{1-x}\text{Ca}_x\text{O}_3$). Error bars indicate a 95% confidence interval for each composition .................................................................169

**Figure 6.16:** Electric field dependence of permittivity and loss tangent for 100 ppm Ca-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $\text{O}_2$, b) $5 \times 10^{-12}$ atm $\text{O}_2$, and c) $5 \times 10^{-11}$ atm $\text{O}_2$ .................................................................171

**Figure 6.17:** Frequency dependence of permittivity and loss tangent for 100 ppm Ca-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $\text{O}_2$, b) $5 \times 10^{-12}$ atm $\text{O}_2$, and c) $5 \times 10^{-11}$ atm $\text{O}_2$ .................................................................171

**Figure 6.18:** Electric field dependence of permittivity and loss tangent for 100 ppm Mg-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $\text{O}_2$, b) $5 \times 10^{-12}$ atm $\text{O}_2$, and c) $5 \times 10^{-11}$ atm $\text{O}_2$ .................................................................171

**Figure 6.19:** Frequency dependence of permittivity and loss tangent for 100 ppm Mg-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $\text{O}_2$, b) $5 \times 10^{-12}$ atm $\text{O}_2$, and c) $5 \times 10^{-11}$ atm $\text{O}_2$ .................................................................172

**Figure 6.20:** Electric field dependence of permittivity and loss tangent for 100 ppm Mn-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $\text{O}_2$, b) $5 \times 10^{-12}$ atm $\text{O}_2$, and c) $5 \times 10^{-11}$ atm $\text{O}_2$ .................................................................172
Figure 6.21: Frequency dependence of permittivity and loss tangent for 100 ppm Mn-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$.................................................................173

Figure 6.22: Electric field dependence of permittivity and loss tangent for 1000 ppm Ca-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$.................................................................174

Figure 6.23: Frequency dependence of permittivity and loss tangent for 1000 ppm Ca-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$.................................................................174

Figure 6.24: Electric field dependence of permittivity and loss tangent for 1000 ppm Mg-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$.................................................................175

Figure 6.25: Frequency dependence of permittivity and loss tangent for 1000 ppm Mg-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$.................................................................175

Figure 6.26: Electric field dependence of permittivity and loss tangent for 1000 ppm Mn-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$ .................................................................176

Figure 6.27: Frequency dependence of permittivity and loss tangent for 1000 ppm Mn-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$ .................................................................176

Figure 6.28: Electric field dependence of permittivity and loss tangent for 1mol% Ca-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$ .................................................................177

Figure 6.29: Frequency dependence of permittivity and loss tangent for 1 mol% Ca-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$ .................................................................177

Figure 6.30: Electric field dependence of permittivity and loss tangent for 1mol% Mg-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$ .................................................................178

Figure 6.31: Frequency dependence of permittivity and loss tangent for 1 mol% Mg-doped barium titanate processed at a) $5 \times 10^{13}$ atm O$_2$ b) $5 \times 10^{12}$ atm O$_2$ and c) $5 \times 10^{11}$ atm O$_2$ .................................................................178
Figure 6.32: Electric field dependence of permittivity and loss tangent for 1mol% Mn-doped barium titanate processed at a) 5x10^{13} atm O_2 b) 5x10^{12} atm O_2 and c) 5x10^{11} atm O_2 ........................................................................................................179

Figure 6.33: Frequency dependence of permittivity and loss tangent for 1 mol% Mn-doped barium titanate processed at a) 5x10^{13} atm O_2 b) 5x10^{12} atm O_2 and c) 5x10^{11} atm O_2 ........................................................................................................179

Figure 6.34: DC leakage current density versus applied bias for a 780 nm thick barium titanate thin film processed at 900°C and 10^{13} atm O_2 without reoxidation........................................................................................................181

Figure 7.1: SEM image of fractured cross section of a barium titanate thin film on copper. ........................................................................................................................................184

Figure 7.2: Equilibrium phase diagram for the system BaO-B_2O_3 ..........................................................185

Figure 7.3: X-ray diffraction patterns for BaTiO_3-B_2O_3 thin films on copper..............................187

Figure 7.4: X-ray diffraction patterns for BaTiO_3 – 869°C eutectic BaO-B_2O_3 thin films ..................................................................................................................188

Figure 7.5: X-ray diffraction patterns for BaTiO_3 – BaO-2B_2O_3 thin films....................................188

Figure 7.6: X-ray diffraction patterns for BaTiO_3 – 899°C eutectic BaO-B_2O_3 thin films ........................................189

Figure 7.7: X-ray diffraction patterns for BaTiO_3 – BaO thin films ................................................189

Figure 7.8: X-ray diffraction patterns of a) pure BaTiO_3 b) BaTiO_3 – 2% 899°C eutectic BaO-B_2O_3, c) BaTiO_3 – 5% 899°C eutectic BaO-B_2O_3, The discontinuous BaTiO_3 diffraction arcs in the 5% sample suggests large-scale grain growth .........................................................................................190

Figure 7.9: SEM topographical micrographs of BaTiO_3 – B_2O_3 with compositions ranging from a) Pure BaTiO_3 to f) 6.9 mole % B_2O_3 .................................................................................................191

Figure 7.10: SEM topographical micrographs of BaTiO_3 – 869°C eutectic BaO-B_2O_3 with compositions ranging from a) 0.5% glass to f) 5% glass. ................................................191

Figure 7.11: SEM topographical micrographs of BaTiO_3 – BaO-2B_2O_3 with compositions ranging from a) 0.5% glass to f) 5% glass ..............................................................192

Figure 7.12: SEM topographical micrographs of BaTiO_3 – 899°C eutectic BaO-B_2O_3 with compositions ranging from a) 0.5% glass to f) 5% glass ..............................................................192

Figure 7.13: SEM topographical micrographs of BaTiO_3 – BaO with compositions ranging from a) Pure BaTiO_3 to f) 5 mole % BaO ..................................................................................................193
Figure 7.14: Average grain diameter versus percent flux phase for barium titanate thin films with B$_2$O$_3$ additions. ................................................................. 194

Figure 7.15: Measured lattice parameter as a function of flux content for barium titanate thin films with B$_2$O$_3$ added................................................................. 195

Figure 7.16: Average grain diameter versus mole percent excess BaO for barium titanate thin films ................................................................. 195

Figure 7.17: Measured lattice parameter as a function excess BaO for barium titanate thin films................................................................. 196

Figure 7.18: Average grain diameter versus percent flux phase for barium titanate thin films with barium borate additions................................................................. 196

Figure 7.19: Measured lattice parameter as a function of flux content for barium titanate-869°C eutectic BaO-B$_2$O$_3$ thin films ................................................................. 197

Figure 7.20: Measured lattice parameter as a function of flux content for BaTiO$_3$-BaO-2B$_2$O$_3$ thin films ................................................................. 197

Figure 7.21: Measured lattice parameter as a function of flux content for barium titanate-899°C eutectic BaO-B$_2$O$_3$ thin films ................................................................. 198

Figure 7.22: X-ray diffraction pattern of the {002} family of planes for 899°C eutectic fluxed barium titanate................................................................. 199

Figure 7.23: SEM micrographs of fractured cross sections of barium titanate films containing a) 0% B$_2$O$_3$, b) 0.5% B$_2$O$_3$, and c) 1 % B$_2$O$_3$ .................................................. 200

Figure 7.24: SEM micrographs of fractured cross sections of barium titanate-869°C eutectic BaO-B$_2$O$_3$ films with concentrations of a) 0.5%, b) 1%, and c) 2%. .................................................. 200

Figure 7.25: SEM micrographs of fractured cross sections of barium titanate-BaO-2B$_2$O$_3$ films with concentrations of a) 0.5%, b) 1%, and c) 2.5% .... 201

Figure 7.26: SEM micrographs of fractured cross sections of barium titanate-899°C eutectic BaO-B$_2$O$_3$ films with concentrations of a) 0.5%, b) 1%, and c) 2% .................................................................................. 201

Figure 7.27: SEM micrographs of fractured cross sections of barium titanate films containing a) 0.5 mol% BaO, b) 1 mol% BaO, and c) 2 mol% BaO .................................................................................. 201
Figure 7.28: Temperature dependence of permittivity and loss tangent for BaTiO$_3$-B$_2$O$_3$. Average grain sizes are shown with 147 nm representing 0%, 179 nm representing 0.5%, and 184 nm representing 1%. .......................................................... 202

Figure 7.29: Temperature dependence of permittivity and loss tangent for BaTiO$_3$-869°C eutectic BaO-B$_2$O$_3$. Average grain sizes are shown with 107 nm representing 0%, 127 nm representing 0.5%, 138 nm representing 1%, and 157 nm representing 2%. .......................................................... 202

Figure 7.30: Temperature dependence of permittivity and loss tangent for BaTiO$_3$-BaO-2B$_2$O$_3$. Average grain sizes are shown with 107 nm representing 0%, 132 nm representing 0.5%, and 144 nm representing 1%. .......................................................... 203

Figure 7.31: Temperature dependence of permittivity and loss tangent for BaTiO$_3$-899°C eutectic BaO-B$_2$O$_3$. Average grain sizes are shown with 107 nm representing 0%, 127 nm representing 0.5%, and 147 nm representing 1%. .......................................................... 203

Figure 7.32: Temperature dependence of permittivity and loss tangent for BaTiO$_3$-BaO. Average grain sizes are shown with 147 nm representing 0%, 158 nm representing 0.5 mol%, and 164 nm representing 1 mol%. .......................................................... 204

Figure 7.33: Maximum relative permittivity as a function of grain size for barium borate-based fluxed barium titanate thin films of varying compositions. ..... 204

Figure 7.34: Relative permittivity at 20°C as a function of average grain size from several barium titanate scaling effects studies .......................................................... 205

Figure 7.35: Field dependence of permittivity and loss tangent for B$_2$O$_3$-fluxed barium titanate thin films on copper .......................................................... 207

Figure 7.36: Permittivity versus temperature plots for fine-grained bulk ceramics, thin films on platinized silicon, a film on copper, and a fluxed film on copper ........................................................................................................... 208

Figure 7.37: Equilibrium phase diagram for the system BaO-P$_2$O$_5$ .......................................................... 209

Figure 7.38: X-ray diffraction patterns for BaTiO$_3$ – 850°C eutectic BaO-P$_2$O$_5$ thin films with compositions ranging from 1 to 5 mol% eutectic composition. .... 210

Figure 7.39: Measured lattice parameter as a function of flux content for BaTiO$_3$-850°C eutectic BaO-P$_2$O$_5$ thin films .......................................................... 211
Figure 7.40: SEM topographical micrographs of BaTiO$_3$ – 850°C eutectic BaO-P$_2$O$_5$ with compositions ranging from a) 1% glass, b) 1.5% glass, c) 2.5% glass, and d) 5% glass. .................................................................................................................. 212

Figure 7.41: Average grain diameter versus percent flux phase for barium titanate thin films with barium phosphate additions. .................................................................................................................. 212

Figure 7.42: SEM micrographs of fractured cross sections of barium titanate-850°C eutectic BaO- P$_2$O$_5$ films with concentrations of a) 0%, b) 1%, and c) 1.5% ........................................................................................................ 213

Figure 7.43: Field dependence of permittivity and loss tangent for a) 1% barium phosphate, b) 1.5% barium phosphate, c) 2.5% barium phosphate, and d) 5% barium phosphate .................................................................................................................. 214

Figure 8.1: Optical micrograph of a platinum electrode on a cofired solution derived barium titanate thin film. .................................................................................................................................................. 219

Figure 8.2: Frequency dependence of capacitance and loss tangent for a nominal 1cm$^2$ capacitor ......................................................................................................................................................... 219

Figure 8.3: a) Optical micrograph of a 3mm electrode cofired after a burnout anneal and b) an optical micrograph of a crack in a BaTiO$_3$ film with a cofired electrode. ................................................................................................................ 220

Figure 10.1: Schematic of the temperature dependent measurement apparatus used in this thesis. ......................................................................................................................................................... 250
List of Tables

Table 6.1: *Typical impurity levels in barium titanate solution precursor chemicals* ........182

Table 7.1: *Compositions of the thin films in the barium borate liquid phase sintering study*................................................................................................................................. 186

Table 7.2: *Compositions of the thin films in the barium phosphate liquid phase sintering study*................................................................................................................................. 209
1. Introduction:

This thesis outlines the development of a commercially viable embedded capacitor technology based upon a high permittivity thin film deposited on an inexpensive metal foil substrate. This work represents a collaborative effort between an industry sponsor, DuPont, and an academic institution, North Carolina State University.

As electronics become increasingly functional and portable, there is a strong driving force toward miniaturization of electronic circuits and the devices in which they operate. Additionally, performance increases in integrated circuits has necessitated advancements in passive technology including a need to place decoupling capacitors with close proximity to reduce inductive losses. The 2-dimensional placement of surface-mount components places limitations on the minimum distance these parts can be placed from ICs. A 3-dimensional embodiment by embedding passives within the layers of a printed wiring board would alleviate several of these issues – size, functionality, and performance. This thesis describes a technology by which decoupling capacitors can be processed and developed in an embodiment suitable for lamination into a printed wiring board for high-performance applications by depositing a high permittivity ferroelectric thin film on copper foil substrates using thermodynamic equilibrium processing conditions to avoid deleterious interactions between the film and the substrate.

1.1 Outcomes:

This research resulted in the following six technical outcomes:

1) A commercially viable and robust chemical solution containing barium and titanium with the potential for large area deposition was developed. The solution is of relatively low toxicity while maintaining reasonable stability, with the chemical flexibility to allow for the addition of several dopants and substituent cations.

2) A process was developed by which a barium titanate chemical solution could be deposited on a base-metal copper substrate and heat-treated such that the organic
precursor crystallizes into barium titanate while the copper substrate remains metallic. In particular, the use of gas-phase reactions to control the level of free oxygen in the firing atmosphere was optimized.

3) The solution chemistry modifications were developed such that unwanted defect concentrations resulting from raw material impurities, non-stoichiometry, and subsequent processing were ameliorated.

4) The correlation between average thin film grain size on the dielectric response was explored. In doing so, the effects of crystallite size and average grain size were decoupled through physical and electrical characterization.

5) The ability to engineer the temperature dependence of the phase transition in barium titanate by $B$-site cation substitution was demonstrated. Attention focused on the so-called ‘phase transition pinchers’ of barium zirconate, barium hafnate, and barium stannate flattening the overall dielectric response with temperature was the primary goal.

6) A composition was developed to improve film densification and crystallinity and increase grain size. The results display unparalleled crystal and dielectric properties for polycrystalline thin film ferroelectric materials.
2: Literature Review

2.1: Embedded Passives

Advanced electronic devices contain two distinct categories of components: active components, such as integrated circuits (ICs) that amplify and process signals and passive components, including resistors, inductors, and capacitors, that condition. The improvements in performance and dimensionality of active components have been well publicized through the scaling trend of Moore’s Law. Perhaps less known is the necessary passive scaling to provide support for advanced active circuits. An example of this is the distance from which decoupling capacitors can be located from an integrated circuit operating at a high frequency. To avoid inductive losses, the distances must be minimized.\(^1\) In addition to reducing inductive losses, this also decreases system noise and provides for cleaner signals.\(^2\) Practically, placing passives close to ICs has limitations based upon assembly and device size. This is particularly clear when examining the latest trends in consumer electronics, which continually demand increased functionality and decreased package size. Current electronics fabricated using surface mount assembly routinely approach this situation where the entire board surface is occupied. By embedding passive components within the layers of a printed wiring board (PWB) two primary advantages are appreciated: 1) lead length is dramatically reduced, and 2) 3-dimensional integration enables much greater density of components to board volume. There are additional advantages to embedding passives including increases in reliability from a reduction of solder joints and decreases in manufacturing costs by replacing pick-and-place assembly with lithography and planar processing many components in parallel.\(^1, 3, 4\) The increase in free surface space allows for more ICs and increased device functionality. This is particular true in the cellular phone market where the number of passive components typically outnumbers integrated circuits by a ratio of 20:1. Embedded passives are of interest to the personal computer industry as well, where the market seeks a decoupling capacitor technology capable of operating at modest frequencies with very low inductance. It has been predicted that by 2009, 40% of passive components in a personal computer will be embedded; the majority of these devices are resistors and capacitors. A major requirement of embedded decoupling capacitors is to
supply a sufficient capacitance per unit area, where suitable capacitance densities range from 0.1 to 100 µF/cm$^2$.\textsuperscript{4}

**Figure 2.1:** Schematic of embedded decoupling capacitors within the layers of a printed wiring board.

Several technologies have been developed for embedded capacitors. These include polymer laminates, barium titanate loaded composites, barium titanate-based thick films, and lead zirconate titanate thin films. To form the composite films, a high permittivity powder is mixed into a polymer matrix and the composite is screen printed onto predefined electrodes and cured at temperatures of less than 200°C. The film is then laminated to the PWB and a polymer composite electrode is printed on top. Thick films are composites of low melting temperature glasses and barium titanate powders that are screen printed onto copper foils and processed at temperature generally less than 1000°C in reductive atmospheres. The foil/dielectric stacks are then laminated into a PWB and electrode areas are defined by photolithography and etching of the copper foil. Thin film technologies are based upon a chemical solution deposition approach using either a spin casting or dip coating technique to coat a nickel or nickel-coated copper foil. The foil/dielectric stacks are processed at temperatures of ~650°C prior to lamination into the printed circuit board. Each of the composite technologies have the capability of supplying 3 to 200 nF/cm$^2$ while the thick film gives 150 nF/cm$^2$ and the thin lead zirconate titanate films give ~ 350 nF/cm$^2$.\textsuperscript{1,3,5} It can be seen that these technologies satisfy just the lower end of the requirements for decoupling. Therefore, a need exists for a higher performance supplying at least 1 µF/cm$^2$ to expand the market and in particular satisfy the computing industry.
2.2: Ferroelectric Crystals

The crystal structures of materials can be classified into 32 distinct point groups, which represent the symmetry present. Inspection of these symmetries reveals several features of technological and scientific interest. Of the 32 point groups, 20 are characterized as piezoelectric -- that is, upon the application of a mechanical stress, an electronic displacement can be induced in the crystal. Equivalently, an applied electric field can induce a mechanical strain, a property known as the converse piezoelectric effect. The 20 point groups, which can support piezoelectricity are non-centrosymmetric. While the lack of a center of symmetry is a necessary condition for piezoelectricity, it is not necessarily sufficient to observe a piezoelectric effect. For example, the cubic point group 432 is the only non-centrosymmetric symmetry that is unable to support piezoelectricity. Further categorization of the piezoelectric point groups reveals that in ten of the twenty, the electronic polarization is spontaneous, remaining finite in the absence of an applied stress or electric field. This spontaneous polarization is characteristic of pyroelectricity and is a consequence of the atomic arrangement within the unit cell where the positive and negative charge centers are not coincident, thus establishing a resultant spontaneous electric dipole. Ferroelectricity occurs in a select number of these 10 polar point groups and is distinguished by having a spontaneous electric dipole that can be reoriented along other equivalent crystallographic directions under application of the proper driving force, i.e. an electric field. From this discussion, it is observed that the necessary conditions for ferroelectricity to exist are a non-centrosymmetric crystal structure, a spontaneous permanent dipole, and the ability to orient this dipole to equivalent crystallographic directions with the application of a suitable field.

2.2.1 Historical Perspective of Ferroelectric Crystals

Ferroelectricity, or Seignette-electricity as it is sometimes referred to in historical literature, is characterized by a spontaneous reorientable electric dipole in crystal. The name ferroelectricity stems from the hysteretic nature of dielectric displacement with applied field,
analogous to the hysteresis in magnetization with magnetic field present in ferromagnets. The word ferroelectricity was thus chosen out of convenience and in no way implies that iron is a necessary component to all crystals displaying the ferroelectric phenomenon. It has even been suggested that the term ferroelectricity had caught on quicker than its synonym Seignette-electricity simply because it was more palatable. 

The first report of the ferroelectric phenomenon was by Valasek in 1921 on single crystal Rochelle salt (sodium potassium tartrate tetrahydrate, NaKC₄H₄O₆•4H₂O, also referred to as Seignette salt). Rochelle salt served as the earliest ferroelectric material studied until the discovery of ferroelectricity in potassium dihydrogen phosphate (KH₂PO₄) by Busch and Scherrer in 1935. While interesting from a scientific standpoint, any practical usage of Rochelle salt or potassium dihydrogen phosphate was limited by their water solubility. As such, ferroelectricity remained a scientific curiosity in its infancy until the discovery of ferroelectricity in the more chemically stable compound barium titanate (BaTiO₃) in 1945 and 1946 independently in Russia and the United States. The Russian group of Vul and Goldman were probably the first to report a non-linear response in the permittivity with applied field and an apparent peak in permittivity at a phase transition, however they did not go so far as to classify the material as ferroelectric. Rather they confirm the unpublished work of Ginsburg who reported a pyroelectric to non-pyroelectric phase transition in the material (there is also an unpublished report that the Japanese group of T. Ogawa may have been the first to record the peak in permittivity at the phase transition). Through X-ray diffraction investigations exploring the crystal structure of the alkaline-earth titanates it was revealed that not all had the cubic perovskite structure at room temperature. Specifically, it was found that barium titanate had a slight tetragonal distortion at 22°C and through hot-stage XRD investigations, Megaw found a transition to cubic symmetry at a temperature below 200°C. With the X-ray evidence of a distortion at hand from Megaw’s work, Vul and Goldman, upon the observation of hysteresis in the dielectric displacement, concluded that barium titanate must exhibit ferroelectricity. Concurrently, von Hippel and coworkers, while investigating the dielectric response of several alkaline earth titanate compounds with temperature, field and frequency, observed a maxima in permittivity at ~116.5°C in BaTiO₃ as well minority peaks at −70 and 10°C. This work went
a step further by investigating dielectric hysteresis as a function of temperature and unambiguously identified a ferroelectric-paraelectric displacive transition with support of temperature dependent X-ray analysis.\textsuperscript{14} Miyake and Ueda observed peak splitting in X-ray diffraction patterns suggestive of a tetragonal distortion that disappeared at temperatures in excess of 110°C. They also observed an anomalous change in specific heat at 112.5°C in BaTiO$_3$ powder, but similarly to Vul and Goldman, did not initially classify the material as a ferroelectric, only as a material possessing a displacive transition.\textsuperscript{10}

### 2.2.2 Perovskite Crystal Structure

The perovskite crystal structure is perhaps the most technologically important structure supporting ferroelectricity. The structure is of space group $Pm\bar{3}m$ in the non-polar cubic state and is characterized by a chemical formula of ABO$_3$ for oxides consisting of 1,2, or 3-valent $A$-site and 5,4, or 3-valent $B$-site cations respectively and 2-valent anions. As indicated by the space group, the perovskite structure is formed from a primitive lattice and one atom of each species per unit cell. The O-anions are located on the face centers of the unit cell in the cubic phase while the $A$-site ions are traditionally denoted as positioned at the cell corners with the $B$-site ions at the cell center. It should be noted that the $B$-site ions could be equivalently denoted as being positioned at the cell corners with the $A$-site ions at the cell center, however the reasons for the former notation become clear when discussing the structure in terms of polyhedra. Figure 2.2 shows the cubic structure of a prototypical perovskite unit cell.
An alternative and perhaps more insightful approach views the perovskite structure in terms of polyhedra packing. In this description the $B$-site ion sits equidistant and at the center of 6 anions, in an octahedral site, and the $A$-site ion is located equidistant from 12 anions and is thus 12-coordinated. If an octahedron is constructed with corners at the anions and in the center a $B$-Site ion, a packing structure is realized with corner-sharing octahedra and $A$-Site ions sitting in the interstices of these octahedra. The lattice in this embodiment is shown in Figure 2.3a. This approach of using polyhedra packing allows one to better visualize the effects that changing cation radii have on the crystal structure of the material. For example, it is known that in SrTiO$_3$ the structure at room temperature is cubic. This is a consequence of the $A$-site strontium cations fitting nearly perfectly in the 12-coordinated interstices of the octahedral packing structure and allows the $B$-site titanium cation to sit in the center of the oxygen octahedra. If a larger alkaline earth cation, such as barium, is substituted for strontium, a distortion of the structure occurs as the barium cations are now too large for their interstice position and the oxygen octahedra must alter its shape to accommodate the larger cation. Consequently the $B$-site titanium ion can no longer be positioned equidistant with its 6 near neighbor oxygen ions. Therefore, the titanium ion will be displaced toward any of the 6 cube faces resulting in a small tetragonal distortion to space group $P4mm$ in the unit cell as illustrated in Figure 2.3b.
In 1927 Goldschmidt formulated an equation to describe this behavior, known as the Goldschmidt tolerance factor.\(^{15}\)

\[
t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}
\]

Equation (2.1)

Where \(R_A\), \(R_B\), and \(R_X\) are the ionic radii of the \(A\)-site, \(B\)-site, and anion ions respectively. Tolerance factors equal to one predict a perfect packing of ions to form a cubic perovskite structure as is seen in room temperature \(\text{SrTiO}_3\). Tolerance factors greater than one occur if the \(A\)-site ion is large or the \(B\)-site ion is small and results in a distortion of the \(B\)-site toward one of the unit cell face anions, as is observed in \(\text{BaTiO}_3\). Tolerance factors less than one occur in the opposite situation and result in the \(B\)-site cation shifting positions toward one of the unit cell corners – a tilting of the octahedron. This occurs in materials such as \(\text{BiScO}_3\).

### 2.2.3 The Ferroelectric Phase Transition

As ferroelectric materials are cooled from high temperatures in their paraelectric phase, the permittivity of the material increases non-linearly as a phase-transition is
approached in accordance with Curie-Weiss behavior as shown in Figure 2.4 for a first-order transition and is governed by the following relation:

\[ \varepsilon_r = \varepsilon_0 + \frac{C}{T - T_0} \]  

Equation (2.2)

Where \( \varepsilon \) is the relative permittivity, \( \varepsilon_0 \) is the permittivity of free space, \( C \) is the Curie Constant, and \( T_0 \) is the Curie Temperature. For barium titanate, typical values for \( C \) are on the order of \( 10^5 \), while \( T_0 \) approximately \( 10^\circ \) below the Curie point, the temperature where the dielectric constant reaches a maximum.\(^{16} \)

![Figure 2.4: Temperature dependence of relative permittivity for a ferroelectric with a first order phase transition displaying Curie-Weiss behavior.](image)

In displacive ferroelectrics, a phase transition includes a change from a non-polar centro-symmetric structure to a polar non-centro-symmetric phase. In barium titanate, this occurs at temperatures around \( 125^\circ \text{C} \) as the crystal structure changes from cubic (\( m3m \)) to tetragonal (\( 4mm \)) and the titanium atom shifts from its position in the center of the oxygen octahedra to a position closer to one of the face centered oxygen ions as shown in Figure 2.3b. The result of the transition to the tetragonal symmetry is an elongation of the unit cell along one cube axis, denoted the \( c \) axis, and a contraction along the 2 remaining equivalent, \( a \) axes. In addition to the paraelectric/ferroelectric phase transition in BaTiO\(_3\), there are two other ferroelectric/ferroelectric phase transitions.\(^{17, 18} \) The first occurs at \( 0^\circ \text{C} \) as the crystal symmetry changes from tetragonal to orthorhombic (\( mmm \)). The second transition occurs at \( -90^\circ \text{C} \) as the crystal symmetry changes to rhombohedral (\( R3 \)).
Viewing the lattice in terms of lattice vibrations, the phase transition can be characterized according to a specific transverse optic (TO) phonon mode known as the soft-mode. The transverse optic mode of interest includes vibration of the $B$-site perovskite ion. This phonon mode decreases in frequency as the temperature approaches the phase transition (as indicated in Equation 2.3 where $K$ is a constant) at which point it condenses and approaches an infinite wavelength and zero-frequency at the Brillouin zone center ($k = 0$) as shown in Figure 2.5.\textsuperscript{19,20}

\[
\omega_{TO}^2 = K(T - T_0)
\]

Equation (2.3)

The lattice vibration that was the soft mode is now “frozen in” and represents a stabilization of the displacive transition, e.g. the displacive shift of a titanium ion toward one of the face centered oxygen ions in barium titanate. It should be noted that there are 3 equivalent TO modes active in the perovskite structure at high temperatures – one for each of the crystallographically equivalent $<00l>$ directions. The condensation of one the modes, for example at the phase transition in barium titanate where the cell elongates along one axis, does not necessarily result in a condensation of the other two TO modes along the equivalent $a$-axes. Condensation of the other modes results in the lower temperature phase transitions in barium titanate. At 0°C, one of the $a$-axis modes condenses and the polar axis changes from $<001>$ to $<011>$. At –90°C the final TO soft mode condenses and the polar axis orients
along the <111>. At temperatures above the phase transition, the finite wavelength of the soft-mode manifests in a situation where the multiple equivalent displacements of the lattice normalize to form a symmetric and thus non-ferroelectric structure. The significance of the soft mode and its temperature dependence on the phase transition is apparent when viewing the relationship of permittivity and frequency of vibration as shown in Equation 2.4 where $\varepsilon$ is permittivity and $\omega_s$ is the soft mode frequency at zero wavenumber.

$$\varepsilon \propto \frac{1}{\omega_s^2}$$  \hspace{1cm} \text{Equation (2.4)}

As the temperature decreases the soft-mode frequency lessens and the permittivity increases. This provides a phenomenological description of the permittivity increase as the phase transition is approached from high temperatures.

The soft mode also provides insight into the cooperative phenomena that allow for ferroelectricity. Notice that the soft mode that condenses in displacive ferroelectrics occurs near the Brillouin zone center where $k \approx 0$. Since $k$ is equal to the inverse of the oscillation wavelength, the soft mode condensation only occurs for very long wavelengths. Therefore, a sufficient number of unit cells must exist in order for the soft mode to condense and support the ferroelectric distortion.

### 2.2.4 Chemical Bonding in Ferroelectrics

While atomic radii and structure give a groundwork that physically shows the necessary conditions that support spontaneous polarizations and ferroelectricity, an important requirement or instability for ferroelectricity is a degree covalency in the bonding. In particular, in perovskite ferroelectrics containing transition metal B-site cations, $d^0$ cations are necessary for the ferroelectric instability to exist (this is with exception to many multiferroics such as BiMnO$_3$ where $d^\alpha$ cations are shown to be able to support ferroelectricity through hybridization of the A-site cations). In this case, the $d^0$ cation refers to ions where the $d$-shell of electrons is empty, for example in Ti$^{4+}$, Nb$^{5+}$, W$^{6+}$, etc. For
barium titanate, the existence of mixed bonding has long been suspected to contribute to stabilizing the ferroelectric phase.\textsuperscript{24-28} Megaw showed that if a significantly large volume is present for Ti to shift, a homopolar (covalent) directional bond, in contrast to a purely ionic bond, can form between the titanium ion and the nearest oxygen. This was supported by a contraction of the bonding distance from those predicted by atomic radii considerations as shown in Figure 2.6.\textsuperscript{26, 27} Similar trends were seen in alkali-niobates and tantalates, also possessing a $d^0$ B-site cation. More recently, through Linear Density Approximations (LDA), Cohen showed that the covalent bonding in ferroelectric titanates was a hybridization of the titanium $3d$ states with the oxygen $2p$ states.\textsuperscript{21} The result of which is a $\pi$-bond that gives effective charges on the titanium ion of $+2.89$ and an oxygen charge of $-1.63$. This $\pi$-bond has been shown to be essential to stabilization of the tetragonal phase and thus a polar structure, and is a direct result of $B$-sites cations whose lowest energy unoccupied states are $d$-states, \textit{i.e.} $d^0$ transition metals. Incorporation of electrons in $d$-orbitals in a perovskite structure such as YTiO$_3$, where the orbital occupancy of the Ti ion is $d^1$, results in a Jahn-Teller distortion of the lattice, which also shifts the Ti atom within the oxygen polyhedra. However, materials with Jahn-Teller distortions do not tend to exhibit ferroelectricity.\textsuperscript{23} The lack of ferroelectricity in Jahn-Teller distorted structures is not well understood at this time.

\textbf{Figure 2.6:} Distorted octahedra in a ferroelectric perovskite with the B-site ion shifted toward one face.
2.2.5 Dielectric Properties

Relative permittivity, $\varepsilon_r$, or dielectric constant, $K$, characterizes a material's ability to store charge. Almost all mechanisms of storing charge in solids are a consequence of internal polarizations. The permittivity of a material is commonly measured as a change in dielectric displacement, $D$, with applied field, $E$, as shown in Equation 2.5.

$$
\varepsilon_r = \left( \frac{\partial D}{\partial E} \right)_{E=0}
$$

Equation (2.5)

Dielectric displacement in turn supplies the relationship of polarization to the permittivity in Equation 2.6 and results in permittivity being essentially the change in polarization with applied field as in Equation 2.7.

$$
D = E + 4\pi P
$$

Equation (2.6)

$$
\varepsilon_r = 1 + 4\pi \frac{\partial P}{\partial E}
$$

Equation (2.7)

This holds particularly true near the ferroelectric phase transition where the change in polarization with field is much larger than unity and dominates the relation. The various polarization mechanisms contributing to permittivity are: electronic polarizations, the shifting and/or stretching of the electron distribution around an ion nucleus, $\alpha_e$; ionic polarizations, the shifting of oppositely charged ions from their equilibrium position by an applied field, $\alpha_I$; dipole polarizations, the rotation of internal dipole moments to align with an applied force, $\alpha_d$; and space charge polarizations, the movement of charged internal defects with applied force, $\alpha_{s.c.}$. The sum of these polarization mechanisms gives the total change in polarization and thus the total contribution to permittivity. These contributions generally have a frequency dependence, revealing dispersive behavior, with all polarizations mechanisms active at low frequencies and only electronic polarizations active at the highest frequencies as shown in Figure 2.7.$^{29}$ As each polarization mechanism reaches its frequency limit, a
subsequent increase in loss is observed. This loss increase can be attributed to a dissipation of heat energy by friction of the space charges and dipoles as they move in the applied field. Electronic and ionic polarizations show loss peaks over much finer frequency ranges than space charge and dipole polarizations. The peaks here are not as strongly related to internal friction, but are due to resonance of the bound electrons to the nuclear cores by high frequency electromagnetic radiation.  

Figure 2.7: Frequency dependence of permittivity and loss tangent for a material containing space charge, dipole, ionic, and electronic relaxations (adapted from Murphy and Morgan).

There is an intimate relationship between loss and the dielectric properties of the material. Expressing the relative permittivity as a complex function, Equation 2.8, shows that the dielectric constant is composed of two components: a real component, \( \varepsilon' \), and an imaginary component, \( \varepsilon'' \).

\[
\varepsilon_r = \varepsilon' - i\varepsilon'' \quad \text{Equation (2.8)}
\]

The loss in the material can then be expressed in terms of a phase angle between the polarizing field and the response of the material commonly called the dissipation factor, loss tangent, or tangent delta:
\[ \tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad \text{Equation (2.9)} \]

Where \( \delta \) is the phase angle as of impedance as shown in Figure 2.8. For perfect insulators the phase angle is \( 90^\circ \), while for perfect conductors the phase angle is \( 0^\circ \). Real materials have values intermediate of the two extremes.

**Figure 2.8:** Schematic of the real versus imaginary components of permittivity separated by a phase angle \( \delta \).

In linear dielectrics (those without a reorientable dipole) the change in dielectric displacement can often be approximated to be linearly proportional to applied field. This is a general approximation, however and there are many exceptions owing to higher order terms contributing to dielectric permittivity. In ferroelectric materials, the dependence of displacement with applied field is hysteretic, owing to the reorientation of dipoles, through the movement of boundaries of mono-poled regions, or domains. It is important here to distinguish between the extrinsic and intrinsic contributions to permittivity. Ionic and electronic polarizations can be attributed intrinsically to the lattice of a crystalline material. While dipole polarizations and their subsequent reorientation of dipoles are considered extrinsic. Using this convention, it is clear that linear dielectrics, in the absence of space charges, will have only intrinsic contributions to permittivities and thus relatively low dielectric constants. Ferroelectrics and other materials with reorientable dipoles will have two contributions, those intrinsic to the lattice and those due to the change in polarization with the change in direction of the dipole moment.
The structure and existence of domains in ferroelectric materials can have strong implications on the dielectric properties. In displacive ferroelectrics that undergo a cubic to tetragonal ferroelectric phase transition, such as barium titanate, there are 6 equivalent crystal directions corresponding to unit cell face normals. These $<100>$ directions can support the tetragonal axis elongation and thus the spontaneous polarization. While elongation along each $<100>$ direction is energetically equivalent in an unclamped crystal, electrostatic and mechanical boundary conditions in real systems impart limitations on the polarization directions that are favored. The result of these conditions are regions within the material that have uniformly oriented polarizations neighboring regions of opposite or perpendicular polarization. Each region of uniform polarization defines a ferroelectric domain, while the separating boundary is a domain wall.

The electrical constraints that contribute to domain formation are a means to compensate for the spontaneous polarization within the material that creates a depolarization field. For example, in a mono-poled single crystal an electric field will form across the crystal as a result of surface charges that develop to compensate for the polarization. This electric field will oppose the polarization and should destabilize it. Since this clearly does not always occur, there must be mechanisms to compensate for the depolarizing electric field. Four suggested mechanisms include compensating surface charge from the surrounding environment, electrical conduction through the crystal, polarization gradients within the crystal, and domain formation as illustrated in Figure 2.9. Here, the ensemble of randomly oriented domains has a net polarization of zero, and strong depolarization fields do not develop.
Figure 2.9: *Polarization compensation mechanisms: a) surface charge, b) electrical conduction, c) polarization gradients, and d) 180° domain wall formation.*

In mechanically constrained ferroelectrics such as thin films adhered to substrates, polycrystalline ceramics where grain boundaries impart constraints, and single crystals with defects or exposed to temperature gradients upon cooling, a domain structure may form to minimize the mechanical strain energy in the system. For example, in barium titanate the formation of 90° domain walls occurs to compensate for stress incongruent with the $c$ and $a$ axes as shown in Figure 2.10.\textsuperscript{32} It is important here to distinguish between the 2 domain wall types in tetragonal barium titanate. The first discussed are those which separate domains related by a 180° rotation, *i.e.* 180° domain walls. These domain walls are purely ferroelectric in that they can move in response to an applied field but are invariant with respect to applied strains. Conversely, 90° domain walls (those relating neighboring domains related by a 90° rotation) can be moved by both applied fields and strains and are thus both ferroelectric and ferroelastic.\textsuperscript{32} While 180° domain walls occur on $(00l)$ planes, 90° domain walls correspond to $(hh0)$ planes.\textsuperscript{35} Finally, the dipole arrangement across 90° domain wall follows a ‘head-to-tail’ arrangement to minimize charge across the wall.\textsuperscript{36}
Domain walls can move in two ways, switching or sub-switching, depending on the strength of the applied field and energy barrier to wall motion. In the sub-switching regime, the field applied is not strong enough to move domain walls. Rather, the domain walls oscillate about a median position. As the field applied is increased, the energy barrier to domain wall motion is overcome and the domain wall moves irreversibly through growing into an adjacent domain. A plot comparing the two regimes in terms of their displacement-field hysteresis loops is shown if Figure 2.11. The plot labeled a is a classic hysteresis loop for a ferroelectric material, while b shows the loop for a ferroelectric material in sub-switching fields.

Figure 2.10: Schematic of a 90° domain wall in a tetragonal ferroelectric crystal.

Figure 2.11: Polarization hysteresis loops for a ferroelectric under a) switching and b) sub-switching fields.
Here the effect of switching the domains on the dielectric response is evident. By converting the hysteresis loop to a permittivity-field plot (also commonly called capacitance–voltage plots or C-V plots) through derivation of a hysteresis loop we can see the effect of domain wall motion on permittivity. There are two distinct regions on a C-V curve that are of interest in characterizing ferroelectric materials. The first is the low field region where the permittivity is high. In this region the movement of domain walls provide large extrinsic contributions, and subsequently permittivities in excess of $10^3$. In the second region, where the permittivity and loss saturate at high fields, the polarization vectors of all domains have effectively aligned with the applied field thus are minimally responsive to the superimposed oscillator. As a result, the permittivity response is dominated by the ionic and electronic polarizations, the intrinsic response of the lattice and a value in BaTiO$_3$ of $\sim 200$. The relative tunability, the percentage change of capacitance from its maximum value to its value at high fields, as shown in Equation 2.10, is then an appropriate measure of the level of extrinsic versus intrinsic response of the material and provides a metric by which the quality can be assessed.$^{37}$

$$tunability = \frac{\varepsilon_{\text{maximum}} - \varepsilon_{\text{minimum}}}{\varepsilon_{\text{maximum}}}$$

Equation (2.10)

Measuring the properties of ferroelectrics under sub-switching fields is a recent and informative method of characterizing the extrinsic response. The principles by which the study of domain wall motion under sub-switching fields are based are from the ferromagnetic analog, specifically observations by Lord Rayleigh.$^{38}$ In what became known as the Rayleigh Law, domain wall motion in magnetic materials was described by simple relations of magnetic permeability, $\mu$; magnetic induction, $B$; and magnetic field, $H$:

$$\mu(H) = \mu_{\text{init}} + vH$$

Equation (2.11)

$$B(H) = \mu_{\text{init}}H + vH^2$$

Equation (2.12)
Where $\nu$ is the Rayleigh coefficient, $\nu H$ is the linear term, and $\nu H^2$ is the parabolic term. The linear and parabolic terms represent the reversible and irreversible contributions respectively.\textsuperscript{39} These relations hold as long as the density and structure of domain walls remains unchanged under a cycling field. Therefore, the validity of the relationship can only hold under low-field conditions. Domain walls are thought to move about in a field of pinning sites of random energy barrier heights and distribution as first suggested be Nèel for antiferromagnets as shown in Figure 2.12.\textsuperscript{39} Microstructural defects acting as pinning sites were further studied and confirmed statistically by Kronmüller in support of Nèel’s theory.\textsuperscript{40}

![Potential energy versus distance schematic showing a random distribution of pinning sites in a lattice.](image)

**Figure 2.12:** Potential energy versus distance schematic showing a random distribution of pinning sites in a lattice.

Recently, Damjanovic and coworkers have expanded the Rayleigh Law study of domain wall motion to ferroelectric and ferroelastic materials.\textsuperscript{41-47} There are two types of domain wall motion to be considered, reversible, where the wall is thought to move within an energy well, and irreversible where the domain wall moves over the apex of an energy barrier into an adjacent well. A distinction needs to be made between the irreversible and reversible motion in sub-switching conditions – those at fields less than the coercive field – and those in switching. Irreversible domain wall motion under fields in excess of the coercive field represents the growth of favored domain orientations into adjacent domains with alternative orientations until all dipoles are aligned parallel. When the field is removed, the domain will remain the same size and orientation, resulting in a remanent equilibrium polarization on a macroscopic scale. Irreversible motion in sub-switching measurements also results in a minor remanent polarization. However, in this case, the domain wall moves over a pinning site on the atomic length scale. Similar to the switching case, the domain wall does not return to its
original position when the field is removed, however the net growth of the domain is minimal. Separating the reversible and irreversible components is possible to do in both piezoelectric and dielectric measurements. The piezoelectric analog to the ferromagnetic form of the Rayleigh Law is:

\[ d_{33} = d_{\text{init}} + \alpha \sigma_0 \]  
Equation (2.13)

\[ Q_0(\sigma_0) = d_{\text{init}} \sigma_0 + \alpha \sigma_0^2 \]  
Equation (2.14)

Where \( d_{33} \) is the direct longitudinal piezoelectric coefficient, \( \sigma_0 \) is the amplitude of the applied cyclic pressure, \( \sigma(t) \), \( d_{\text{init}} \) is the piezoelectric contribution from the lattice and reversible displacements of domain walls, \( \alpha \) is the Rayleigh coefficient and \( Q_0 \) is the amplitude of the piezoelectric charge density, \( Q(t) \). During low stress cycling, the piezoelectric charge will lag in phase from the applied stress. The result is a low stress hysteresis loop as shown in Figure 2.13.

![Piezoelectric hysteresis with applied stress under sub-switching conditions.](image)

**Figure 2.13:** Piezoelectric hysteresis with applied stress under sub-switching conditions.

Using the Rayleigh Law, the shape of the piezoelectric hysteresis loop can be described by:

\[ Q(X) = (d_{\text{init}} + \alpha X_{\text{max}})X \pm \frac{\alpha}{2} \left( X_{\text{max}}^2 - X^2 \right) \]  
Equation (2.15)

Where the sign “+” is for decreasing stress and “-” is for increasing stress. While this has been shown to be valid for piezoelectric materials where only non-180° domain walls are
active, a dielectric analog was developed that could take into account the dielectric subswitching ferroelectric properties and thus 180° and non-180° domain wall motion:

\[ \varepsilon = \varepsilon_{\text{init}} + \alpha E \]  

\[ P(E) = \varepsilon_{\text{init}} E + \alpha E^2 \]

Equation (2.16)  
Equation (2.17)

Where \( \varepsilon \) is the relative permittivity, \( \varepsilon_{\text{init}} \) is the initial permittivity due to lattice contributions and pinning sites with barrier heights less than thermal energy \( (k_B T) \), \( E \) is the oscillating electric field amplitude, and \( \alpha \) is the Rayleigh coefficient.\(^{45, 48} \) Taking into account the complex form of permittivity, these equations can be modified to isolate the real and imaginary contributions:

\[ \varepsilon' = \varepsilon'_{\text{init}} + \alpha'E \]  

\[ \varepsilon'' = \alpha'E = \frac{4}{3\pi} \alpha'E \]

Equation (2.18)  
Equation (2.19)

\[ P(E) = (\varepsilon'_{\text{init}} + \alpha'E)E_{AC} \pm \frac{\alpha'}{2}(E^2 - E_{AC}^2) \]

Equation (2.20)

Where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary components to the complex permittivity, respectively, \( E \) is the amplitude of the oscillating driving field, \( E_{AC} \) is the time dependent amplitude (which can be expressed by \( E_{AC} = E \sin(\omega t) \)), \( P \) is the dielectric polarization, \( \varepsilon'_{\text{init}} \) and \( \alpha' \) are the reversible and irreversible Rayleigh coefficients, respectively, and \( \alpha'' \) is the imaginary Rayleigh coefficient.\(^{49} \) Analogous to the piezoelectric Rayleigh Law, the polarization versus oscillator field hysteresis loop can be described by Equation 2.20 as shown in Figure 2.14.\(^{46, 49} \)
Figure 2.14: *Polarization hysteresis loop with applied field under a sub-switching bias.*

Measuring the Rayleigh coefficients can be accomplished by subjecting a ferroelectric material to an increasing oscillating electric field with amplitude less than the coercive field. Subsequently measuring the complex dielectric constant and plotting both the real and imaginary components as a function of field reveals plots similar to Figure 2.15. The interpolated intercept of the permittivity at zero field gives the reversible component to dielectric constant and domain wall motion while the slope of the curve in the linear portion gives the irreversible Rayleigh coefficient. Similarly, the slope of the imaginary component of permittivity versus field gives the imaginary Rayleigh coefficient. In some cases there is a threshold field that is observed before irreversible processes are revealed. In observing a plot of either the dielectric constant or piezoelectric constant versus oscillator strength, the threshold field is the field level at which the slope of the response deviates from zero. The threshold field represents the existence of strong pinning sites in the material that require large fields to overcome and thus provide insight into the degree of the pinning.\textsuperscript{44,49-52}

Figure 2.15: *Sub-switching field dependence of the real and imaginary components to permittivity for a ferroelectric with a degree of domain wall pinning. The dashed line represents the region where the Rayleigh Law holds.*
The implications of reversible and irreversible components are in describing the extrinsic and intrinsic contributions to the dielectric properties. Domain wall motion in ferroelectric materials is known to be strongly dependent on such features as crystal structure, microstructure, and the presence of impurities, dopants, defects, and microscopic composition gradients.\textsuperscript{44} By measuring the ratio of irreversible to reversible contributions to the dielectric response, these features can be probed thus providing structure/processing/property relations. Large irreversible components indicate mobile domain walls that are able to traverse the energy barriers resulting from pinning sites, which can contribute more to the dielectric response.\textsuperscript{49} Small irreversible, and thus linear, components can indicate one of three cases: i) there is limited wall mobility and they stay within local energy wells between pinning sites ii) the domain walls move reversibly throughout the investigated field strength, or iii) there are no domain walls or mobile interfaces in the material being measured.\textsuperscript{52} In cases i and iii, the change of polarization with field is small, thus the measured dielectric response will be relatively independent of applied oscillator field. Materials that fit case ii could have large changes in polarization with applied field and therefore could have a large extrinsic response. In such cases full switching hysteresis loops or C-V curves would provide further insight into the level of extrinsic response. In general however, the higher the irreversible contribution to the dielectric response the higher the extrinsic contribution.

2.3 Scaling and Size Effects

The dependence of ferroelectric properties on crystal dimensions has been routinely observed. Two phenomena are typically discussed. First is an increase in permittivity as grain size decreases to around 1 micron followed by a subsequent reduction in the room temperature permittivity with further size reductions.\textsuperscript{53-60} Second is a shift of the paraelectric/ferroelectric phase transition to lower temperatures as crystallite dimensions are reduced below 100 nm.\textsuperscript{33, 61-69} These effects have strong implications on the usefulness of ferroelectric materials in practical applications. Particularly, as devices scale to smaller
dimensions, the dimensional properties must be understood so that designs and materials can be modified to achieve the desired performance.

Before discussing size dependent phenomena in ferroelectric materials, it is important to make a distinction between finite size and scaling effects. Size effects represent theoretical limitations to a ferroelectric material forming a stable spontaneous polarization. True size effects are predicted to occur in systems involving extremely small dimensions. In such cases, frustrations to the paraelectric/ferroelectric phase transition result from an insufficient number of dipoles being present for the soft mode to condense and stabilize the ferroelectric distortion – however, unambiguous experimental evidence for this has yet to be reported.\textsuperscript{70, 71} Furthermore, depolarization fields present at electrode/ferroelectric interfaces can become significant as dimensions approach levels of multiple unit cells.\textsuperscript{72} Scaling effects incorporate all of the features of true size effects, but in addition have additional limitations and features that are imparted from the complexities of real systems including: limitations in processing technology to form defect free and phase pure materials, porosity, the existence of phase, domain, and grain boundaries and interfaces, compositional homogeneity, and residual strain present due to mechanical boundary conditions.\textsuperscript{73} Scaling effects may be divided into two systems: 1) Scaling in bulk ceramics with a randomly oriented polycrystalline microstructure and 2) scaling in thin films. Note that thin films can encompass many microstructures, ranging from epitaxial films to fiber textured polycrystalline films to randomly oriented, equiaxed polycrystalline films. Each case will be discussed in further detail in the following paragraphs.

2.3.1 True Size Effects

Over the past two decades there have been great efforts toward identifying the crystal dimensions below which a spontaneous ferroelectric polarization is unstable. We describe these studies as finite size effects. Much of this work has shown that by extrapolating the phase transition temperature as a function of particle size, a limit is reached where the transition should occur below 0 K. This ultimate size has been deemed the critical size for
ferroelectricity and has been suggested to be on the order of 20 to 30 unit cells.\textsuperscript{61} Theoretical calculations have predicted that the critical size is on the order of $10 – 100 \text{ nm}^3$ using the mean-field Ginzburg-Landau free energy approach,\textsuperscript{74} while \textit{ab initio} models suggest that ferroelectricity can be supported in films or particles with only a few unit cells in dimension.\textsuperscript{72, 74, 75} The latter has been supported by work on 3 unit cell thick PbTiO$_3$ films as studied by synchrotron X-ray scattering and work on 40 Å thick PbZr$_{0.20}$Ti$_{0.80}$O$_3$ films as studied by piezoforce and electric-field microscopy.\textsuperscript{67, 69, 76} The success of this work shows that through either 180° stripe-domain formation, or compensating charges from a conductive electrode or the surrounding atmosphere a stable polarization can be maintained without significant reduction from depolarization. Thus demonstrating that the scale on which finite size effects must be considered is quite small. It was however, observed that as film thicknesses decreased toward 1 nm, the phase transition temperature decreased by several hundred degrees.\textsuperscript{66, 67, 69}

### 2.3.2 Observed Scaling Effects in Bulk Ferroelectrics

Scaling effects in bulk ceramics were observed soon after the discovery of ferroelectric barium titanate. Initially, several groups observed an increase in the room temperature permittivity in polycrystalline materials to greater than 3000, with at least one group reporting a permittivity of 6000.\textsuperscript{55, 58, 60, 77, 78} This increase in permittivity was accompanied by a subsequent decrease in tetragonality as the grain size decreased toward 1 micron.\textsuperscript{55, 58} Single crystal barium titanate has an $a$-axis permittivity of 4000 and a $c$-axis permittivity of 400.\textsuperscript{17, 18} Assuming random orientations of single crystalline grains, as is present in a polycrystalline ceramic, this would suggest that the room temperature permittivity could not exceed 4000. Therefore, simple mixing rules are insufficient to describe the effect that fine grain size has on the permittivity. The first successful model to describe this behavior was an internal stress model developed by Buessem and coworkers.\textsuperscript{53} In ceramic materials, the grain boundaries provide for complex mechanical boundary conditions that require domain formation upon cooling to minimize the free energy associated with the phase transition. It was suggested that the minimum domain width in barium titanate was $\sim 0.4 \mu\text{m}$, thus it was unlikely that twinning could occur in materials with
grain sizes less than 1 μm. With domain formation prohibited, it was suggested that each grain was under a higher degree of stress (than in a coarse-grained analog) in order to oppose the spontaneous deformation. This internal stress would work to minimize the degree of tetragonality in each grain, and thus maintain the material in the cubic state, as was identified in X-ray diffraction investigations. Using free energy minimization, it was shown that a stress level between 600 and 800 kg/cm² was sufficient to increase the room temperature permittivity to greater than 3000. Furthermore, the calculated stress levels corresponded well with the measured decrease in tetragonality observed in the experimental work. The Beussem model successfully described several scaling phenomena in bulk ceramics until further TEM investigations of the sub-grain structure of fine-grained barium titanate was performed by Arlt et al.

By preparing a comprehensive ceramic BaTiO₃ sample set with grain sizes varying between 0.3 and 50 μm, Arlt et al. was one of the first groups to fully characterize the effect of grain size on the dielectric properties of polycrystalline ferroelectrics. In measuring the dielectric properties as a function of grain size, the authors developed a plot of room temperature permittivity as a function of grain size as shown in Figure 2.16.

![Figure 2.16: Room temperature relative permittivity as a function of average grain diameter for barium titanate ceramics (adapted from Arlt et al.)](image)

Two phenomena are observed in this plot. First, as the grain dimensions decrease from 50 μm, there is an increase in the room temperature permittivity with a peak at approximately
0.7 µm. Second, subsequent reduction in grain size results in a decrease in the measured permittivity. This was also apparent in plots of permittivity as a function of temperature for several different grain size materials. In observing the domain structure of these materials, it was noted that as the grain size reduced from 10 to 0.7 µm, the domain width scaled as the square root of grain size. It was this increase in domain wall density per volume and the subsequent increase in the domain wall contribution to permittivity that was responsible for the increased room temperature permittivity, rather than a stress effect alone. Through TEM investigations of sub-0.7 µm grains, it was revealed that the density of domain walls dropped, with many grains showing no 90° domains walls. X-ray diffraction studies in the same report demonstrated that the room temperature crystal structure changed with decreasing grain size. As the grain size decreased below 1 µm, the tetragonality decreased with an increase of diffraction peaks attributed to the orthorhombic and rhombohedral structures. The existence of room temperature orthorhombic phases has been observed in by other groups studying fine-grained barium titanate, as well as a trend of increasing transition temperatures for the 2 lowest symmetry phases. This appears to be a consequence of scaling and appears to be an affect of scaling and has been predicted by a refinement of the internal stress model by Bell et al. It should be mentioned that while Arlt’s work was groundbreaking, and provided insight into the sub-micron grain size effects, there are several issues which confound interpretation. The sample set used was developed from three different materials and preparation methods, with sets of equivalent preparation methods used in ranges from 0.3 – 0.5 µm, from 0.7 – 1.2 µm, and from 10 – 50 µm. Investigation of Figure 2.16 shows clear data discontinuities at the edges of each of these data ranges, thus adding some uncertainty to the results.

Further refinement of the scaling effect in barium titanate was conducted separately by Frey and McCauley and coworkers. The former demonstrated through the chemical preparation of barium titanate powders and polycrystalline ceramics several scaling trends. (1) At room temperature, the global crystal structure of barium titanate, as studied by X-ray diffraction, changes from tetragonal to cubic as grain size is reduced. This is direct agreement with other studies on similarly sized materials. (2) Raman spectroscopy revealed that the local structure of the materials ranged from orthorhombic to tetragonal within
materials defined to be cubic by X-ray diffraction. This suggests that X-ray diffraction may not be sensitive to the small distortions in these materials due to line broadening and overlap of split peaks as particle size decreases. (3) Through thermal analysis it was shown that in materials as fine as 100 nm in grain size, a phase transition is present at slightly lower temperatures than large, 10 µm, grain-sized material. TEM investigations revealed similar findings to Arlt’s work in that the domain twin boundaries were identified in materials as fine as 0.4 µm, however no evidence of domains were found in finer grained material. This suggests that in materials with grains smaller than approximately 0.4 µm each grain is a mono-domain.\(^{81}\)

Further investigations on chemically derived barium titanate in the form of ceramic disks provided more insight into the apparent suppression of dielectric constant as grain size decreases below \( \sim 0.5 \) µm. Through careful preparation at high pressures, Frey was able to develop a sample set of fine-grained barium titanate where the composition and density were approximately identical, and where grain size is the independent variable. Permittivity versus temperature plots for materials ranging in grain size from 70 to 1700 nm are shown in Figure 2.17.

![Figure 2.17: Temperature dependence of permittivity for a grain size series of pure barium titanate bulk ceramics (adapted from Frey et al.\(^{57}\)).](image)

From this plot a room temperature permittivity maximum at \(~0.7 \) µm, analogous to the report of Arlt, is shown. Furthermore, Frey demonstrates that the phase transition temperature for

30
materials as fine as 70 nm does not appreciably shift. In materials as fine as 40 nm a ferroelectric hysteretic polarization was observed at room temperature. While it was suggested that the lack of a domain wall contribution to permittivity is responsible for the reduction in dielectric constant of sub-micron grain size material, it does not explain why further reductions in grain size suppresses permittivity.\textsuperscript{54} To this point, Frey and coworkers explained that simple series-mixing model could describe the subsequent reduction. The model proposed is based upon the brick wall model developed by Payne and Cross where bricks are formed of high permittivity grain cores and mortar of low permittivity grain boundaries. TEM analysis revealed grain boundary thicknesses on the order of 8Å, which would require a permittivity of the defective grain boundary to be approximately 130.\textsuperscript{57} Both numbers are reasonable and clearly demonstrate a key feature of scaling effects. That is that reductions in permittivity previously attributed to depolarization fields and dead-layers could be better explained through microstructural features present in the material.

While Frey’s work investigated the scaling effects of barium titanate ceramics with defective grain boundaries, it is interesting to note that the existence of adjacent grains with dissimilar polarizations and the defective nature of grain boundaries that could act as a source of charge within a material that could compensate for the depolarization field within each grain. McCauley and coworkers developed a sample set of barium titanate fine crystallites within a glass matrix through a precipitation process.\textsuperscript{33, 65} The importance of this work lies in the electrical boundary conditions that develop in the glass – ceramic embodiment. The insulating nature of the glass matrix makes it possible to probe the effect of crystallite size in a system where surface charges cannot rapidly accumulate. In this situation, depolarization fields could not be compensated. It was shown that a decrease in both dielectric constant and phase transition temperature occurred as crystallite size decreased from 80 to 25 nm as shown in Figure 2.18.
Figure 2.18: Temperature dependence of permittivity for a barium titanate glass-ceramic of varying grain size (adapted from McCauley et al.\textsuperscript{33}).

It was also shown that the phase transition became broader with decreasing crystallite dimensions. All three of these features provided evidence that the Binder model of finite scaling in ferroelectric crystals is correct.\textsuperscript{83, 84} Simply put, the Binder model shows that the polarization across a thin ferroelectric layer should have a gradient at each surface. This results in a shift of its phase transition temperature according to Equation 2.21:

\[ T_c(N) - T_c(\infty) = N^{\gamma/D} \]  

Equation (2.21)

Where \( N \) is the number of unit cells, \( D \) is the dimensionality, and \( \gamma \) is the critical shift exponent. The Binder model also predicts an increase in broadness of the phase transition as can be described by Equation 2.22:

\[ \Delta T_{\text{Rounding}} \propto N^{\theta/D} \]  

Equation (2.22)

Where \( \theta \) is the rounding exponent and \( D \) is again the dimensionality.
2.3.3 Observed Scaling Effects in Thin Film Ferroelectrics

To this point the effect of scaling has been discussed with regard to bulk systems. The thin film community has pursued similar, if not more, activity in exploring scaling effects in thin ferroelectric layers. Scaling effects in thin films differ from their bulk counterparts. While bulk materials with sub-100 nm grains can routinely reach permittivities in excess of 1000, these values are rarely seen in thin films, especially those with refractory constituents, such as barium titanate. The thin film microstructure tends to differ from bulk ceramics in that a fiber-textured or columnar microstructure grown with a preferred crystallographic orientation is common. The specific morphology and orientations are often dependent on the substrate and preparation method used. This microstructure is characterized by grains and grain boundaries that exist throughout the entire film thickness rather than having several grain boundaries present parallel to the electrodes.

There have been two primary models for the apparent decrease in the dielectric properties as ferroelectric are formed in thin film layers. The dead-layer model predicts that there is a layer that is ferroelectrically damped at each free surface or interface.85, 86 Proponents of this model point to extrapolations of inverse capacitance density versus film thickness that results in a non-zero intercept as evidence of a temperature independent lower capacitance interfacial layer.87-90 The other model is the Binder model that was previously discussed for ferroelectric crystallites where a polarization gradient is present throughout the thickness of the films. The dispute over the correct model or interpretation has been contentious at best. To date, perhaps the most convincing argument to the decrease in permittivity and phase transition temperature with a decrease in film thickness was put forth by Maria and Parker et al.91 This work utilized MOCVD deposited (100) fiber textured barium strontium titanate thin films on platinized silicon substrates in a thickness range of 15 to 580 nm. Temperature dependent measurements of the permittivity and dielectric loss revealed that decreasing the film thickness resulted in a decrease in the maximum permittivity, a decrease in the phase transition temperature, and an increase in broadness of the phase transition. All three phenomena scale with film thickness as predicted by the Binder model. In spite of the work’s successes, questions still remain on the scaling effect.
origins. The Binder model’s predictions should not begin to dominate the dielectric response until film thickness approaches 10 nm. This suggests that other extrinsic scaling effects are predominant. In addition, the width of the columnar grains was on the order of 10s of nanometers. It was outside the realm of the study to investigate the possible influence of this fine dimension on the properties of the films, however it should not be ignored when considering the potential contribution. The films used in the study were non-stoichiometric with a composition consisting of 53.1% Ti and 46.9% A-site. This non-stoichiometry was used to limit the DC leakage in the films, however its possible effects on the dielectric properties, including possible poorly crystalline second phases need to be kept in consideration.

Some recent work by Strukov and coworkers sought to decouple a grain size and film thickness effect in thin films of barium titanate. Fiber-textured films were prepared by RF magnetron sputtering with thicknesses ranging from 20 to 1100 nm with a constant column width of 150 nm. A second set of samples was prepared with a constant thickness of 500 nm while the column width was varied from 30 to 150 nm by varying the deposition temperature and power. While the authors did not measure the dielectric response, measurement of the specific heat of the phase transitions revealed similar trends with respect to film thickness and grain size. In both sample sets the phase transition was suppressed in temperature and increased in broadness as the dimensions decreased. While no groundbreaking conclusions were drawn, it was demonstrated that the effects of film thickness and grain size are linked and should be considered in scaling studies.

Recently, it was demonstrated that true bulk characteristics could be had in thin layers by Saad et al. A freestanding 75 nm thick film was formed by cutting a thin section into bulk single crystal of barium titanate using a focused ion beam. By plating the thinned area with gold electrodes and annealing out defects caused by the sample preparation process, it was shown that bulk properties including a permittivity of 25,000 are possible. The sample measurements displayed clear Curie-Weiss behavior with a Curie point of 122°C, extremely close to what is regularly measured in coarse-grained bulk and single crystal samples. This suggests that depolarization fields and electrode screening effects are unlikely to be
responsible for observed scaling effects in thin film ferroelectrics. Rather, especially in
consideration of the bulk work of Frey, the cause of the diminished response is more likely to
be due to some extrinsic processing effect, which will be addressed in this thesis.

2.3.4 Extrinsic Effects to Scaling

There are several possible extrinsic effects that have been and can be attributed to
causings the observed scaling effects in ferroelectric materials. Three in particular that will be
discussed are the limited processing temperatures utilized, the effect of stress, and the effects
of hydroxyl groups in the lattice. The former two are commonly present in thin film
materials, while the third can be present in either thin films or bulk ceramics depending on
the material preparation methods.

Thin films suffer from an inability to be processed at high temperatures due to
thermo-physical instabilities of the films, electrodes, and substrates.\textsuperscript{96, 97} Often films are
limited to temperatures of less than 800°C, much less than the 1000+°C temperatures typical
for bulk processing. These lower temperatures could result in a higher defect density or
poorly crystalline materials.\textsuperscript{73} Many deposition processes, such as sputtering and pulsed laser
deposition, utilize high-energy species to form a dense film. In these processes there exists a
finite amount of gas phase charged anion species that can be accelerated into and bombard
the film during growth. The lattice damage that occurs in such processes requires thermal
energy to repair. Unfortunately, the temperature limits imposed upon most thin film systems
precludes full annealing of the defective lattice. Processes that are based on metal-organic
chemical precursors suffer the disadvantage of having to remove the organic species prior to
and during crystallization and densification. It is well known in the barium titanate system
that temperatures in excess of 600°C are necessary to drive off carbon, which commonly
complexes with barium and titanium during heating to form barium titanate oxycarbonate or
barium carbonate.\textsuperscript{98-103} This practically leaves a processing window of 150° to crystallize and
densify the material before substrate instabilities impart further temperature limitations. For
complex oxides, such as barium strontium titanate, it is possible that a random distribution of
common site ions does not occur with the limited thermal budgets used in thin film
processing, resulting in a variation of phase transition temperatures spatially through the material.

Thin films are most often constrained to rigid substrates, which result in residual strains due to differing thermal expansion coefficients. In light of this, it is important to discuss the effect that stress could have on ferroelectric properties of materials. Two types of stress will be discussed. The first is hydrostatic pressure as applied to single crystals and bulk ceramics. The second is 2-dimensional pressure as applied to single crystals, bulk ceramics, and thin films.

Hydrostatic pressure acting on single crystal barium titanate has been shown to decrease the Curie point at a rate between $-5.2^\circ\text{K/kbar}$ and $-5.8^\circ\text{K/kbar}$ respectively.\textsuperscript{104-106} The effect of pressure on the other ferroelectric transitions in barium titanate are somewhat less pronounced with measured values of approximately $-2.90^\circ\text{K/kbar}$ and $-1.23^\circ\text{K/kbar}$ for the tetragonal to orthorhombic and orthorhombic to rhombohedral transitions respectively. Under pressures up to 24 kbar the Curie point and Curie Temperature both decrease linearly and similarly suggesting that the order of the phase transition remains one over a relatively large range and that the peaks simply shift and do not significantly change shape or become dramatically more diffuse.\textsuperscript{105} It was also demonstrated that the maximum permittivity increases with increased pressure.\textsuperscript{104} Interestingly, both of these phenomena point toward a decrease in lattice parameter with increased pressure as can also be accomplished by substituting strontium for barium in the perovskite lattice – a point that will be discussed in more detail in a following section. The effect of hydrostatic pressure on polycrystalline barium titanate was similar in showing a linear decrease of the Curie point, however the increases in permittivity were not observed, rather the maximum permittivity decreased with increasing pressure, which was not discussed further by the author.\textsuperscript{106}

While hydrostatic pressure was shown to drive all phase transition temperatures to lower values, the effect of 2-dimensional pressure is markedly different. By applying a 2-D pressure to a crystal or bulk ceramic it is expected that a stabilization of dipoles most closely aligned perpendicular to the applied stress will occur as the crystal will contract along two
axes and expand in the third. Forsbergh tested this hypothesis on a cylinder cut from a single crystal of barium titanate. The results showed that by increasing the 2-dimensional pressure the Curie point also increased.\textsuperscript{107} Contrary to the linear dependence of hydrostatic pressure on phase transition temperature, 2-dimensional pressure revealed a parabolic dependence according to Equation 2.23.

\[ T_c = T_{c_0} + 3.1 \times 10^{-5} P^2 \]  
Equation (2.23)

Where \( T_c \) is the Curie point, \( T_{c_0} \) is the Curie point at ambient conditions, and \( P \) is the applied 2-D pressure in atmospheres. While the dependence of the other phase transitions were not measured in the study, it was suggested that the 2-dimensional pressure, if applied equally in a radial fashion, should stabilize the tetragonal distortion. Thus it was argued that the orthorhombic and rhombohedral phase transition temperatures would be suppressed. In studying 2-dimensional pressure on coarse and fine-grained barium titanate ceramics, it was observed by Buessem and coworkers that the room temperature permittivity increased for materials with grain sizes of approximately 1 \( \mu \)m.\textsuperscript{108} For coarse-grained material, the room temperature permittivity decreased with the application of a biaxial stress. These results were interpreted as being indicative of a decrease in domain wall density and motion in the fine-grained material and thus an increase in the internal stress.\textsuperscript{108} In this case, the 2-dimensional pressure may aid the elongation of a polar axis in the material, thus increasing the polarization and permittivity.

A model of the effect of 2-D strain was expanded to epitaxial thin film ferroelectrics by Pertsev \textit{et al.}\textsuperscript{109} Modeling the effect of 2-D epitaxial mismatch stress on a thin ferroelectric film revealed results similar to those experimentally measured by Forsbergh on bulk single crystals. Specifically, for a thin film clamped to a sufficiently thick substrate with lattice registry through the interface, the phase transition temperature should increase under both compressive and tensile stress as specific polarization axes are stabilized. The success of this model has been demonstrated experimentally by several groups growing epitaxial barium titanate and strontium thin films on a multitude of substrates.\textsuperscript{110, 111} While
the model and experimental data describe well the effect of biaxial strain on epitaxial thin films, the case with polycrystalline and relaxed single crystal films is not as easily described.

The phase transition temperatures of polycrystalline thin films are typically suppressed from those measured in bulk ceramics and single crystals.\textsuperscript{64,112,113} Strain effects are commonly attributed as a contributor to this behavior. However, in light of previous studies one would expect the phase transition temperature to increase as a result of thermal expansion mismatch with the substrate (regardless of sign). A recent study by Maria et al. sought to elucidate the effect of strain on the phase transition temperature of barium strontium titanate grown by MOCVD on platinized silicon substrates.\textsuperscript{114} By separating the platinum bottom electrode from the rigid silicon substrate, the strain in the BST film could be reduced. In comparing the temperature response of permittivity prior to and after removal from the silicon substrate it was revealed that the permittivity maximum increased, as did the phase transition temperature. This surprising result is in contradiction to the decrease in transition temperature as would be expected by relieving biaxial strain. It was hypothesized that the growth conditions resulted in a film with a preferred polarization normal to the film surface and was supported by its inability to switch ferroelastically. The origin of the preferred orientation was unknown but was speculated to be an extrinsic effect such as a composition gradient present from the growth process. Similar effects could be expected in materials grown by other vapor deposited methods where ion bombardment and cation flux may be difficult to control. This work provides further evidence that extrinsic defects are a likely cause of observed scaling effects.

Several methods have been used to form fine-grained ferroelectric bulk and thin film materials. The most advanced methods utilize chemically derived precursors or hydrothermal synthesis to develop highly pure materials. These precursor materials have the drawback that each contains a large amount of oxygen and hydrogen and thus potential hydroxyl (OH\textsuperscript{-}) forming compounds. It has been shown that hydroxyl groups can be easily incorporated into the perovskite lattice and can act as a mobile electrically active charge carriers and/or a significant concentration of hydroxyl groups could expand the lattice stabilizing the cubic phase.\textsuperscript{115-123}
As electrical charge carriers, hydroxyl groups carry a net positive charge and can conduct through the lattice as protons.\textsuperscript{122, 123} In order to have a stable polarization a material must be insulating. Therefore, the existence of readily available and mobile charge carriers has been considered as a potential contributor to a destabilization of the spontaneous polarization in ferroelectrics. It is for this reason that hydroxyl defects, and all potential charge carrying defects, must be considered when discussing scaling effects in ferroelectrics.

An observation consistent to many researchers studying the effects of the lattice hydroxyl group is a volume expansion of the unit cell associated with the hydroxyl group, and a stabilization of the cubic paraelectric phase to lower temperatures.\textsuperscript{117, 119-121} It has been suggested that the existence of charged defects in the crystal can reduced the Coulomb attraction between neighboring ions promoting longer bond lengths and an increase in lattice parameter.\textsuperscript{117} Along similar lines, Wada et al. have suggested that the lattice defects present due to hydroxyl groups can act as scattering sites for lattice vibrations. As the concentration of defects increases, the spacing between scattering sites decreases and can approach the correlation length necessary for the cooperative condensation of the soft mode. As a result, the cubic to paraelectric phase transition is not allowed to occur and the material remains cubic at room temperature.\textsuperscript{121} Corroborating the defect model of scaling effects with phase transition temperature predictions of Abrahams et al. (Equation 2.24)\textsuperscript{124} and assuming a logarithmic dependence of correlation length on spontaneous deformation ($c/a$), the authors were able to show similar scaling effects trends to other experimental work.

\[
T^c = \left(\frac{K}{2k_B}\right) \times (\delta z)^2
\]  

Equation (2.24)

In Equation 2.24 $K$ is a force constant, $k_B$ is Boltzmann’s constant, and $\delta z$ is the displacement of the titanium ion in the lattice. The success of this model provides important insight in distinguishing true size effects – actual correlation lengths – from scaling effects – the observed diminishment in properties as material size decreases.
2.4 Barium Titanate Based Solid Solutions

Barium titanate is one of the most widely used ferroelectrics for capacitor applications. Pure barium titanate however, suffers from strongly temperature dependent capacitance as a consequence of its sharp phase transitions. These sharp phase transitions and the existence of the ferroelectric phase at room temperature limits the usefulness of the pure material in practical applications. In the following sections several solid solutions will be discussed which can either pinch or shift the Curie point of barium titanate to provide for a more desirable temperature response. First some brief definitions will be discussed. Phase transition shifters are solid solution end members that decrease the cubic to tetragonal phase transition temperature while either decreasing or maintaining the tetragonal to orthorhombic and orthorhombic to rhombohedral transitions. Phase transition shifters are often solid solution end members where the A-site is substituted for by an isovalent cation. Phase transition pinchers decrease the temperature of the cubic to tetragonal transition while increasing both the tetragonal to orthorhombic and orthorhombic to rhombohedral transition temperatures. Typical phase transition pinchers are B-site substituents that are isovalent with Ti. Figure 2.19 shows a plot of the phase transition temperatures as function of mole percent substituent for various common phase transition shifters and pinchers (adapted from Jaffe, Cook, and Jaffe).125
It should be noted that in bulk systems, such as multilayer capacitors, there are several combinations of phase transition pinchers and shifters, which are used to achieve the desired temperature response. Furthermore, special microstructures have been developed to flatten the overall response. These microstructures utilize a high permittivity ferroelectric grain core and a lower permittivity and temperature stable shell in a microstructure known as a core-shell structure. Because these structures utilize ferroelectrically active grain cores with domain structures, their usefulness in fine-grained thin film embodiments is limited and thus will not be a part of the following discussion.

### 2.4.1 Barium Titanate – Strontium Titanate (Barium Strontium Titanate)

Perhaps the most common solid solution former with barium titanate is strontium titanate to form barium strontium titanate ($\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, BST). In this fully miscible system, strontium substitutes for barium in the perovskite lattice. The Curie points of the two end member compounds are 398 K for barium titanate and approximately 0 K for strontium titanate. Strontium titanate is an insipient ferroelectric, meaning that the phase transition does not occur at any temperature, however with the application of stress the phase transition can be realized. The result of solid solution formation is a linear decrease in the Curie point.
with a slope of approximately 3.7° per mole strontium titanate. The tetragonal – orthorhombic phase transition decreases linearly with the addition of strontium, however the slope is less than the cubic – tetragonal transition at approximately 2° per mole substituent. The orthorhombic – rhombohedra transition remains relatively constant.\textsuperscript{125, 126} Plotting the permittivity versus temperature for bulk ceramics of barium strontium titanate shows that there is an increase in permittivity as the strontium level increases to approximately 30 percent and then decreases again, however the effect of grain size is not discussed. There has been some single crystal work in the barium strontium titanate system, however stoichiometry and purity of the materials are questionable and could lead to ambiguous results.\textsuperscript{127, 128}

Incorporating strontium into the lattice results in an overall decrease in the lattice parameter as the smaller strontium ion is incorporated. It is interesting to note that the change in lattice parameter and phase transition temperature with strontium incorporation parallels that of hydrostatic pressure and provides a connection to structure property relations in these materials.

A wealth of data exists on barium strontium titanate in bulk ceramics and thin film form. It has been shown that thin film materials can be grown by a variety of methods ranging from chemical solution deposition (CSD),\textsuperscript{100} metalorganic chemical vapor deposition (MOCVD),\textsuperscript{129} pulsed laser deposition (PLD), and radio frequency (RF) magnetron sputtering,\textsuperscript{130, 131} and for a variety of applications ranging from DRAM to frequency agile tunable devices.\textsuperscript{132, 133} In these materials scaling effects are almost always observed with decreased phase transition temperatures, decreased permittivities, and increased broadness of the transition.

2.4.2 Barium Titanate – Barium Zirconate (Barium Titanate Zirconate)

Barium titanate zirconate (BaTi\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{3}, BTZ) is probably the second most common solid solution based on barium titanate for dielectric applications. In this fully miscible system, zirconium substitutes for titanium in the perovskite lattice. Unlike strontium titanate,
barium zirconate is a linear dielectric and is not an insipient ferroelectric. This changes some of the properties of these materials as zirconium is substituted into the lattice. For example, this material is a phase transition pincher rather than a shifter. The lattice parameter and the unit cell volume of barium zirconate are larger than barium titanate, indicative of the larger Zr$^{4+}$ cation compared to Ti$^{4+}$.

The Curie point in this material, from here forward described as $T_{\text{max}}$, the temperature of the dielectric constant maximum, decreases linearly at a rate of $-5.3$ °C per mole barium zirconate. The tetragonal to orthorhombic transition increases in temperature at a rate of $+7$ °C per mole and the orthorhombic to rhombohedral transition increases at a rate of $+18$ °C per mole for low levels of barium zirconate substitution. It should be noted that these values have been obtained from a combination of electrical and X-ray diffraction studies on bulk ceramic samples. While there exists at least one study of single crystalline barium titanate zirconate, the quality is suspect and will not be used to elucidate information on the system. In light of this, any conclusions concerning the effect of zirconium on permittivity must be taken in context and the microstructure of the system must be considered. Fortunately all studies discussed have used materials with grain sizes in excess of 1 μm, so the effect of scaling on the phase transition behavior would be limited and allows for further analysis.

Several distinct features occur as the amount of zirconium substituted into the lattice is increased. First is the pinching effect of the phase transitions. The result of which is a broadening of the dielectric maximum that can flatten the overall temperature response of permittivity. Between 0 and 15 mole percent barium zirconate the material acts as a ‘normal’ ferroelectric with each of the phase transitions remaining distinct. A critical point in the phase transition pinching occurs between approximately 10 and 15 mole percent barium zirconate. Around these substituent levels, all phase transitions have converged and the material is thought to transition from cubic directly to rhombohedral at a temperature of approximately 40°C. In compositions ranging from 15 to 25 mole percent barium zirconate there is a phase transition behavior that has been defined as ‘diffuse.’ Here the permittivity versus temperature curves show a large and broad peak. Above approximately 25 to 26 mole percent zirconium the phase transition behavior begins to exhibit relaxor...
behavior, characterized by a frequency dependence of \( T_{\text{max}} \) and a broad maximum in the permittivity.\(^{137,139}\) An example of the each phase transition behavior is shown in Figure 2.20.

![Figure 2.20: Schematic of three ferroelectric phase transitions a) normal, b) diffuse, and c) relaxor.](image)

The origin of the changes in phase transition behavior is not well understood at this time. However, it has been suggested by Wada and coworkers that zirconium in the lattice acts to lessen the depth the free energy well in the free energy versus polarization model. In this model the polarization states of a ferroelectric can be modeled in terms of free energy wells with an energy barrier separating the various equivalent polarization states. Wada describes a ‘normal’ ferroelectric as having a well of energy lower than \( k_B T \), the thermal energy of a system. In such a case a phase transition will be first order and will not display significant frequency dependence and the phase transition will remain sharp. In the ‘diffuse’ state, with increased zirconium concentration, the well depth is very slightly greater than \( k_B T \) and the material will display second order phase transition characteristics with continuously increasing polarization as the temperature decreases through the phase transition. Above 25 mole percent zirconium the well depth is equivalent to \( k_B T \) and the material shows the characteristics of a relaxor ferroelectric.\(^{137}\) That is, the material is thought to contain polar microregions (PMR) that can change dipole orientation through thermal energy alone. An alternative, though linked, view of Smolensky in describing the diffuse state was proposed for the chemically similar barium titanate stannate system. It was suggested that there may be composition gradients within the material that result in a spatial variation of phase transition temperatures throughout the material.\(^{140}\) Modeling of such a system successfully
accounted for several of the observed experimental phenomena in diffuse phase transition materials, such as unusual domain morphology and relaxation of the polarization.

While less literature exists for BTZ than does for BST, the technological importance of the system should not be underestimated. Many multilayer capacitor applications utilize barium titanate zirconate based compositions for some of the highest performance devices.\textsuperscript{141-143} In spite of this heavy usage of BTZ in the bulk systems, it has received decidedly less attention in the thin film community, especially in comparison with BST. A few groups have studied the effects of zirconium on the properties of barium titanate thin film using CSD,\textsuperscript{144-148} MOCVD,\textsuperscript{149, 150} and PLD.\textsuperscript{151} From the unambiguous results, similar scaling effects to those observed in thin films of BST can be found. Those include: decreased permittivity, decreased phase transition temperature, and an increase in broadness of the ferroelectric anomaly.\textsuperscript{144-150} Relaxor behavior was also observed in BTZ thin films occurring across a range from 15 to 40 mole percent barium zirconate depending on the group investigating the behavior.\textsuperscript{146, 150} No work on thin film or bulk barium titanate zirconate successfully investigated scaling behavior in the system, or the link between zirconium content and permittivity.

\textbf{2.4.3 Barium Titanate – Barium Stannate (Barium Titanate Stannate)}

Barium titanate stannate (BaTi\textsubscript{1-x}Sn\textsubscript{x}O\textsubscript{3}, BTS) behaves similarly to the barium titanate zirconate system as barium stannate is a linear dielectric. In this solid solution, tin substitutes for titanium in the perovskite lattice and shows a phase transition pinching effect as the level of tin is increased. The permittivity maximum, $T_{max}$, decreases linearly with increasing barium stannate concentration at a rate of $-8^\circ$C per mole solution. The tetragonal to orthorhombic transition, as in the barium titanate zirconate system, increases by $+5^\circ$C per mole and the orthorhombic to rhombohedral transition increases by $+16^\circ$C per mole.\textsuperscript{125, 152-155} As with barium titanate zirconate, all numbers quoted are for ceramic samples and not single crystals. One study exists in the literature on single crystals of barium titanate stannate with levels up to 17 mole percent tin, however no measurements of the phase transition behavior were made.\textsuperscript{156}
As the phase transitions converge with increased tin content, a critical point is reached where the material has a single phase transition. Compositions containing approximately 10 mole percent barium zirconate transition directly from cubic to rhombohedral with no stable tetragonal or orthorhombic phases present.\textsuperscript{152, 155, 157} Like BTZ, the three phase transition regions can be characterized according to their solid solution concentration. For materials containing less than 10 mole percent barium stannate the materials exhibit ‘normal’ first order phase transition behavior. At concentrations larger than 10\% the transition changes from first order to second order with the ‘diffuse’ transition previously identified in BTZ becoming predominant.\textsuperscript{140} The diffuse phase transition remains up to levels between 20 and 25 mole percent barium stannate. At this level the phase transition broadens further and frequency dispersion is seen in the temperature of $T_{\text{max}}$ – characteristics of a relaxor ferroelectric.\textsuperscript{157, 158}

Barium titanate stannate has received considerably less attention than either BST or BTZ especially for thin film studies. The limited number of groups working on the system have used CSD,\textsuperscript{159-161} PLD,\textsuperscript{162} and RF magnetron sputtering\textsuperscript{163}. Similar to the other solid solution thin film systems, BTS films grown to date suffer from the same diminished dielectric responses, including permittivities that rarely exceed 500, diffuse phase transition behavior, and low dielectric tunabilities. The effect of tin content on microstructure and dielectric properties was studied by Zhai and Yoon.\textsuperscript{160, 161} It was observed that increasing tin content resulted in a decrease in the average grain size, as was attributed to a diminished diffusion coefficient of tin in the lattice compared to titanium or a higher nucleation density as the tin content increased.\textsuperscript{161} The phase transition temperatures occurred at similar, if not higher temperatures than the bulk materials, including a pure barium titanate peak at 150°C.\textsuperscript{161} Such increased temperatures may bring into question accuracy of the measurement apparatus used. The work of Zhai also shows differing saturation values of permittivity for each composition, which again brings into question the measurement accuracy. Relaxor behavior was identified in a composition containing 10\% barium stannate by Halder and coworkers, however the films showed a large permittivity contribution due to space charges that were not considered in their analysis.\textsuperscript{162}
2.4.4 Barium Titanate – Barium Hafnate (Barium Titanate Hafnate)

Of the three systems discussed, barium titanate – barium hafnate (BaTi$_{1-x}$Hf$_x$O$_3$, BTH) solid solutions have received the least attention in the literature, most likely due to the limited availability of barium hafnate and the high costs of pure hafnium. Barium titanate and barium hafnate are both perovskites and form fully miscible solid solutions. As would be expected from the chemical similarity of hafnium and zirconium, the effect of barium hafnate on the properties of materials are virtually identical. The phase transition temperature decreases linearly with increasing hafnium content at a rate of – 5°C per mole percent. The tetragonal to orthorhombic transition increases by + 7°C per mole and the orthorhombic to rhombohedral transition increases by 16°C per mole barium hafnate.\textsuperscript{125, 164, 165} The critical composition where all three phase transitions occur at the same temperature is 16 mole percent barium hafnate. Compositions containing greater amounts of hafnium transition directly from the cubic phase to the rhombohedral.\textsuperscript{164} The phase transition behavior of BTH appears similar to that of BTZ, with an increase in diffuseness as the hafnium concentration increases. There have be no studies to determine if relaxor behavior will occur in barium titanate hafnate as it does in both BTZ and BTS. While it was observed that the peak permittivity increased with hafnium concentration to a level of 16 mole percent, it should again be noted that the samples used in the study were bulk ceramics and the effect of hafnium on the grain size and morphology was not determined. One study exists in the literature of barium titanate hafnate single crystals, however the materials contain less than 5 mole percent hafnium and no mention of phase transition behavior is made.\textsuperscript{166}

There exist few examples of barium hafnate containing solid solution thin films in the literature. It has been demonstrated that the films containing both hafnium and zirconium as substituents for titanium can be deposited by CSD\textsuperscript{167} and PLD.\textsuperscript{168} As a result of using processing temperatures in excess of 800°C, both groups were able to obtain samples with peak permittivities greater than 725.\textsuperscript{167, 168} The effect of hafnium on the microstructure and phase transition behavior has not been reported by any previous group in the literature.
2.5 Chemical Solution Deposition of Thin Films

Chemical solution deposition (CSD) describes a wet chemical method by which thin films are formed and encompasses a multitude of solution preparation and processing techniques. Perhaps the most well-known and widely used solution process is known as sol-gel. Sol-gel preparation of ceramic materials dates to the 1840s when Ebelmen used a chemical technique to form silicon dioxide. Since that time, sol-gel techniques have successfully been used to form a wide range of oxide materials, including complex oxides and ferroelectrics. Films formed from chemical solutions hold several advantages as well as disadvantages over other popular thin film deposition techniques, ironically with some of the advantages also being the process’s weakness. As solutions are prepared by dissolving metalorganics in solvents, the mixing that occurs is on a molecular level, ensuring a high level of chemical homogeneity in films. Solution derived materials can be formed from chemical precursors of extremely high purity as a result of distillation, thus providing for materials of higher purity than is available in many solid state methods. By adjusting the viscosity and concentration of solutions, films of various thicknesses can be formed over large areas with limited necessity for complex and expensive capital equipment. Solution derived materials have a distinct advantage over many other techniques in the flexibility to tailor composition quickly and easily. Unfortunately, the flexibility of chemical solution deposition is also its greatest weakness. The ability to repeat precisely a composition is difficult in small batches. Furthermore, while there has been a great deal of attention to the chemical reactions that occur within the solutions, the complexity of the systems often make it difficult to fully characterize and predict reactions that may occur.

While there are a vast number of solution chemistries that have been used for solution deposition, there are three that have become the most widely used. These are: sol-gel processes, hybrid-chelate processes, and metalorganic decomposition (MOD). Sol-gel processes refer to chemistries that use alcohols as both solvents and reactants. Hybrid-chelate chemistries use modifying ligands to react and stabilize a solution or component of the solution. MOD uses solutions that are based on water-insensitive metalorganic compounds.
Sol-gel is the most widely used term to describe the solutions used in chemical solution deposition. Unfortunately, its use is often a misnomer as many of the solution chemistries described as sol-gel are more closely related to hybrid-chelate processes. In true sol-gel processes an alcohol such as 2-methoxyethanol (2MOE) is used as a solvent and reactant for alkoxide metalorganic precursors. Here alkoxide refers to a chemistry of a metal, M bonded to oxygen, O, that is bonded to an alkyl group, R, (M(OR)_n). In forming a gel from the solution, two common reactions occur. First is a hydrolysis reaction where water in the solution reacts with the metalorganic and condensation where the hydrated alkoxide precursor react to form water and a complex metalorganic oligimer with oxygen bridging two metal ions as shown in Equations 2.25 and 2.26.

\[
M(OR)_n + H_2O \rightarrow M(OR)_{n-1}(OH) + ROH \text{ (hydrolysis)} \quad \text{Equation (2.25)}
\]

\[
2M(OR)_{n-1}(OH) \rightarrow M_2O(OR)_{2n-2} + H_2O \text{ (condensation)} \quad \text{Equation (2.26)}
\]

Methoxyethanol can react with some alkoxide metal precursors to form methoxyethoxide molecules that are less reactive and thus more stable through the following reaction, where OR' is a methoxyethoxy group.

\[
M(OR)_n + nROH \rightarrow M(OR')_n + nROH \text{ (alkoxy exchange)} \quad \text{Equation (2.27)}
\]

This reaction, in limiting the reactivity of the products, can be used to control the levels of condensation and hydrolysis that occur. The simplicity of the reactions involved in true sol-gel systems make it an ideal system for studying the preparation of new compounds. By controlling temperature, water content, and reflux/distallation conditions the nature of the oligimeric species formed can be controlled. Solutions formed from sol-gel chemistries tend to be stable over long periods of time because the reactions themselves can be controlled during preparation. While this particular solution chemistry has many advantages, it also has its drawbacks. Solution preparation of sol-gel precursors requires extensive knowledge of
chemistry and chemical preparation techniques as well as specialty equipment, such as a Rotary-evaporator. Additionally, 2-methoxyethanol is a known teratogen, which makes large-scale or industrial use unattractive.\textsuperscript{170-173}

Hybrid-chelate chemistries share many similarities with traditional sol-gel processes. Both chemistries use metal-alkoxides as starting materials and both form oligimeric species upon reacting. The differences stem from the use of a chelating or stabilizing agent to modify the metal alkoxides and make them less reactive to moisture. Typical chelating agents are acetic acid (AcOH), acetylacetone (2, 4 pentanedione or acac), and diethanolamine (DEA). Similar to sol-gel, a hybrid-chelate process can utilize a chelating agent as a solvent, however the agent is no longer an alcohol. For example, it is common for acetic acid to act as both the chelating ligand and the parent solvent. An example of a chelating reaction is given below for the chelation of a metal-alkoxide with acetic acid.

\[
M(OR)_n + xCH_3COOH \rightarrow M(OR)_{n-x}(OOCCH_3)_x + xROH \quad \text{Equation (2.28)}
\]

In addition to metal-alkoxides, metal-carboxolates are often used as starting reagents. This is particularly true for precursors that become low valence cations in the final film or ceramic. The hybrid-chelate process of solution preparation has one major advantage over sol-gel and that is the ease of solution preparation. Complex equipment and in-depth knowledge of chemistry are not necessary to form stable and complex solutions. Unfortunately, while solutions are easy to prepare, predicting the reactions that occur within is not easily done due to the number of components present. Furthermore, hybrid-chelate systems tend to remain reactive for the life of the solution, changing its properties with time and eventually leading to solution precipitation. In spite of these drawbacks, hybrid-chelate chemistries may be the most popular and the solutions discussed in this thesis fit in this family.\textsuperscript{171-173}

Metalorganic deposition differs from the previously discussed sol-gel and hybrid-chelate chemistries in that the solutions are relatively unreactive. In this solution chemistry, the reagents contain large carboxylate groups that are then mixed in an organic solvent. This chemistry is quite stable and is not as sensitive to water. In spite of its simplicity and
unreactive nature, this is one of the least common solution deposition chemistries used. The primary reason being large-scale cracking that occurs as a result of the large carboxylate group evaporation during subsequent drying and pyrolysis steps.\textsuperscript{171-173}

Processing solution deposited films occurs in three steps that are common to all solution systems. Films are wet deposited onto a substrate followed by a drying step to drive off solvents and consolidate the film into an amorphous gel and finally subject to a crystallization step to evolve the desired crystalline phase and microstructure.

The most common solution deposition method is spin-casting. In this process a solution is flooded onto a substrate, which is then spun at a rate varying between 1000 and 8000 revolutions per minute depending on the solution viscosity and desired layer thickness. This process is the simplest technique for laboratory-scale investigations and for that reason remains the most popular. Other wet deposition techniques include spray or mist coating and dip coating.\textsuperscript{173, 174}

Once a wet film is cast onto a substrate, the process of gellation begins. Gellation and the gel state are perhaps the least understood and most difficult parameter to characterize in solution-derived materials. The as-deposited film is typically amorphous and can contain a large volume fraction of organics. Schwartz has divided the nature of the as-deposited state into three subgroups.\textsuperscript{172, 173} The first is a chemical gel; here a significant level of condensation reactions has occurred during and/or after deposition and the films cannot be re-dissolved in the parent solvent. The second group is that of a physical gel. Physical gels show a physical aggregation of the oligimers present in the solution. The condensation reactions leading to extensive polymerization in chemical gels has not occurred and the films can be re-dissolved in the parent solvent. The third group is that of non-gelling films. Similar to physical gels in that a limited amount of condensation has occurred, these films tend to remain wet in appearance owing to high boiling points and low volatility of solvents and chemicals present in the solution.
Film consolidation may have occurred during or immediately after deposition resulting in a chemical gel. In other cases, the films must be exposed to higher temperatures (or allowed to sit in ambient conditions for some time to allow organic evaporation) to drive out remaining organics and to consolidate the gel. The thermal processes that are used to consolidate gels can be described by two categories. Thermolysis is a general term describing the removal of organics by heat. It can include either combustion or heating in a reducing atmosphere to drive organics through heat and partial pressures alone. Pyrolysis is a form of thermolysis that is specific to heat treatment in oxidizing atmospheres, such as air. Here organics are reacted with oxygen in the air to break bonds and form species that are easier to extract. Pyrolysis is by far the most utilized term in the literature, however many processes may actually be better described by thermolysis. The most common thermolysis treatment of thin films is a hot-plate ‘dry.’ Here the film is taken directly from the spin coater and placed onto the surface of a hot-plate with a temperature ranging between 200 and 400°C. During this step, the films experience significant shrinkage -- as much as 30% of the original thickness. The relatively high temperatures of the hot-plate thermolysis are necessary to remove a large fraction of the organic constituents prior to a collapse of the amorphous structure upon later heat treatments that would trap remaining organics. A secondary thermolysis step is commonly employed following the hot-plate treatment. This step, most commonly referred to as pyrolysis is typically conducted at temperatures between 500 and 700°C and is used to remove any remaining organic or hydroxyl species. Rapid thermal anneals, slow ramps, or hot-furnace insertion have all be used in this ‘pyrolysis’ anneal affectively. The films now are either crystallized at higher temperatures and recoated, or a crystallization step is skipped and the film is recoated. This process can be conducted several times to achieve the desired film thickness.

The final processing step is crystallization of the amorphous film. Crystallization and film morphology depend on several factors including, but not limited to: substrate, film composition, and prior thermolysis steps. Films deposited on single-crystalline or textured substrates maintain a possibility to grow with atomic registry to the substrate in an epitaxial fashion. Observing well-known free energy equations for crystallization (Equations 2.29
through 2.31), we can see how interfacial energy plays a role in determining the type of nucleation that occurs.

\[ \Delta G^*_{\text{homogeneous}} = \frac{16\pi\gamma^i}{3(\Delta G_v)^2} \]  
Equation (2.29)

\[ \Delta G^*_{\text{heterogeneous}} = \frac{16\pi\gamma^i}{3(\Delta G_v)^2} f(\theta) \]  
Equation (2.30)

\[ f(\theta) = \frac{(2 - 3\cos\theta + \cos^3\theta)}{4} \]  
Equation (2.31)

Where \( \gamma \) is the interfacial energy, \( \Delta G_v \) is the driving force for crystallization, and \( \theta \) is a contact angle for nuclei with a substrate or defect. As the driving force for nucleation increases, the probability of a homogeneous nucleus forming increases. An increase in driving force for crystallization in an amorphous film would include an increase in process temperature. Film composition very strongly can modify the final grain morphology. It is known that films that have a transient phase can show a preference for heterogeneous nucleation as this phase forms at lower temperatures where heterogeneous nucleation is favored and then transforms. This is likely the case for PZT thin films, which can crystallize as pyrochlore and then transform to perovskite.\(^{172} \) This argument does not hold for barium titanate systems, which first form an oxycarbonate phase and is known to crystallize homogeneously. However the structure of the oxycarbonate compared to perovskite is unknown and may provide for an additional barrier to perovskite formation. This provides a clear demonstration of the effect of composition on the resulting microstructure, as PZT based films generally form textured films that are one grain thick and barium titanate based films show more of an equiaxed morphology. Prior pyrolysis and heat treatments steps also can affect film morphology. If every layer is crystallized, it is possible to obtain a textured morphology, even in barium titanate systems.\(^{100} \)
2.5.1 Solution Processing of Barium Titanate Thin Films

Barium titanate thin films have been deposited using many different techniques including MOCVD,\textsuperscript{175} PLD,\textsuperscript{176} vacuum evaporation,\textsuperscript{177} RF magnetron sputtering,\textsuperscript{178} and MBE.\textsuperscript{179} This section discusses the deposition of barium titanate thin films using a chemical solution technique. While hundreds of papers exist in the literature concerning solution deposition of BaTiO$_3$, only those that introduced important chemistries, microstructures, and grain morphologies will be discussed.

The first example in the literature of a barium titanate film from a wet chemistry was a derivative of a true sol-gel approach by Yanovskaya \textit{et al.}\textsuperscript{180} The authors report the ability to crystallize films at 800°C on glass and platinum substrates, with secondary metatitanates forming at higher temperatures, indicating a difficulty in controlling stoichiometry. Films fired 800°C displayed dielectric constants of approximately 80 at room temperature, however the authors show a capacitance versus temperature curve that displays a sharp ferroelectric/paraelectric transition. This data is not well discussed and permittivity values of the sample are not reported. A true sol-gel approached was used by Campion and coworkers who deposited barium titanate on a platinized silicon substrate. The authors fired the film at 725°C and observed grain diameters as large as 250 nm, however ferroelectricity was not observed in the film.\textsuperscript{102} Using the same solution chemistry and processing at 750°C, Frey saw an average grain size of approximately 25 nm, which brings into question the 250 nm diameter measured by Campion. Frey’s materials again showed no ferroelectric hysteresis and had a peak permittivity of 230. The measurements did not reveal any phase transition behavior between –85 and 200°C.\textsuperscript{181} Hayashi and coworkers were the first to unambiguously measure ferroelectric properties in a solution derived thin film. Using a dip coating technique with a sol-gel chemistry and processing at 650°C, the authors formed films with average grain sizes of approximately 50 nm and saw permittivities between 800 and 1000 with loss tangents of 7 to 9%. The authors also measured dielectric hysteresis and confirmed that the material had a coercive field of 25kV/cm with a remanent polarization of 8μC/cm$^2$.\textsuperscript{182}
Some of the first work utilizing a hybrid-chelate chemistry for the deposition of barium titanate thin films was by Schwartz et al.\textsuperscript{183} In this work, barium acetate was dissolved in acetic acid and titanium butoxide was added to the solution. The precursor was diluted to 0.3M with methanol. It was found that the solution was stable for approximately 1 week. Processing on platinized silicon substrates revealed an equiaxed microstructure, commonly observed in barium titanate films. This was explained by the existence of barium carbonate and titanium dioxide phases prior to the onset of perovskite formation at 590°C. The dielectric properties of the films showed dielectric constants ranging from 180 to 300 and loss tangents of 1.5 to 6.5%. These properties were explained by the fine grain structure present with regard to inhibiting the permittivity.

In attempting to control the morphology of solution deposited films and thereby improve the dielectric properties, Hoffmann and Waser described a method by which columnar grains could be formed.\textsuperscript{100} The authors formed solutions of various hybrid-chelate chemistries; unlike Schwartz’s work, acetylacetone was used as a chelating agent for titanium butoxide in contrast to acetic acid. Barium precursors used were barium acetate dissolved in acetic acid and diluted with 2-MOE, barium propionate dissolved in propionic acid and diluted with butanol, and barium 2-ethylhexanoate dissolved in a carboxylic acid and diluted with 2-ethylhexanoate. It was observed that the longer the chain on the barium precursor, the lower the crystallization temperature. For example, the ethylhexanoate containing materials formed perovskites at temperatures less than 450°C. The other chemistries formed the often-observed barium titanium oxycarbonate phase prior to perovskite formation. By diluting the short chain solutions to 0.1M and firing each layer deposited at 750°C, films with a columnar structure were formed. Using typical processes with a 0.3M solution and a pyrolysis step, the authors formed films with a random, equiaxed morphology. In comparing the dielectric properties of the two morphologies, it was observed that a peak permittivity of approximately 1000 could be obtained in the columnar films, however a peak of approximately 500 was seen in the randomly oriented material. Schwartz built upon this technique and was able to show that a single seed layer of a dilute solution is necessary for columnar growth. That is, by depositing a layer of a dilute solution and
processing at high temperatures, subsequent layers can be deposited with less dilute solutions, so long as each layer is crystallized.\textsuperscript{183}

2.6 Controlled Atmosphere Processing

Traditional oxide processing methods, in particular thin film processing, have relied on noble metal or conductive oxide electrodes primarily to limit chemical interaction of the thin film materials with the substrate. In the multilayer capacitor industry, for example, the traditional electrode materials utilized were alloys of palladium and silver. As the usage of capacitors in circuit elements increased, as did the demand for such noble metals. Ultimately, a worldwide shortage of palladium in the 1990s drove the cost levels prohibitively high. This necessitated a need for less expensive metallization that could withstand the high processing temperatures required for the sintering of refractory oxide dielectric materials.\textsuperscript{184, 185}

In 1963 Herbert published a paper describing a method by which barium titanate could be processed in contact with a basic metal, nickel.\textsuperscript{186} By sintering a barium titanate ceramic in an atmosphere rich with hydrogen (and ultimately deficient in oxygen), with a small amount of manganese oxide, an electroded body of high permittivity barium titanate could be co-fired with either nickel or iron electrodes without oxidation of the base-metal.\textsuperscript{186, 187} The role of manganese oxide will be discussed in detail in the following section, however, it was speculated by Herbert that manganese might substitute for titanium in the lattice to compensate for oxygen loss from the lattice during firing.

Herbert’s observations and processing conditions have been reinforced in the multilayer capacitor industry as billions of barium titanate based devices are manufactured yearly using the reducing firing atmosphere with nickel electrodes.\textsuperscript{184, 188} With nickel being the most common base metal electrode used, it should be noted that it is not the only electrode material being considered. Recently it has been shown that copper could be used if the processing temperatures could be sufficiently lowered such that electrode melting could be avoided.\textsuperscript{189}
The success of base metal electrodes owes itself to the thermodynamics of metal oxidation. Considering a generic equation of the reaction of a metal with oxygen to form a metal oxide as in Equation 2.32. We can calculate a free energy associated with the reaction that is proportional to the temperature at which it occurs, and a reaction equilibrium constant, $K$, as in Equation 2.33, where $R$ is the universal gas constant. The equilibrium constant is equal to the ratio of the activities of the products to reactants as shown in Equation 2.34. Assuming that the activities of pure solids are unity, the free energy is now proportional to the temperature and the partial pressure of oxygen present.

$$2M + O_2 \rightleftharpoons 2MO$$  \hspace{1cm} 

Equation (2.32)

$$\Delta G^\circ = -RT \ln(K)$$  \hspace{1cm} 

Equation (2.33)

$$K = \frac{a_{MO}^2}{a_M^2 pO_2} = \frac{1}{pO_2}$$  \hspace{1cm} 

Equation (2.34)

$$\Delta G^\circ \approx RT \ln\left(\frac{1}{pO_2}\right)$$  \hspace{1cm} 

Equation (2.35)

Tables of the free energy of reactions are readily available for many metals and allow equilibrium reaction conditions to be calculated.$^{190}$ Plotting the equilibrium reaction lines of metals, metal oxides, and oxygen as a function of temperature and partial pressure of oxygen for the barium, titanium, nickel, and copper results in a phase diagram that can be used to predict thermodynamic stability of oxide and metallic species. Additionally, it reveals processing regions where the base metals are in thermodynamic equilibrium with the oxides of barium and titanium as shown in Figure 2.21.$^{190}$
Figure 2.21: Oxygen pressure versus temperature phase diagram for the equilibrium metals, oxygen, and metal oxides. Figure b) shows the equilibrium processing space where the oxides of barium and titanium are stable with metallic nickel and copper and oxygen.\textsuperscript{190, 191}

Failure to co-process the dielectric base-metal stacks under the proper conditions may result in interaction of the oxide dielectric with the electrode and deleterious effects. Considering the reactions that occur between barium oxide and copper oxide by observing their equilibrium phase diagram reveals several stable compounds that could form as shown in Figure 2.22.\textsuperscript{192} Similar effects are expected if copper were allowed to oxidize in contact with barium titanate.
While the success of base-metal processing apparent in the bulk ceramic industry is evident, the use of base metals as electrodes and substrates in thin film oxides has been limited. The first attempts at the deposition a thin film on a non-noble substrate was by Yi et al. for lead zirconate titanate thin films on stainless steel sheets in 1988. No data was presented for this material stack but it was noted that the films were processed at 550°C, presumably in air. The same group reported the deposition of PZT thin films on alumel wire using similar conditions. Again, no dielectric or phase information was reported. Chen et al. continued the PZT thin film on base-metal approach by demonstrating the film on nickel-titanium shape memory alloys. Very little data is available for this demonstration such as X-ray diffraction patterns that would identify phase formation and suggest the absence/presence of interfacial phases. Mercado et al. attempted to deposit the same material set and was able to demonstrate that process temperatures less than 650°C in air are necessary to prevent oxidation of the NiTi substrate. PZT was also studied on foil substrates, fired in air at temperatures of less than 650°C by several groups. Substrates used include stainless steel, titanium, brass, nickel alloys, and nickel foils coated with lanthanum aluminate (LaNiO₃). Films processed on bare foils suffer from low permittivities and high loss tangents. The addition of an interfacial conductive oxide allows for increased

---

**Figure 2.22:** Equilibrium phase diagram for system BaO-CuO (adapted from Zhang et al.192).

![Equilibrium phase diagram for system BaO-CuO](image)
permittivities and lower loss values, but adds complexity to the system. Representative electrical data for a typical PZT film on a base-metal substrate is shown in Figure 2.23. Work by Maria’s group has previously demonstrated PZT-based thin films on nickel coated copper foils using a flowing nitrogen high temperature anneal. Again temperatures less than 650°C were used for crystallization and an interfacial phase of NiP was formed from a reaction of phosphorus in the initial electroless nickel layer. The results were promising with lower loss tangents and low temperature coefficients of capacitance, however, the interfacial phase caused a subsequent loss in permittivity to below 400. All of these examples utilized leaded compositions in an effort to reduce processing temperatures and thereby kinetically limit the interaction between film and substrate.

**Figure 2.23:** Field dependence of permittivity for PZT deposited on stainless steel (adapted from Zou et al.200).

The first example of an oxide thin film processed using the thermodynamic approach outlined previously was by Dawley et al. Using chemical solution deposition, strontium titanate (ST) and barium strontium titanate (BST) were deposited on biaxially <100> textured Ni tapes. By firing the films in an atmosphere of wet 3% H₂ balance N₂, at 900°C, for a pO₂ of ~10⁻¹⁸ atmospheres, chemical stability between the metallic nickel substrate and the oxide could be accomplished. Electrical measurements indicate low permittivies (ε_r ~ 450) for randomly oriented grains in spite of high process temperatures and clean interfaces. Templating the films from the textured substrate resulted in permittivities approaching 1500 at room temperature for a Ba₀.₆₇Sr₀.₃₃TiO₃ thin film.
This thesis describes the first demonstration of a complex oxide thin film being deposited and fired on a copper substrate using the thermodynamic approach. Stemming from its success, other analogous attempts have been made. Laughlin et al. were able to show that barium strontium titanate could be deposited and fired on copper foils using the thermodynamically stable conditions and have demonstrated random polycrystalline films with low loss and permittivities approaching 1000. Sigman and Clem have begun work depositing barium strontium titanate on copper substrates and Trolier-McKinstry and coworkers are using a similar approach for deposition barium titanate on nickel.

In attempting to apply the equilibrium processing approach to PZT films, Losego discovered that the low temperatures used to minimize lead loss are not amenable to preventing substrate oxidation. These complications required an innovative kinetic approach to processing that utilized sophisticated binder burnout techniques and kinetics to mitigate substrate oxidation. This work for the first time demonstrated the ability to process a thin film oxide containing a volatile component in direct contact with a base metal substrate. Additionally, the work demonstrated the first report of a PZT thin film on a base-metal foil with properties equivalent or better than those on conventional noble metal electrodes.

2.7 Defect Chemistry in Barium Titanate

It has long been known that the processing of oxide materials in reducing atmospheres is not without consequence as the resistivity tends to decrease. Though oxide phases are thermodynamically stable at extremely low levels of oxygen, the thermodynamics of the environment dictate that the material will gain or lose oxygen to remain in equilibrium with the partial pressure at its surface. Consequently, under reductive atmospheres, an oxide material will release oxygen from the lattice forming vacant oxygen sites, as shown in Equation 2.36, and more specifically for barium titanate in Equation 2.37.

\[
O_o \leftrightarrow \frac{1}{2} O_2(g) \uparrow + V_o^{''} + 2e'
\]  

Equation (2.36)
\[ BaTiO_3 \leftrightarrow Ba^{2+}_{\text{Ba}} + Ti^3_{\text{Ti}} + 2O^2_0 + \frac{1}{2}O_2(g) \uparrow + V^0_o + 2e' \]  
Equation (2.37)

All variables are written using Kröger-Vink notation.\textsuperscript{210} The consequences of losing oxygen now become clear (in the limit of electronic compensation); the two electrons freed for each oxygen vacancy formed have to potential to electrically conduct, thus limiting the insulating nature of the material.

Concentrations of oxygen vacancies can be calculated from some basic thermodynamic parameters. If the enthalpy of reduction is known, the concentration of oxygen vacancies can be calculated. The calculation for barium titanate reveals the dependency of vacancy concentration as a function of temperature and oxygen partial pressure expressed in Equation 2.38. For barium titanate the enthalpy of reduction was determined experimentally to be \(-568\) kJ/mol.\textsuperscript{211}

\[
\left[ V^0_o, \ldots \right] = \left[ \frac{1}{4} pO_2^{1/2} \exp\left(\frac{-\Delta H}{RT}\right) \right]^{1/2} \]  
Equation (2.38)

Assuming electronic charge compensation for each vacancy formed (as has been suggested by Smyth to be most likely scenario for barium titanate\textsuperscript{212}), two electrons will be localized around each site. Using this model, the oxygen vacancy can be seen as a donor level in the bandgap of the insulating barium titanate. Each electron will have an activation energy to ionize to the conduction band. For the first activation to a singly ionized state, the energy required is \(0.1\) eV. The barrier to a second ionization is \(1.3\) eV.\textsuperscript{213} Reports of the bandgap of barium titanate vary, however it is believed to be in the range of \(2.9\) to \(3.41\) eV.\textsuperscript{212,213} Figure 2.24 shows a schematic of the band diagram for reduced barium titanate showing the effect of temperature on the ionization as controlled by Equations 2.39 through 2.42, where \(n\) is the charge carrier concentration, \(E_g\) is the bandgap energy, \(k_B\) is Boltzmann’s constant, \(T\) is the absolute temperature and \(E'_d\) and \(E''_d\) are the activation energies of singly and doubly ionized vacancies respectively.
For $V_o^+$ ionizing to $V_o^+$, with one electron being excited to the conduction band:

$$n_1 = V_o^+ = V_o^+ \exp \left( \frac{-E_d'}{k_B T} \right)$$  \hspace{1cm} \text{Equation (2.40)}

For $V_o^+$ ionizing to $V_o^{++}$, with the second electron being excited to the conduction band:

$$n_2 = V_o^{++} = V_o^+ \exp \left( \frac{-E_d''}{k_B T} \right)$$  \hspace{1cm} \text{Equation (2.41)}

Finally the total charge carrier density is equal to the sum of the two ionization events:

$$n = n_1 + n_2 = V_o^+ \exp \left( \frac{-E_d'}{k_B T} \right) + V_o^+ \exp \left( \frac{-E_d''}{k_B T} \right)$$  \hspace{1cm} \text{Equation (2.42)}

In the barium titanate system the difference of greater than 1 eV separating the first and second ionization events makes it likely that the electron carrier density is dominated by the first event with small contribution from the doubly ionized vacancies.
2.7.1 Doping in Barium Titanate

Material doping may be most familiar to those working with semiconductors where aleovalent doping can be used to increase the conductivity and to form junctions between regions containing different dopant species for device applications. Similar doping principles can be applied in oxides to alter the electronic and optical properties. For oxides processed in reducing atmospheres, it has long been recognized that the addition of small amounts of second phases prior to sintering can improved the final material resistance. Specifically for barium titanate it was observed early on that small amounts of iron impurities could improve the insulation resistance.\textsuperscript{214, 215} Remeika astutely surmised that the iron atoms were acting as acceptors for intrinsic donors in the material. Since that time many groups have studied the effects of impurities on the dielectric properties of barium titanate. Herbert was the first to connect the use of manganese as an acceptor to compensate for processing in reducing atmospheres as described earlier.\textsuperscript{186, 187} Burn expanded on Herbert’s work by demonstrating that elements of lower valence and similar size as Ti\textsuperscript{4+} could be used as acceptor dopants to compensate for low $p\text{O}_2$ processing.\textsuperscript{216, 217} Combined, this work has laid a backbone for the advancement of multilayer capacitor technology to the current form today with complex dielectric compositions finely-tuned to perform after co-processing with base metal electrodes.

Perhaps the most rigorous and complete study of the effects of reducing atmospheres and dopants on the properties of barium titanate was done by Chan and Smyth in the late 1970s and early 1980s.\textsuperscript{211, 212, 218, 219} Their work supplies the foundation for much of the defect chemistry outlined below. As shown previously in Equation 2.37, the processing of barium titanate under reducing conditions results in the formation of oxygen vacancies compensated electrically by electrons. If a small concentration of titanium ions were substituted by a lower valence ion of similar size, $A$, an oxygen vacancy can be formed that is now electrically compensated by the excess charge present by the substituted acceptor. Alternatively, the acceptors can be compensated electronically by holes. The acceptors
described in this thesis concern those ions with 2+ and 3+ charge as represented in Equations 2.43 and 2.46.

\[ AO \xrightleftharpoons{TiO} \rightarrow A''_{Ti} + O^+_O + 2h^+ \quad \text{Equation (2.43)} \]

\[ A_2O_3 \xrightleftharpoons{2TiO} \rightarrow 2A'_{Ti} + 3O_O + V''_O \quad \text{Equation (2.44)} \]

\[ AO + \frac{1}{2}O_2 \xrightleftharpoons{TiO} \rightarrow A''_{Ti} + 2O^+_O + 2h^+ \quad \text{Equation (2.45)} \]

\[ A_2O_3 + \frac{1}{2}O_2 \xrightleftharpoons{2TiO} \rightarrow 2A'_{Ti} + 4O_O + 2h^+ \quad \text{Equation (2.46)} \]

Schematically viewing the above reaction in a band diagram, the two electrons that previously were bound to the oxygen vacancy and subject to ionization now drop in energy to fill the acceptor state as shown in Figure 2.25, or are neutralized by the holes.

**Figure 2.25:** Band diagram showing annihilation of charge carriers associated with oxygen vacancies by acceptor states.

Practically speaking this can be achieved with many of the elements from the periodic table. The most common elements that fill the requirements of size and charge are: Mn, Ca, Mg, Co, Al, Fe, Ni, and Zn.\textsuperscript{211, 216-220} The utility of a multivalent cation like Mn becomes clear when considering the control necessary in doping a material at the part-per-million and part-per-billion levels needed to compensate for typical vacancy concentrations. Because of this, manganese is one of the most popular and widely used dopants, as it can change from Mn\textsuperscript{2+}
to Mn$^{4+}$ depending on the local environment and processing conditions. Monovalent dopants replacing barium are also feasible, however their usage is limited due to volatility at high temperatures.\textsuperscript{217}

For the sake of comparison, consider the effect of a donor dopant on the defect chemistry of barium titanate. Considering only the titanium oxide sublattice, if a 5+ valent cation were substituted for titanium we might expect the formation of electrons as represented in Equation (2.45).

$$2D_2O_5 \rightarrow 4D_{\text{Ti}}^* + 8O_O + O_2(g)^\uparrow + 4e'$$  \hspace{1cm} \text{Equation (2.45)}

Alternatively, this could be represented as the formation of a titanium vacancy in the titanium sublattice, as tends to be the case if doping levels are high, as illustrated in equation Equation 2.46.\textsuperscript{212}

$$2D_2O_3 \rightarrow 4D_{\text{Ti}}^* + V_{\text{Ti}}^{d'} + 10O_O$$  \hspace{1cm} \text{Equation (2.46)}

Donors on the $A$-site are more common than acceptors due to the lower volatility of many 3+ cations. Considering only the barium oxide sublattice, a 3+ substituent on the barium site would be expected for form electrons bound with the excess positive charge on the $A$-site as shown in Equation 2.47, or could be compensated by the formation of an $A$-site vacancy as in Equation 2.48.

$$D_2O_3 \rightarrow 2D_{\text{Ba}}^* + 2O_O + \frac{1}{2}O_2(g)^\uparrow + 2e'$$  \hspace{1cm} \text{Equation (2.47)}

$$D_2O_3 \rightarrow 2D_{\text{Ba}}^* + 3O_O + V_{\text{Ba}}^*$$  \hspace{1cm} \text{Equation (2.48)}

Typical $B$-site donors for barium titanate include Nb and W. La is the most common $A$-site donor.
The usage of acceptors in barium titanate based capacitors has been well documented. Upon studying the literature however, it is apparent that a much more commonly used dopant for reliability and lifetime of capacitors are amphoteric rare-earth and yttrium dopants that possess a $3^+$ charge and fit equally well on either the $A$-site as a donor or the $B$-site as an acceptor.$^{221}$ Generally speaking, it has been found that depending on firing conditions and stoichiometry, ions with radii between 0.87 and 0.94Å (in 6-coordination) can sit on either site. These include Y, Ho, Dy, Sm, Er, and Gd.$^{188, 222}$ A general expression for a rare-earth ion of appropriate amphoteric size in the barium titanate lattice is shown below.

$$R'_{Ba} + V'^{4'}_{Ti} \leftrightarrow R'^{'}_{Ti} + V''_{Ba}$$

Equation (2.49)

Under reducing conditions, this site balance of dopants has been shown to be proportional to the oxygen vacancy level:$^{223}$

$$\frac{[R'_{Ba}]}{[R'^{'}_{Ti}]} \propto \frac{[V''_{Ba}]}{[V'^{4'}_{Ti}]} \propto [V'^{4'}_{O}]$$

Equation (2.50)

There are several hypotheses to explain the reason for improved lifetimes in materials doped with amphoteric ions. It is possible that the dopant ions organize themselves on both $A$ and $B$ sites and therefore self-compensate and form donor-acceptor complexes throughout the lattice.$^{185}$ These donor-acceptor complexes could also be formed by compensation doping with traditional acceptors and donors, however the self-balancing nature of the amphoteric dopants could simplify the process. If a rare-earth ion sat on the $A$-site and stabilized an barium vacancy as in Equations (2.47) and (2.50), then a defect complex with an oxygen vacancy present from low $pO_2$ processing could form and would act to suppress the drift of the oxygen vacancy (i.e. $V''_{Ba} - V''_{O}$).$^{224}$ A rare-earth on the $B$-site would act to stabilize the oxygen vacancies formed during reductive processing, but would prevent the existence of easily ionized electrons. Such site occupancy could also form defect complexes with oxygen vacancies and would suppress drift (i.e. $2D'^{'}_{Ti} - V'^{4'}_{O}$).$^{223}$ Alternatively, it has been proposed that the amphoteric dopants may expand the single phase field region of barium titanate, thus making for a more homogeneous material that may limit the level of defective secondary
phases and limit oxygen vacancy transport. Rare-earth dopants seem to preferentially locate closest to grain boundaries as well. This being the most defective region in the material, it is likely to be the path of least resistance for oxygen vacancy migration and higher concentrations of dopants in these regions may impede vacancy motion. It is likely that all of the above-discussed mechanisms occur to an extent and contribute to the improved lifetimes and seen in materials with amphoteric dopants.

It is worth mentioning that Chan, Sharma, and Smyth were able to show using defect chemistry arguments that most commercially available barium titanate powders contain a modest level of acceptor impurities. By measuring the electrical conductivity as a function of $pO_2$ and temperature, a minima separating $n$-type and $p$-type conduction was found under reducing conditions. The only reasonable explanation is the existence of an acceptor impurity that compensates oxygen vacancies to a level allowing for the most insulating state to be produced by slight reduction. This provides a concise example regarding the difficulties in measuring the intrinsic properties of many oxide systems as such slight chemical modifications can impart dramatic property differences. It is worth mentioning that many groups use oxygen anneals in an attempt to “fully oxidize” ceramics and thin films. In light of this knowledge on impurities, in many cases such anneals may actually degrade material properties by driving excess oxygen into the lattice, in a defect reaction represented by Equation 2.51 where the material becomes $p$-type.

$$\text{Ba}_{ba}^+ + A_{t_i}^+ + 2O_{o}^+ + V_{o}^{**} + \frac{1}{2}O_2(g) \downarrow \rightarrow \text{Ba}_{ba}^+ + A_{t_i}^+ + 3O_{o}^+ + 2h^* \quad \text{Equation (2.51)}$$

It is clear that care must be taken when characterizing materials to recognize that almost all materials are not intrinsically pure and assuming so can lead to erroneous models and descriptions of data.

In addition to vacancy formation being a known cause of increased conductivity in oxides, their existence in materials with mobile domain or phase boundaries may alter behavior. Domain walls may become pinned on or their motion dampened by vacancies in the lattice, thus limiting the extrinsic contribution to permittivity.
2.7.2 Reoxidation of Barium Titanate

Discussed in the previous section were commercially practiced methods of compensating for oxygen vacancies that forms during firing with base-metal electrodes using compensation doping. In this section, the alternative thermal approach, called reoxidation, is considered. Following Equation 2.38, if a lower temperature and higher $pO_2$ could be used during processing, the level of oxygen vacancies would decrease. Limitations of base-metal oxidation prevent the use of higher $pO_2$ levels during sintering, however it has been shown that introducing higher oxygen levels during cooling can be introduced to increase resistivity of the dielectric, a process known as reoxidation. In principle, given enough time, the vacancy concentration should reach the equilibrium level for the conditions.

Studies on the effects of reoxidation have been conducted on Ni-base-metal multilayer capacitors. For compositions containing multi-valent cations e.g., Mn and Fe, it has been shown that reoxidation anneals between 800 and 1100°C in atmospheres containing 1 to 50 parts per million (ppm) oxygen result in a change in valence state of the dopant cations from 2+ to 3+ or 4+. This allows for a slight decrease in the oxygen vacancy concentration. For materials containing stable valence dopants, such as Y$^{3+}$, the oxygen vacancy concentration is controlled by the dopant level and thus cannot change even under oxidizing conditions. It is interesting that regardless of the dopant type used the effect of reoxidation on the dielectric properties is similar. That is, an enhancement of the dielectric constant at the phase transition, an increase in loss in the ferroelectric phases, and a decrease in loss in the paraelectric phase. That this occurs with valance stable and unstable dopants suggests that either grain boundaries are oxidized or an ordering of dopants and vacancies occurs. Impedance spectroscopy and TEM investigations have revealed that reoxidation anneals tend to reduce the levels of oxygen vacancies and increase the homogeneity of their distribution in the materials. Reoxidation increased the resistance of all circuit elements modeled in impedance spectroscopy, decreased the free carrier concentration and increased in the Schottky barrier height at the grain boundaries and electrode interfaces.
In multilayer capacitors, it was observed through $^{18}$O tracer studies that the reoxidation process is controlled by the Ni inner electrodes. At higher $pO_2$ values the Ni/NiO equilibrium conditions set the $pO_2$ seen by the dielectric, for conditions that do not significantly oxidize the electrodes. Therefore, in monolithic capacitors, oxygen diffuses along the Ni electrodes with an activity equivalent to the equilibrium $pO_2$ at the given temperature and then proceeds into the dielectric governed by Fick’s second law with an activation energy of $\sim 151$ kJ/mol.\textsuperscript{225} For $pO_2$ values higher than that of equilibrium for Ni/NiO, oxidation of the electrodes into a semiconducting state occurs, diminishing device performance.

### 2.8 Flux and Liquid Phase Assisted Sintering

Grain growth in ceramics can be inhibited by several factors, including segregation of impurities or solutes, secondary phases, porosity, space charges, liquid phases (especially if the liquid wets a grain boundary), and initial grain/particle morphology. In refractory systems, liquid phases or fluxes have long been utilized to improve densification and to lower process temperatures. There are two varieties of liquid-phase sintering. The first is reactive liquid-phase sintering and applies to systems where a small amount (typically less than 5 volume percent) of a liquid forming compound is added to a powder to drive diffusion and transport through dissolution and precipitation. An important distinction of reaction liquid phase sintering is that the solid phase must show limited solubility in the liquid. The second is named vitrification and applies to systems where significantly larger amounts (greater than 25 volume percent) of a liquid forming compound is added, which is enough to fill in porosity and interstices separating grains. In reactive liquid phase sintering, extensive grain growth and densification can occur due to dissolution of the solid, which allows for efficient mass transport through the liquid, and precipitation. In both varieties of liquid phase sintering densification is aided by the presence of a liquid phase through particle rearrangement as a result of capillary pressure. During vitrification, the glass compositions are chosen such that the glass wets the solid and thereby decreasing the solid-liquid interface energy, which decreases the driving force for grain growth. Therefore, vitrification processes
are generally used to form dense solids with little grain growth. High-density materials are achieved by proper selection of compositions and temperatures such that the viscosity and surface tension of the glass facilitates pore-filling. Two varieties of liquid phases are possible for liquid-phase sintering. Persistent liquid phases are present throughout the sintering process and remain as a glassy phase in the grain boundaries after cooling. Transient liquid phases form liquids at high temperatures and disappear during the firing process either through vaporization or consumption by the matrix ceramic.\textsuperscript{228, 229}

There does not exist a hard definition of a fluxing agent. Fluxes can either be glasses or crystalline phases that incorporate themselves into the lattice and promote diffusion. A key distinction between a flux and a liquid-phase sintering aid is that liquid-phases are generally used to aid densification, whereas fluxes are added to enhance grain growth.\textsuperscript{230} Fluxing agents need not form a liquid state during sintering. In some systems using liquid-phase sintering, a great deal of grain growth and densification is observed before the melting point of the glass. In scenarios such as these, the glass agents act as fluxes aiding diffusion in a process known as activated sintering, which is not well understood, but probably is related to cation vacancy formation.

\textbf{2.8.1 Binary and Ternary Fluxes and Liquid Phases}

In barium titanate systems, a number of liquid-phases and fluxes have been investigated. Perhaps the earliest used transient fluxes were barium chloride and potassium fluroide in barium titanate and barium titanate solid solution single crystal growth.\textsuperscript{128, 231} The advent of multilayer capacitors and the necessity of low-firing temperatures for compatibility with metal electrodes has lead to a substantial research on fluxes for the polycrystalline systems.\textsuperscript{232} Unfortunately, much of the work on fluxes has been proprietary and therefore unavailable in the open literature (see for example \textsuperscript{233-236}). Burn was one of the first to openly publish information on flux-sintered barium titanate.\textsuperscript{230} All experiments were aimed at improving densification and growing grains at sintering temperatures of 1100°C. Therefore, binary and ternary systems with compositions with melting points less than the sintering temperature were investigated. Each system was composed of a glass former
(B$_2$O$_3$, GeO$_2$, or SiO$_2$) and a modifier (CdO, Bi$_2$O$_3$, ZnO, CuO, or BaO). Burn observed that optimal grain growth and densification were achieved with glass former levels of 1 to 2 mole percent without deteriorating the permittivity. Typically modifier levels did not correspond to eutectic points or glass forming compositions. This was suggestive that the fluxing compositions were acting in some form of activated sintering and that the additives were being incorporated into the lattice. This proved especially true of systems containing bismuth, which was believed to be acting as a donor dopant in the lattice. It is interesting to note that the author did not investigate the incorporation of the glass formers in the lattice and drew all dielectric property conclusions based on the effect of the modifiers.

In developing a barium titanate based dielectric for use with copper electrodes, Song and Randall investigated the binary ZnO-B$_2$O$_3$ system and found that a eutectic composition allowed for densification below 1000°C with an optimum at ~ 2.9 wt% flux and a firing temperature of 1100°C. No mention of grain growth was made, however reasonable dielectric properties could be had with room temperature permittivities of 2700 and losses less than 1% with a small amount of LiO added to the composition.$^{189}$

Lead borate (PbO-B$_2$O$_3$) glasses have been investigated as possible fluxes for lowering the sintering temperature of barium titanate and other perovskites. Kuromitsu and coworkers investigated the system by mixing equimolar ratios of glass with fine-grained BaTiO$_3$ and firing at 850°C. It was demonstrated that as the PbO-B$_2$O$_3$ ratio decreased to less than 50% PbO, a BaTiB$_2$O$_6$ phase developed. Furthermore, through an apparent substitution process of lead for barium, a BaB$_2$O$_4$ phase was evident throughout the composition range. High boron content glasses showed interfacial titanium oxide and titanium boron oxide phases separating barium titanate from the glass, which was suggested to be an intermediate step in the reaction to form the BaTiB$_2$O$_6$ phase. Significant grain growth was observed for dwell times as low as 10 minutes. Thermodynamic arguments suggested that boron must be present for the lead substitution and subsequent formation of barium borate to occur.$^{237, 238}$ Closer investigation of this system by Hirata and Yamaguchi suggested that in order for the BaTiB$_2$O$_6$ phase to form, a substantial amount of barium must
be previously dissolved in the glass, leaving behind the previously mentioned TiO$_2$ interfacial phase.\textsuperscript{239}

Barium borate fluxes have been used in the sintering of barium titanate by several authors. Burn noted that compositions of BaO-2B$_2$O$_3$ were successful in densifying the ceramic materials and producing homogeneous samples at sintering temperatures of 1100°C.\textsuperscript{230} Goto and Cross studied the phase diagram of BaTiO$_3$-BaB$_2$O$_4$ in an effort to develop fluxes to form single crystals of barium titanate. They observed a simple eutectic at approximately 32 mole percent BaTiO$_3$ with a eutectic temperature of 942°C. No stable intermediate phases were observed in the system.\textsuperscript{240} In studying the BaO-TiO$_2$-B$_2$O$_3$ ternary system, Goto observed that there are two stable compounds that contain stoichiometric barium and titanium ratios and boron oxide – BaTiB$_2$O$_6$ and Ba$_2$Ti$_2$B$_2$O$_9$. BaTiB$_2$O$_6$ was stable below 1055°C, above which it undergoes a peritectic reaction to form TiO$_2$ and liquid while no mention was made of the stability of the Ba$_2$Ti$_2$B$_2$O$_9$ phase.\textsuperscript{241} The sintering behavior of donor doped barium titanate ceramics was investigated with additions of BaO and 2BaO-B$_2$O$_3$ by Drofenik et al. Sintering with 2 mole percent excess barium oxide alone did not reveal any abnormal grain growth at temperatures up to 1400°C while 2 mole percent of the glass composition showed dramatic densification at 900°C indicative of liquid formation and then showed anomalous grain growth at temperatures as low as 960°C. Excess barium oxide alone did result in a second phase of Ba$_2$TiO$_4$ forming at the grain boundaries of the material, while no secondary crystalline phases could be observed in samples with boron oxide added.\textsuperscript{242}

2.8.2 Unary Fluxes and Liquid Phases

LiF is the most historically significant unary flux for barium titanate.\textsuperscript{232, 243-246} LiF acts as a transient flux in during sintering, and is explained through an evaporative mechanism: Flourine and lithium volatilize rapidly at temperatures above 600°C and 800°C respectively. It is interesting to note that the decrease in fluorine level occurs prior to the formation of a liquid phase thus suggesting a reaction of the lithium fluoride with barium titanate and a form of activated sintering.\textsuperscript{244} In two of the more complete studies of this
system, Randall and Wang et al. were able to show that excess barium in the form of BaCO₃ was instrumental in forming a low temperature eutectic with LiF and BaTiO₃ at temperatures below 700°C. Without excess BaCO₃, the BaTiO₃ – LiF reaction does not occur until temperatures in excess of 750°C. The reaction has been suggested to form a cubic perovskite with lithium substituting for titanium and fluorine for oxygen (chemical analysis suggests that most of the fluorine is volatilized during firing and little remains in the lattice) and forms a second phase of LiTiO₂ as excess titanium is expelled from the lattice to react with the excess Li that remains as a result of the low temperature fluorine volatility.²⁴⁵, ²⁴⁷ In the BaTiO₃ – LiF – BaCO₃ system, densification occurs without grain growth at temperatures between 700 and 800°C for compositions containing 0.25 to 1.5 weight percent LiF. Holding the temperature at 850°C and increasing the LiF content from 0.5 to 1.5 weight percent showed a transition from normal homogeneous grain growth to discontinuous grain growth. At 950°C abnormal grain growth is observed for all LiF levels. For samples sintered at 850°C, a core-shell structure forms with a pure BaTiO₃ core and a doped shell. Consequently, the dielectric constant versus temperature measurements show a diffuse phase transition with $T_{\text{max}}$ at approximately 0° and a minority peak at ~125°C. The diffuseness and shifting that occurs was attributed to chemical inhomogeneity in the grain shell with a range of phase transition temperatures. Computer modeling of such a structure showed a nearly identical response to the experimental data.²⁴⁷ Heating to higher temperatures resulted in a homogenization of the microstructure to form a lithium containing cubic perovskite.²⁴⁵, ²⁴⁷

SiO₂, Al₂O₃, and P₂O₅ have been investigated for liquid-phase sintering. Unlike LiF and many of the binary glasses these additives show an ability to densify BaTiO₃ with minimal grain growth. For P₂O₅, it has been reported that a secondary phase of Ba₃(PO₄)₄ forms at grain boundaries and may inhibit the motion of these boundaries in the sintering process. This grain growth inhibition occurs at temperatures below 1200°C. Increasing the temperature results in a titanium-rich secondary phase that melts and promotes abnormal grain growth.²⁴⁸, ²⁴⁹

Boron oxide without glass modifiers has been used as a fluxing agent for barium titanate sintering. Conflicting results exist for the material set with debate regarding the
solubility and site occupancy of boron in the perovskite lattice. Castelliz and Routil were the first group to investigate the usage of boric oxide as a sintering aid for barium titanate. Optimal properties including high density and low room temperature loss were achieved with a 10 mole percent addition of boron oxide with a sintering temperature of 1100°C. X-ray diffraction studies revealed a contraction of the unit cell volume with boron oxide addition and a segregation of a secondary $\text{BaTi}_4\text{O}_9$ phase. The authors explained the unit cell contraction and second phase formation by a substitution process of boron sitting on octahedral sites in the perovskite lattice and expelling titanium to form a second phase.\textsuperscript{250} The use of boron nitride as a fluxing agent has been investigated by multiple groups.\textsuperscript{251, 252} The authors found that approximately 4 mole percent BN addition resulted in the highest density samples with densification occurring at around 950°C, which was presumed to be due to the decomposition of BN to from liquid boron oxide and nitrogen gas. Contrary to previous work, a $\text{BaB}_2\text{O}_4$ phase was identified and no variation in unit cell size was observed. Conflicting results were obtained on the electrical properties with one group observing a decrease in resistivity as the boron level increased and attributed this to boron incorporating on interstitial sites in the lattice and subsequently acting as donors.\textsuperscript{252} The other work saw no change in resistivity or unit cell dimensions with boron addition and suggested that boron exists only at grain boundaries and also volatilizes during sintering.\textsuperscript{251} Boron oxide has been added to barium strontium titanate ceramics with similar results. Sintering at 1150°C with varying levels of boron oxide showed that secondary phases formed with additions of 1 weight percent and greater. Furthermore, 0.5 weight percent boron oxide addition resulted in discontinuous grain growth, while increasing to 2 percent limited grain growth. Electrical measurements of the material showed no change in the phase transition behavior and for materials containing 0.5 weight percent boron oxide also showed no increase in zero bias and room temperature loss tangent with increasing boron level.\textsuperscript{253} Vapor transport has been used as a means to incorporate a boron phase into barium titanate without directly adding materials to the powder prior to sintering. X-ray measurements of samples doped via the vapor transport method showed a net increase in unit cell volume in addition to an increase in the tetragonal distortion at room temperature, suggestive of boron occupying interstitial sites in the lattice. It was also observed that the temperature of the paraelectric to ferroelectric phase transition increased with boron addition as would be expected for
ferroelectrics with a more pronounced polar distortion. The proposal of an interstitial boron occupancy also suggests that the material should be donor doped with either cation vacancy or electron compensation necessary for electroneutrality.\textsuperscript{254}

2.8.3 Fluxes and Liquid Phase Sintering in Thin Films

Several groups have investigated liquid phases or fluxes to improve the properties of thin ferroelectric films. Saegusa has probably contributed the most to the literature on the subject, in particular to the lead titanate and lead zirconate titanate systems.\textsuperscript{255-259} Specifically he has studied PbTiO$_3$ and Pb(Zr,Ti)O$_3$ ferroelectrics with lead borate, lead silicate, and lead borosilicate glasses, all deposited from chemical solutions on either platinized silicon wafers or foils of aluminum, titanium, and stainless steel. For the lead borate glasses, the crystallization temperatures were decreased by 20 to 40° (460-480°C) with higher lead content glasses forming perovskite phases directly and lower lead content glasses first forming a pyrochlore phase. Lead silicate glasses delayed crystallization to 500°C where a pyrochlore phase formed prior to perovskite formation at 700°C, which was ascribed to the pyrochlore being of higher density and therefore is stable until the glass phase softens. The amount of glass phase used ranged from 10 to 40 mole percent and grain growth was proportional to the level of glass. The microstructure of the boron containing glasses were shown to have grain sizes increasing with firing temperature up to 700°C, at which point no further increases were observed, however grains in excess of 1 µm in diameter were observed at these relatively low temperatures. The silicate glasses tended toward finer grain sizes. The dielectric constants of the glass-ceramic thin films were less than 300 with loss tangents ranging between 1 and 8 percent. The low dielectric constants could be explained by a mixing model with the high volume fractions of glass phases diluting the composite permittivity.

Bismuth-silicon oxide and borosilicate glass have been studied for use as a fluxing agent to form ultra-thin layers of lead zirconate titanate for use as gate dielectrics. Materials were deposited on platinized silicon substrates and were prepared using chemical solution techniques. It was found that the crystallization temperatures decreased with increasing
second phase content and that the dielectric properties are diluted relative to that expected for pure materials with peak permittivities greater than 800. For the glass-ceramic fired at 700°C, permittivities were below 600, but these films showed extremely uniform and dense microstructures.  

Boron and borosilicate glasses have been added to barium titanate and barium strontium titanate solutions for thin film deposition by a number of groups. The systems show similarities to the leaded perovskite systems in that increasing the glass content increases the average grain size for a given firing temperature. For the case of boron addition only, secondary phases were not observed for boron additions of up to 10 mole percent while the average grain size for a 700°C crystallization anneal increased from 23 nm to approximately 31 nm for compositions ranging from 0 to 10 mole percent boron. Interestingly, the increase in grain size was not accompanied by an increase in permittivity. Pure BST had a permittivity of approximately 500 while the addition of 10 percent boron decreased the permittivity to less than 200. This was again attributed to the boron glass wetting the grain boundaries and diluting the dielectric constant. Similar results were observed for the borosilicate glass system with permittivities decreasing with increasing glass additive level. It was, however, shown that increasing the glass level from 0 to 10 mole percent resulted in an increase in the insulation resistance prior to a decrease with more than 10 mole percent additive.
Chapter 3: Barium Titanate Solution and Thin Film Preparation and Properties

In this chapter the initial barium titanate thin film preparation methods are discussed. This includes the development of the solution chemistry, deposition methods, and studies of the crystallization behavior. The work begins by investigating low-toxicity solutions that can be deposited via a spin casting technique. All preliminary studies of the solution chemistry and its crystallization behavior were conducted on platinized silicon substrates to limit complications that could result from deposition and processing on copper foils. With a suitable solution chemistry devised that demonstrates clear evidence of perovskite barium titanate formation upon crystallization, the technology is transferred to depositions on copper foil substrates. Construction and operation of the controlled atmosphere furnace for crystallization anneals is discussed and the initial properties of barium titanate thin films on copper substrates are demonstrated.

3.1: Barium Titanate Solution Chemistry

In developing a commercially viable chemical solution deposition technique for the formation of barium titanate thin films, several factors needed consideration, including the availability, cost, and safety protocols related to the chemicals used. As discussed in section 2.5 there are a variety of solution chemistries in the literature that have been utilized in the deposition of barium titanate thin films including sol-gel, hybrid-chelate, and MOD. Of these, sol-gel is the most popular and widely used, primarily because of the chemical stability of the solutions that form. For this project, solutions based on sol-gel chemistry were eliminated from the possible approaches due to the inherent toxicity of 2-methoxyethanol -- the primary solvent. Metalorganic decomposition approaches were not considered because of the limited availability of literature concerning the preparation and processing and because of the cracking issues known for the technique. For these reasons, a hybrid-chelate chemistry was chosen.
The solution preparation chemistry and process were loosely based on the works of Hoffmann and Schwartz.\textsuperscript{100,183} Two methods of solution preparation will be discussed in this section. The first is representative of all initial results and includes the use of methanol as a dilution agent to control solution stability and viscosity. The second method eliminates methanol from the formulation and uses acetic acid as both the solvent for barium acetate and as the dilution agent. The phase formation and properties of films grown from both systems is similar and the motivation for the change was elimination of the volatile methanol component as required by the industry sponsor.

While Hoffmann’s work showed a preference toward barium propionate as a barium source, the availability and use of barium acetate by Schwartz made it preferable. Titanium isopropoxide was chosen as the titanium source based upon the availability of high purity (99.999\%) chemicals in comparison with titanium butoxide. While Schwartz chose to chelate titanium isopropoxide with acetic acid, the stronger chelating agent of acetylacetone was chosen based upon the work of Hoffmann, and solutions formed with this chemistry had a significantly longer shelf life.

The chemical solutions were prepared in a glove box under dry nitrogen atmospheres and room temperature in an effort to minimize the level of water vapor present that could react with the precursors and solutions prior to deposition. In particular, it is known that titanium isopropoxide is strongly reactive with water vapor and causes degradation of the precursor with exposure. Relative humidity levels present during preparation were consistently less than 20\%. To form the barium precursor, barium acetate (99\% Sigma-Aldrich) was dissolved in glacial acetic acid (\textgeq99.99\% Sigma-Aldrich). For methanol diluted solutions, 6.000 grams of barium acetate were measured using a Mettler-Toledo AT201 5-decimal digital balance and added to a 50 mL screw-top Erlenmeyer flask (Kimble Kimax). 23.48 mL of glacial acetic acid was added using a pipette (BrandTech Transferpette) and the mass was recorded to calculate the molar mass of the barium precursor. For acetic acid diluted solutions, 6.000 g of barium acetate were measured and placed in a 50 mL Erlenmeyer flask. 51.000 g of glacial acetic acid was added to the powder using a micropipette and eyedroppers to achieve higher precision. The mixtures were capped
with Teflon lined screw caps (Qorpak) and allowed to stir at room temperature and 200 RPM with a 0.625” Teflon coated magnetic stir bar for approximately 2 hours until the barium acetate was fully dissolved. In each case an excess amount of the barium precursor was prepared to ensure that a stoichiometric solution could be formed without being barium deficient. Titanium precursors were prepared by massing 0.02 moles (approximately 5.6852 g) of titanium isopropoxide (99.999% Sigma-Aldrich) in a screw-top Erlenmeyer flask. 0.08 moles (approximately 4.048 g) of acetylacetone (≥99% Sigma-Aldrich) was added drop wise via an eyedropper to the titanium isopropoxide. The solutions were capped with the Teflon lined screw caps and allowed to stir under identical conditions to the barium precursors. It should be mentioned here that the chelation reaction of acetylacetone with titanium isopropoxide is strongly exothermic with the solution temperatures increasing by several tens of degrees for the first few minutes of mixing. All masses were recorded and the precise number of moles of titanium was calculated. With the molar mass of the barium precursor and the number of moles of titanium calculated, a stoichiometric amount of the liquid barium precursor was added to the titanium precursor using a pipette and an eyedropper. The barium precursor was added while the titanium flask was on the balance to best enable the preparation of a solution containing a 1:1 ratio of Ba:Ti. Based upon the calculations, most solutions formed using this method have equivalent barium to titanium levels within 100 ppm – which is at the edge of the precision of the balance and molecular weights of the raw materials. The solution was then recapped with a Teflon coated screw cap and allowed to stir overnight (~12 hours). The molarity of the acetic acid diluted solutions at this point was approximately 0.3. After the 12 hours of mixing, methanol was added to the methanol-diluted solution to a reach a molarity of 0.3. The solution preparation procedures are outlined schematically in Figure 3.1.
Figure 3.1: Solution preparation procedure for a) methanol-diluted and b) acetic acid diluted barium titanate solutions.

3.2: Barium Titanate Thin Films on Platinized Silicon Substrates

The as-prepared solutions were deposited via a spin-casting technique using a Cookson Electronics P-6000 spin coater. Substrates used in initial studies were platinized silicon wafers (Si/SiO₂/Pt) prepared by e-beam evaporation with the platinum bottom electrode films possessing a <111> fiber-texture. The wafers were sectioned into approximately 2 cm² sections and placed on the spin-coater chuck. A syringe (Becton-Dickinson) with a 0.2 μm filter (Fisher Scientific) was used to dispense the solution onto the substrate by flooding the surface. Films were cast by spinning at 3000 RPM for 30 seconds. Substrates were immediately removed from the spin coater chuck and placed directly on a 250 °C hotplate for 5 minutes to drive off solvents and to consolidate the film. The hotplate drying process was followed by a 400°C pyrolysis step in a tube furnace in air for 15 minutes. This process was repeated 4 times to increase film thickness.

Samples on platinized silicon substrates were crystallized at temperatures ranging between 350°C and 750°C for 30 minutes in a tube furnace in an air atmosphere. Phase development during crystallization was studied via X-ray diffraction using a Bruker D-5000 X-ray diffractometer equipped with a Hi-Star area detector with a focusing circle of 15 cm. The area detector allows approximately 35° of 2θ to be collected for a single ω setting. Furthermore, the detector acts as a section of a Laue camera and therefore can provide insight
into texturing of the sample by collecting diffraction events in the $\chi$ angles. Because of the area detector capability, this instrument is particularly useful for identifying low volume fraction phases through integration along the $\chi$ circle. X-ray diffraction patterns for each crystallized film are shown in Figure 3.2. A logarithmic intensity scale was used to amplify the intensity at low count levels to distinguish between secondary phases and the background. From this plot the development of peaks associated with a perovskite crystal structure are apparent at temperatures in excess of 550°C. The peaks increase in intensity with the $111$ peak becoming clear at 700°C.

![Figure 3.2: X-ray diffraction patterns for barium titanate thin films on platinized silicon substrates processed in air in a temperature range of 350 to 750°C.](image)

To prepare capacitor structures for dielectric measurements, top electrodes were deposited through a shadow mask. For convenience, platinum was chosen as a top electrode material. The electrodes were deposited via DC magnetron sputtering using a 4-inch magnetron sputtering gun with a power of 300 Watts and argon as the ionized gas at a pressure of 30 mTorr. The sputtering chamber used was designed to handle UHV conditions and used the Moore method of Conflat® flange assembly. Electrodess were deposited to a thickness of approximately 30 nm with sizes ranging from $6 \times 10^{-4}$ to $2 \times 10^{-3}$ cm$^2$.  

82
The dielectric properties of the barium titanate thin film on a platinized silicon substrate processed at 750°C were investigated using an HP 4192A low frequency impedance analyzer. Figure 3.3a shows a capacitance density versus applied bias curve for a barium titanate thin film measured at 100 kHz with an rms oscillator level of 0.1V. Capacitance density is plotted, as film thickness is not known. The measurement reveals a small amount of dielectric tunability characteristic of a ferroelectric material. Loss tangents are relatively low and suggest a material with low levels of electrical leakage and space-charge. To verify the existence of space-charge a capacitance density versus frequency plot was taken with the identical oscillator condition over a frequency range of 1 kHz to 1 MHz as shown in Figure 3.3b.

![Figure 3.3: Capacitance density versus a) applied bias and b) capacitance density versus frequency for a BaTiO$_3$ thin film on platinized silicon.](image)

Over the measurement range there is limited dispersion in capacitance density of approximately 1% per decade. No dramatic dispersion is over the measurement range is identified and is indicative of a material with very low levels of space-charge. The increase in loss at high frequencies can be attributed to a resonance in the impedance bridge associated with the relatively large capacitance of the device under test.

Each of the data described in this section point toward the successful deposition of a barium titanate thin film via the chemical solution approach. Ultimately though, the rigidity and cost of platinized silicon substrates deem them unsuitable for use in embedded passive applications. For these reasons subsequent sections deal exclusively with flexible copper foil substrates.
3.3: Barium Titanate Thin Films on Copper Substrates

The success of forming stable barium titanate solutions of limited toxicity capable of being spin-cast and processed to form barium titanate was the initial step in achieving the ultimate goal of this thesis – a demonstration of barium titanate thin films on a copper foil substrates. In this section there will be a discussion of the principles of low $pO_2$ processing as it pertains to deposition barium titanate on copper as well as a description of the equipment necessary to achieve controlled atmospheres at high temperatures.

3.3.1: Principles of Low $pO_2$ Processing of Barium Titanate Thin Films

As discussed in section 2.6, the reaction of metal with oxygen to form metal oxides is governed by the oxide free energy of formation, the temperature, and the oxygen partial pressure. Using this knowledge, phase diagrams showing the equilibrium phase fields of metals, oxygen, and metal oxides can be developed. As shown in Figure 3.4, such a diagram for a system containing barium, titanium, and copper establishes a large process zone where copper metal is in equilibrium with oxygen gas and the oxides of barium and titanium. For example, Fig. 3.4 teaches that to process barium titanate on copper at a temperature above the temperature of barium titanate crystallization e.g. 700°C, an atmosphere with less than $\sim 10^{-11}$ atm of oxygen is necessary. Practically achieving such an atmosphere would be difficult using vacuum technology, especially with a film containing a large fraction of organics that would be thermalized during heating. A more reasonable system would take advantage of gas phase reactions to reduce the level of oxygen in the processing atmosphere.
Figure 3.4: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides. The shaded region represents the conditions where barium and titanium oxidize and copper is reduced.

A furnace was constructed for the controlled atmosphere processing of barium titanate thin films as shown in Figure 3.5. The system consists of a Lindberg-Blue M glowbar tube furnace and controller with a 2” fused silica tube. Furnace tube ends are terminated with CVD end caps and sealed with Viton® o-rings. Process gases are introduced through an H$_2$O bubbler to pick up water vapor to be used in the gas phase reactions to control $pO_2$ and are plumbed in through one of the endcaps. The exhaust end of the furnace is equipped with a second H$_2$O bubbler to act as a check-valve for the process gases to eliminate backstreaming.

The gas phase equilibrium between oxygen, hydrogen, and water vapor governs oxygen partial pressure as shown in Equation 3.1. By establishing a fixed furnace temperature and the level of water vapor in bubbled gas mixture, the $pO_2$ can be controlled as shown in Equation 3.2.

$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$$  \hspace{1cm} \text{Equation (3.1)}

$$pO_2 = \frac{pH_2O^2}{pH_2^2} \exp \left( \frac{2\Delta G}{RT} \right)$$  \hspace{1cm} \text{Equation (3.2)}
The gas mixtures used in the processing of barium titanate thin films are nitrogen from a liquid source, which acts a carrier gas and contains approximately 1 ppm of oxygen impurity and forming gas containing 1 mol% H$_2$ with a balance of N$_2$. By passing the mixture through the H$_2$O bubbler at room temperature, the water vapor for the balanced reaction is gathered. To obtain a $pO_2$ of less than $10^{-11}$ atm at 700°C a gas mixture of 400 sccm N$_2$ carrier gas with 5 sccm of the hydrogen forming gas was used. Typical processing of barium titanate on copper utilized a $pO_2$ several orders of magnitude less than that required for Cu-Cu$_2$O equilibrium in order to provide a margin of error and used flows of 400 sccm of N$_2$ carrier gas with 55 sccm of forming gas. An Australian Oxytrol Systems DS-Series solid-state $pO_2$ sensor was passed through one furnace end cap with an ultra-torr seal. The solid oxide sensor was located in the center of the furnace hotzone and is used to monitor the oxygen partial pressure in situ during the high temperature processing. The oxygen sensor generates a voltage due to the concentration gradient of oxygen on each side of the solid oxide cell. Combining the sensor voltage output and the temperature reading from a thermocouple on the temperature sensor allows $pO_2$ to be calculated using the manufacturer supplied Nernst Equation where 0.209 represents the ambient level of oxygen in the atmosphere in atm, $E$ is the signal from the sensor, and $T$ is the absolute temperature of the sensor:

$$pO_2 = 0.209 \exp\left(-\frac{46.42 \times E}{T}\right)$$

Equation (3.3)

Copper foils used in these experiments are 18µm thick PLSP foils supplied by Oak-Mitsui. Because of the foil flexibility, vacuum cannot be used to affix foil sections to the spinning chuck. Consequently, foils are cut into sections approximately 1.5” on a side and taped on two edges to a 4” silicon wafer using Scotch$^\text{®}$ tape. The wafer is then placed on the vacuum spin chuck. The barium titanate solutions are applied to the as-received foils using a syringe and filter by flooding the surface of the foil with the solution. Films are spun at 3000 RPM for 30 seconds. Immediately after spinning, the tape is removed from the foil and the foil is placed directly on the surface of a 250°C hotplate. After drying for 5 to 10 minutes, the foils are removed from the hotplate. Due to the possibility of copper foil oxidation during pyrolysis at higher temperatures, this step is skipped and foil is recoated with solution.
using the above procedure. The coating and drying process is repeated between 2 and 5 times to achieve the desired film thickness. Films are then loaded onto a fused silica boat and copper bars are placed onto the corners to prevent curling during firing. The boat is then loaded into the idle furnace at 150°C; the furnace endcaps are replaced and the gas flows are set with mass flow controllers. The furnace is then ramped to the desired temperature at a rate of 30°C/minute and allowed to dwell for 30 minutes. At temperature greater than 700°C (the lower limit of usability of the oxygen sensor) $p_{O_2}$ values are recorded. The furnace is allowed to cool to 150°C via Newtonian cooling prior to sample removal. The process flow is shown schematically in Figure 3.5.

![Figure 3.5: Process flow of the formation of barium titanate thin films on copper substrates.](image)

### 3.3.2: Phase Development of Barium Titanate Thin Films

X-ray diffraction was used to study phase development in the thin films after firing in a range of 300 to 900°C as shown in the X-ray diffraction patterns in Figure 3.6. All films were processed as above with gas flows of 400 sccm $N_2$ and 55 sccm 1%$N_2/H_2$. For temperatures where $p_{O_2}$ measurement is appropriate, the $p_{O_2}$ value during processing is shown in comparison with the equilibrium line of copper, copper oxide, and oxygen in Figure 3.7.
Figure 3.6: X-ray diffraction patterns for barium titanate thin films on copper substrates processed in reducing atmospheres in a temperature range of 300 to 900°C.

Similar to the samples fired in air on platinized silicon substrates, the evidence of perovskite formation does not begin until moderately high temperatures, in the case of low $pO_2$ processing this occurs at 650°C. The formation of the perovskite phase is preceded by a crystalline phase that corresponds to a carbon containing complex of barium and titanium, barium titanium oxycarbonate, that forms at 600°C and disappears by 650°C. $Ba_2Ti_2O_5CO_3$ has been reported previously in the literature for barium titanate prepared from chemical solutions and is a known transient phase.\textsuperscript{98-103} No card exists for the phase in the Powder Diffraction File, so it remains un-indexed, however the peaks correspond to those attributed to barium titanium oxycarbonate as determined by Frey.\textsuperscript{98,266}
An interesting feature of the X-ray diffraction data is the existence of a Cu$_2$O phase at the same temperature as the crystallization of BaTiO$_3$. This also corresponds to the temperature at which decomposition of the Ba$_2$Ti$_2$O$_5$CO$_3$ occurs by the reaction in Equation 3.4 to form barium titanate and carbon dioxide.

$$\text{Ba}_2\text{Ti}_2\text{O}_5\text{CO}_3 \rightarrow 2\text{BaTiO}_3 + \text{CO}_2(g) \uparrow$$

Equation (3.4)

$$2\text{CO}_2 \leftrightarrow 2\text{CO} + \text{O}_2$$

Equation (3.5)

By plotting the thermodynamic equilibrium reaction of CO, CO$_2$, and O$_2$ as represented by Equation (3.5) as a function of $pO_2$ and temperature$^{191}$ and comparing with the actual measured process conditions for samples fired between 700°C and 900°C reveals an interesting feature as shown in Figure 3.8.
Figure 3.8: Oxygen pressure-temperature phase diagram for the reaction of copper and oxygen to form copper oxide and the reaction of carbon monoxide with oxygen to form carbon dioxide.\textsuperscript{190,191}

The process conditions used correspond to conditions that border the equilibrium reaction of the CO\textsubscript{2} and CO gases. It is hypothesized that close to the barium titanate/copper interface, the CO\textsubscript{2} gas that evolves during the decomposition of Ba\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5}CO\textsubscript{3} is favored to form CO and O\textsubscript{2} and this excess O\textsubscript{2} is free to react with the copper substrate. Even though the equilibrium conditions suggest that copper oxide is unstable under these furnace conditions, it is possible that the oxygen is trapped close to the interface because of a capping effect by the dense film of BaTiO\textsubscript{3}. This in turn raises the local oxygen activity to a level that promotes copper oxidation. Despite the instability of the Cu\textsubscript{2}O phase, at temperatures below 900°C, kinetics are sufficiently slow that some remains after cool down. At 900°C, however, the oxygen transport appears to be sufficient to allow interfacial Cu\textsubscript{2}O decomposition to oxygen and metallic copper. For this reason, conditions of 900°C will be used for most experiments in this thesis.

3.3.3: Physical Characterization of BaTiO\textsubscript{3} Thin Films

This section discusses the methods and tools used to characterize the physical properties of the barium titanate thin films on copper substrates. Particular attention is paid to tools that can give information about grain size and morphology. All data represented in this section are for the original barium titanate thin films on copper foils. The films were deposited from methanol-diluted solutions in three layers with 250°C, 5:00 minute hotplate dry steps after each layer.
The X-ray diffraction pattern of a typical barium titanate thin film on a copper foil prepared using this equipment and procedure to a temperature of 900°C is shown Figure 3.9. From the plot we see clear evidence of perovskite formation, as expected from the previous crystallization study. Importantly, the reducing conditions and 900°C process temperatures were sufficient to prevent the formation of copper oxide. Closer inspection of the pattern reveals sharp and narrow diffraction peaks of barium titanate with low and flat background levels. These features are suggestive of a material of crystalline quality and grain sizes comparable to bulk ceramics.

![X-ray diffraction pattern](image)

**Figure 3.9:** X-ray diffraction pattern for a solution deposited barium titanate thin film on a copper substrate processed under reducing conditions.

Film microstructure and grain morphology was investigated using atomic force microscopy (AFM). A CP-Research Thermomicroscope AFM in contact mode was used for all AFM micrographs developed in this research. Figure 3.10 shows a typical microstructure of a barium titanate thin film on a copper substrate in a 5 µm x 5 µm scan. The surface microstructure reflects that of an polycrystalline equiaxed grain morphology with grain sizes ranging between 85 and 280 nm and an average grain size of approximately 180 nm as measured using the linear intercept method.\textsuperscript{267}
Cross sectional microstructure of the barium titanate thin film on copper was studied with transmission electron microscopy (TEM). The instrument used was a JEOL 2100-F transmission electron microscope. A cross-section of the film was prepared by adhering a small section of the film and substrate between two portions of a silicon wafer. A wedge polishing technique was used to thin the samples to appropriate thickness. To achieve electron transparency, the films were ion-milled. Figure 3.11 is a bright field TEM image of the cross section a 3-layer barium titanate thin film on a copper substrate. The image is taken from the same film as the AFM image in Figure 3.10. It is clear from the TEM image that the equiaxed grain morphology exists throughout the thickness of the film. The film has low levels of internal porosity and the microscopy reveals no evidence of the presence of a secondary phase at the interface with copper. The average film thickness is approximately 450 nm.
Due to the relatively high processing temperature used to crystallize the barium titanate thin films, the possibility of copper diffusion through the film needed to be taken into account. X-ray photoelectron spectroscopy (XPS) is a surface sensitive characterization technique that can provide chemical information. The measurement was conducted in a vacuum chamber at $10^{-10}$ torr equipped with a VG Clam semi-hemispherical electron spectrometer and a dual anode X-ray source. The source used in the XPS scan was Al K$_\alpha$. The survey and copper spectra were obtained with 50 and 20 eV pass energy, respectively. Figure 3.12 shows the XPS spectra. The data shows that copper is present on the surface of the film in trace concentrations. However it should be noted that the equilibrium vapor pressure of copper at 900 °C is $\sim 10^{-8}$ atmospheres. Consequently, the likelihood of copper condensation on the BT top surface upon cooldown must be considered when interpreting these very surface sensitive data. As such we interpret this result as indicating negligible copper diffusion through the BT film. Note that this result is expected given the very low solubility of Cu in BaTiO$_3$.\textsuperscript{268}

![XPS spectrum for a barium titanate thin film on copper.](image)

**Figure 3.12:** XPS spectrum for a barium titanate thin film on copper.

### 3.3.4: Dielectric Properties of Barium Titanate Thin Films on Copper

In this section the dielectric properties of the barium titanate thin films on copper substrates are discussed. The section starts with a description of the measurement equipment, specifically the apparatus used to measure the temperature dependence of the dielectric properties. The dielectric properties will be discussed as a chronology of the
development of film processing technology, starting with the first films made and continuing on to films with optimized microstructures with methanol-diluted solutions, and finally to the latest films deposited from all acetic acid solutions.

As discussed in section 2.3, the phase transition behavior is the most important indicator of ferroelectric material quality. For this reason the temperature dependence of the permittivity and loss is of interest. The apparatus used to measure the temperature dependent material properties in this thesis is a modified MMR Inc. cryogenic temperature stage. The system consists of a machined quartz arm with a small resistively heated stage on the tip. The quartz arm has several micromachined tubes running through its length opening up into an enclosed cavity in the tip of the arm. By passing high-pressure gas (~1700 psi) through the tubes and allowing it to expand in the cavity, cooling can be achieved through the adiabatic expansion of the gas. The cooling rate is practically limited by the boiling point of the gas used, heat capacity and conductivity of the quartz arm and sample on the stage, and heat from the atmosphere surrounding the arm. By choosing a low boiling point gas such as N\textsubscript{2} or Ar and limiting the sample size the first two limiting factors can be avoided. A rough vacuum atmosphere is used to minimize the heat flow from the surroundings. The quartz arm has a region approximately 1 cm from the stage that also has an enlarged cavity and cools. This section of the stage is intended to getter moisture from the atmosphere to prevent water from condensing on the cold sample. The original factory setup used a small volume enclosure surrounding the quartz arm to achieve the vacuum and limit the amount of water vapor in the system. Unfortunately, such a system requires the use of chip carriers and wire-bonds to make electrical contact to the sample within the chamber. Wire bonding to the copper foils proved difficult, so the cold stage system was modified to allow for direct probing of the sample using micromanipulators. The stage was stripped of its small enclosure and was attached to a 14” Conflat flange. Electrical and gas feed-throughs were run through smaller flanges on the main flange. Two micromanipulators were mounted above the stage with a microscope on a moving arm used to observe the sample on the stage during probing. To achieve vacuum, a 10” bell jar was placed over the entire stage and probe setup and vacuum was achieved with the use of a mechanical rotary vane pump. The modified temperature dependent measurement system, named K-8, is shown in Figure 10.1
in the Appendix. Temperature dependent measurements were conducted by attaching the
leads from the HP4192A impedance analyzer to the temperature dependent measurement
system and heating the sample in a vacuum of approximately 10 mTorr to 510 K. The
samples are then cooled to 100 K at a rate of ~5°C/min.

Prior to measuring the dielectric properties of the films, a reoxidation anneal was
employed to limit the amount of easily ionized charge carriers in the samples. An anneal at
600°C and 10^{-7} atm of O_2 was conducted in a vacuum furnace for 20 minutes and allowed for
films with reasonable dielectric properties. Figure 3.13 shows a permittivity versus field
curve for a 3-layer barium titanate thin film on a copper substrate – the sample from which
the AFM and TEM images above were taken. The measurements were conducted at 10kHz
with an rms oscillator signal of 0.05V. The curve displays tunabilities of approximately 90%
with reasonable saturation at high fields. Peak permittivities are in excess of 1850 with a
zero bias room temperature permittivity of 1600. There is clear evidence of hysteresis with
coercive fields of approximately 10 kV/cm.

![Figure 3.13](image)

**Figure 3.13:** Field dependence of permittivity and loss tangent for a 450 nm thick, 180 nm
grain-sized barium titanate thin film on copper.

Figure 3.14 shows the temperature dependence of permittivity and loss tangent of the
3-layer film. The phase transition behavior is diffuse in character with a peak permittivity of
1890 at approximately 70°C. Due to issues with sample mounting in the original cold stage
arrangement, properties at temperatures higher than 120°C could not be measured, so the full
phase transition behavior could not be characterized.
3.3.5: Material Optimization

While successful, the first demonstration of barium titanate on copper had poor electrode yield and generally high loss. Several processing parameters were altered in attempts to increase yield, film thickness, and the ultimate improve dielectric properties. To this point very little processing optimization has been attempted, rather the necessary process conditions have been established. This section describes the optimization of hotplate dry steps and the solution chemistry to deposit thicker and more robust films. All optimizations were conducted qualitatively by assessing the effect of each parameter on the microstructure of the film. The microstructure was analyzed by observing the plan-view top surface of the films using scanning electron microscopy. All images are of the collected secondary electrons generated by a 5 kV electron beam. The instrument used was a Hitachi S-3200 scanning electron microscope equipped with a thermionic emission electron gun and was operated at high vacuum. No conductive coatings were applied to the samples.

The optimizations were conducted with 0.3M methanol-diluted solutions. Microstructures of the methanol and acetic acid diluted solutions were virtually identical therefore only the methanol solutions are shown. Films were spun and then placed directly on the hotplate at varying temperatures and for varying amounts of time. The process was repeated 3 times and the films were then crystallized at 900°C under appropriately reducing conditions.
The first optimization involved the affect of hotplate dry temperature on BaTiO$_3$ microstructure. The temperatures used ranged from 100°C to 275°C and the dry times used were all 5 minutes. Figure 3.15 shows the microstructures of a representative set of samples processed between 200°C and 275°C. Trends between drying temperature and film porosity were used to identify the optimal temperature of 250°C, using this temperature, final film porosity was minimized, and further improvements did not occur with higher temperatures.

Figure 3.15: SEM micrographs of barium titanate thin films dried from a) 200°C to d) 275°C for 5 minutes.

Dry time was optimized in a similar manner to the dry temperature. Films were dried on the 250°C hotplate for times ranging from 2.5 to 10 minutes. Figure 3.16 shows the microstructures of a representative set of samples. The lowest open porosity level was observed on films dried at 250°C for 7.5 minutes with no discernible improvements in microstructure upon longer dry times.
Figure 3.16: SEM micrographs of barium titanate thin films dried at 250°C for a) 2:30 to d) 10:00 minutes.

The results of these film drying studies are consistent with that observed in the literature by Schwartz and coworkers on chelate-solution deposited zirconia thin films.\textsuperscript{269} It was observed that higher temperature heat treatments on a hotplate resulted in higher degrees of gel consolidation as characterized by measuring film thickness \textit{in situ} with ellipsometry. Furthermore, the film consolidation was found to saturate over a period of time at a given temperature. For example, for a hotplate dry of 200°C, the thickness became asymptotic with 30\% of the original thickness, \( t_{\text{original}} \), at approximately 1500 seconds. For a dry of 400°C a final thickness of 0.2\( t_{\text{original}} \) was achieved in less than 400 seconds. The rate of change of film consolidation slowed as the temperature increased -- greater increases in temperature had diminishing returns. Finally, it was observed that films with a higher degree of film consolidation resulted in materials with higher as-crystallized densities, which appears to be consistent with the current study.

The initial solution chemistry suffered from an inability to prepare \( \text{BaTiO}_3 \) films thicker than approximately 500 nm. This was generally approached with a 3-layer deposition procedure. Dawley \textit{et al.} have shown that the use of higher boiling point chemicals in solution preparation can allow for a relaxation of the film during drying and thereby
eliminate some of the stresses that lead to cracking.\textsuperscript{270} The boiling point of the solvents used to this point are 65°C and 117°C for methanol and acetic acid. Diethanolamine, which was used by Dawley, has a boiling point of 217°C and therefore was investigated as an additive to act as a stress-reliever during drying. DEA is also a known chelating ligand for titanium. For this reason, the amount of DEA added to the solutions is referenced as a molar ratio with the titanium content. Reagent grade DEA (\textgtrapprox 98.5\% Sigma-Aldrich) was added to the solutions following the mixing of barium and titanium. In the case of methanol-diluted solutions, DEA was added at the same time as the methanol dilutant. The final preparation procedure for solutions containing DEA is shown in Figure 3.17.

![Figure 3.17: Solution preparation procedure for a) methanol-diluted and b) acetic acid diluted barium titanate solutions.](image-url)

The ratio of DEA to Ti was optimized based on cracking behavior, solution stability, and resulting film microstructure. It was discovered that solutions containing a 1:1 ratio of DEA to Ti were unstable and resulted in precipitation in less than 24 hours. A 1:2 ratio was stable but was too viscous and led to films with thickness non-uniformities after the spinning step. A 1:4 ratio was determined to be optimal and allowed for films that were up to 5 layers thick with no obvious signs of cracking. Previously, the same solution chemistry allowed just 3 layers to be deposited prior to the onset of cracking. Figure 3.17 shows SEM micrographs of a progression of thicknesses of barium titanate thin films with a 1:4 DEA to Ti ratio. An important result of the DEA optimization was an increase in capacitor yield and an increase of the film thickness from \textsim 450 nm to \textgtrsim 600 nm without cracking.
Initial films deposited had higher loss values than generally desired. It was identified that the loss could be improved by using a secondary anneal after the high temperature firing at lower temperatures and higher $pO_2$ levels. In light of this behavior, the effect of firing temperature and atmosphere on room temperature conductivity was investigated theoretically with an expected value of approximately $3 \times 10^{-5}$ $(\Omega \cdot \text{cm})^{-1}$. The calculations, based on free energies of vacancy formation and electronic defect compensation can be found in the Appendix.

From these calculations it is clear that the lowest temperature and highest tolerable oxygen pressure would yield the most insulating material. Practically speaking, these conditions either would not be feasible or may not yield the best results with two factors limiting the usefulness of such an approach. First, the process of driving oxygen into the lattice is reliant on the kinetics of diffusion, thus the optimal conditions could take a prohibitively long amount of time. Second, the intrinsic level of impurities in the dielectric from the source materials is not precisely known. With the level of impurities and in some cases their site occupancy unknown, the appropriate defect chemistry reactions to calculate the extrinsic oxygen vacancy and donor and acceptor doping levels cannot be completed. Due to these factors, an empirical study of reoxidation conditions was used to find the conditions that could best improve the dielectric quality in an anneal time of 30 minutes. While studying leakage current or conducting reliability testing may be the most desirable metric for evaluation, loss tangent at zero bias was used for the following reason: a statistical
analysis of the results was desired which requires a large sample set, and the time and instrumentation necessary to complete such a study was not available.

Films were prepared on single copper foil sheets by depositing 4 layers of a methanol-based solution and using all of the prior material optimizations. The single foil was then fired under a reducing atmosphere at 900°C and a $pO_2$ of $10^{-12}$ atm. The film was divided into several sections which were then annealed under a range of temperatures from 450°C to 650°C and $pO_2$ values from $10^{-4}$ to $10^{-6}$ Torr ($\sim 10^{-7}$ to $10^{-9}$ atm) of oxygen in a vacuum furnace. The samples were loaded into the furnace, which was then evacuated to a pressure of approximately $10^{-7}$ Torr. Samples were moved to the hot-zone of the furnace using a transfer arm and the pressure was raised to the desired level by providing a controlled leak of oxygen. The dynamic atmospheres were controlled throughout the length of the run. After 30 minutes, the samples were removed from the hot-zone via the transfer arm and allowed to cool to room temperature in a cold end of the furnace under the anneal atmosphere prior to removal. Platinum top electrodes were then deposited on the film surface through a shadow mask. It should be mentioned that the conditions used are sufficient to oxidize copper. However, with the dense film covering the surface of the foil, the amount of oxygen reaching the copper/film interface is limited, and the formation of copper oxide is negligible. Figure 3.18 shows an X-ray diffraction pattern for a film prior to and after annealing at 450°C and $10^{-4}$ Torr of oxygen and shows the lack of copper oxide formation.
Figure 3.18: X-ray diffraction patterns for a pure barium titanate thin film after firing. The lower pattern is an as-fired film. The top pattern is a film reoxidized at 450°C and 10^4 Torr O₂.

Film testing was conducted by applying a DC bias of 3 volts for 10 seconds and then measuring the loss tangent at 0 bias and with oscillator conditions of 10 kHz and 0.05 volts 10 seconds after field removal. This allowed each capacitor to be equivalently poled such that the domain response of each capacitor to the oscillating field would be similar. These measurements were conducted on 40 capacitors for each firing condition. The statistical analysis and the measurements were done by Alisa Hunt-Lowery and the complete work can be found in her Master’s thesis. The pertinent results to optimizing the reoxidation conditions can be seen in Figure 3.19. The optimal properties are found for anneals at 550°C and 10^4 and 10^6 Torr oxygen atmospheres, the increase in loss for the 10^-5 Torr condition could be attributed to the failure of an o-ring seal on the furnace during that run and the trend suggests that the optimal condition may be 550°C and 10^-5 Torr of O₂.
Figure 3.19: *Loss tangent distributions for barium titanate films reoxidized under varying conditions (adapted from Hunt-Lowery [27]).*

Employing all of the optimizations discussed in section 3.3.5 including the addition of DEA to the solution chemistry and the use of a 550°C 1x10^-5 Torr reoxidation anneal resulted in films of greater thickness and improved dielectric properties. Figure 3.20 is a permittivity versus field plot of an optimized 4-layer barium titanate thin film on copper with the DEA addition to improve thickness. The film thickness was increased to approximately 580 nm as measured with SEM. This curve displays similar properties with an increased permittivity to greater than 2100 at the coercive field of approximately 10 kV/cm. Loss tangents are greatly improved and saturate at high field to approximately 1.5% with peaks of approximately 10%. The high loss at the coercive field is a strong indication of domain wall motion during switching and is indicative of a high-quality ferroelectric crystal.

Figure 3.20: *Field dependence of permittivity and loss tangent for a 580 nm thick, 140 nm grain-sized barium titanate thin film on copper.*
The temperature dependence of permittivity and loss tangent was measured for the optimized material and is shown in Figure 3.21. A diffuse phase transition is again observed with a peak permittivity of 1830 and a $T_c$ of 110°C. The decrease in loss tangent with the optimizations is evident.

![Figure 3.21: Temperature dependence of permittivity and loss tangent for a 580 nm thick, 140 nm grain-sized barium titanate thin film on copper.](image)

The frequency dependence of permittivity was investigated for an optimized film as shown in Figure 3.22. The measurement was conducted at 0 bias and at 8V (~140 kV/cm) to identify any possible contribution from space charges. No dramatic dispersions at low frequencies were observed, indicating that the space charge contribution to the dielectric properties was minimal.

![Figure 3.22: Frequency dependence of permittivity (closed circles) and loss tangent (open circles) for a barium titanate thin film at 0 bias (red) and 8V bias (140 kV/cm) (blue).](image)
With the industry desire to eliminate methanol from the solution chemistry, acetic acid diluted solutions were prepared. To achieve similar thicknesses to the methanol solutions, 6 coats were needed. Films were then processed in an identical procedure resulting in materials with as-fired thicknesses of 600-750 nm.

Polarization versus field measurements were conducted with an AixACT TF 2000 ferroelectric tester at 100 kHz across a voltage range of −15 to 15V. Figure 3.23 shows a typical hysteresis loop for a 600 nm thick barium titanate thin film on a copper foil substrate. The loop displays narrow hysteresis with reasonable saturation and a coercive field of approximately 5 kV/cm and has a spontaneous polarization of approximately 8 µC/cm².

![Figure 3.23: Polarization versus field for barium titanate on copper.](image)

For a similar film the permittivity versus field plot is shown in Figure 3.24. The material has an average grain size of 161 nm as determined using the linear intercept method on an SEM image. Similar to the previous examples, the properties of this film exhibit tunabilities in excess of 93% (15.8:1) with a peak room temperature permittivity of 2000. The curve displays excellent high field saturation with loss tangent values of less than 0.5%. The coercive field of the material is 9 kV/cm.
Figure 3.24: Field dependence of permittivity and loss tangent for a 780 nm thick, 161 nm grain-sized barium titanate thin film on copper.

Figure 3.25 shows the temperature dependence of permittivity for a 6-layer acetic acid diluted barium titanate thin film on a copper foil substrate. The phase transition is diffuse in character with an apparent $T_c$ of 118°C. Possible evidence of the tetragonal to orthorhombic transition can be observed at 55°C. This transition temperature is higher than would be expected for single crystalline barium titanate, however a great deal of evidence exists in the literature for the increase in temperature for the tetragonal-orthorhombic transition as grain size scales to smaller sizes.\textsuperscript{56, 81} It is interesting to note that the maximum in permittivity of 1800 does not coincide with the Curie point of the material rather, the peak occurs at what appears to be the tetragonal-orthorhombic transition. This phenomenon is not well understood however it is possible that his behavior is the result of a type of morphotropc phase boundary in the material with a maximum number of variants of the polarization occurring at the tetragonal-orthorhombic phase transition. Furthermore, that the films are only a few grains in thickness, the 12 polarization directions in the orthorhombic phase in comparison with the 6 in the tetragonal may create a situation where the polarization is more easily aligned with the applied field in the orthorhombic orientation, and thus resulting in higher permittivity at this phase transition – it should be emphasized that this is purely conjecture and no experimental evidence exists to back this up.
The dielectric properties of the barium titanate thin films on copper substrates show superior properties in comparison with thin films from literature. This is best portrayed in a comparison of the properties of BaTiO$_3$ films on copper and on traditional platinized silicon substrates. Figure 3.26 shows a comparison of the field dependence of permittivity for a film on copper and a film on platinized silicon from the literature. The literature film was deposited using a similar solution technique and was fired at 700°C. It is observed that the film processed on silicon displays dramatically diminished ferroelectric properties in comparison with films on copper. The peak permittivity of the film on silicon is approximately 430, a factor of 4 lower than the copper sample. The coercive field also differs in the two samples; while the films on copper have values around 10 kV/cm the film on silicon has roughly twice the value.
Figure 3.27: Permittivity versus temperature plots for fine-grained bulk ceramics, thin films on platinized silicon, and a film on copper (adapted from Arlt et al., Frey et al., Hoffmann et al., and Parker et al.).

The high permittivities and low losses coupled with the low coercive field values of the films on copper are more consistent with well-prepared bulk ceramic barium titanate materials than typical thin films. In particular the coercive field values are low for a thin film and compare favorably with the value of 30 kV/cm measured by Sharma on pure bulk-ceramic barium titanate. Since very little field dependent permittivity data exists for bulk materials, perhaps the best comparison can be made through the temperature dependence. Figure 3.27 shows permittivity versus temperature for the bulk ceramic studies of Frey et al. and Arlt et al., for the thin film studies by Hoffmann et al. and Parker et al., and from this work. In as far as possible, the data chosen are for materials with grain sizes similar to those of the material in this study. It can be seen from Figure 3.27 that while the exceptionally high permittivities of Frey are not equaled, films on copper compare favorably with the Arlt data, even though the grain size is more than 100 nm less. It is also apparent that the films on copper have dielectric properties well in excess of those achieved by the other thin film studies - and indeed ANY other report for BaTiO₃ or SrTiO₃ with reliable electrical characterization. Comparing the films on copper with others from the literature, we see that these observations are consistent. That is, for thin films of similar and smaller grain sizes, the permittivities are much lower. This holds also for barium strontium titanate thin films as measured at their peak permittivity. It is believed that the differences distinguishing the barium titanate thin films on copper from those on conventional substrates
stem largely from the processing conditions used. The copper substrate affords a substantially higher processing temperature than platinized silicon. It is this increase in thermal budget (by firing a film at 900°C versus 700°C, a temperature much closer to typical bulk processing temperatures) that is hypothesized to result in properties consistent with bulk ceramics. The higher temperatures and thermal budgets afford material with improved crystallinity and chemical homogeneity for a given grain size. These features are consistent with the properties observed in these films, specifically the high tunabilities, low coercive fields, and low loss tangents, all of which could be predicted for a material with low barriers to domain wall motion.
Chapter 4: Scaling Effects in Barium Titanate Thin Films

The previous chapter described the processing of barium titanate thin films on copper substrates and through electrical characterization it was identified that the films exhibit properties more consistent with bulk ceramics than traditional thin films. It was hypothesized that the improvement in properties was due to the higher thermal budgets allowed by processing on the copper substrates as opposed to platinized silicon or other rigid substrates. In order to further isolate the effect of processing temperature on the properties of the films, a scaling study was devised. Most scaling studies for thin film ferroelectrics use film thickness as the independent variable. The barium titanate thin films on copper afford a unique opportunity where films can be crystallized under a variety of conditions such that grain size is controlled while thickness remains constant. We note however, that crystallinity will also change with temperature, thus limiting our ability to ultimately isolate grain diameter as the isolated control variable.

To prepare the appropriate sample set a six-layer film from an acetic acid based barium titanate solution was deposited on a single copper foil. The foil was then divided and fired under reducing atmospheres for 30 minutes in a temperature range of 700 to 900°C at 50° intervals. The processing atmosphere used an identical flow rate of 410 sccm N₂ and 55 sccm 1% H₂ and resulted in pO₂ levels of 10⁻¹⁷ to 3x10⁻¹³ for the samples fired at 700° and 900°C respectively. These values are comparable to those in the pressure-temperature phase diagram in Figure 3.7. This procedure ensures a set of films where film composition and thickness are identical while the grain size and crystallinity is varied.

Figure 4.1 shows the X-ray diffraction patterns for each film. The existence of a copper oxide phase is again identified and results from the decomposition of the barium titanium oxycarbonate phase. The presence of the copper oxide should not be ignored when considering the measured dielectric properties, however it should be noted that Cu₂O is a known intrinsic p-type semiconductor with a conductivity of 10²-10⁴ Ω-cm at room temperature. Additionally, the volume fraction of Cu₂O is very small, existing only at the
limit of our ability to detect by x-ray diffraction. Note that on a linear scale, these peaks cannot be appreciated. This small volume fraction coupled with the semiconducting behavior assures that any decrease in capacitance due to the series arrangement of layers is minimal.

Figure 4.1: X-ray diffraction patterns for barium titanate thin films processed between 700° and 900°C on copper.

Figure 4.2 shows AFM topographical micrographs of representative films processed at 700°, 800°, and 900°C respectively. In each condition the film morphology is polycrystalline and equiaxed with low levels of open porosity; the increase in average grain size with firing temperature is apparent. Cross-sectional SEM micrographs of the representative films are shown in Figure 4.3. The resolution of the previously used Hitachi thermionic emission SEM was too low for meaningful cross-sectional imaging, so a JEOL 6400F field emission SEM operated at 5 kV in secondary electron mode was. The cross-sections were prepared by cutting the films and observing them along the fracture surface. The shear motion during cutting resulted in areas where the substrate peeled away from the film allowing clear inspection of the film cross-sections. No obvious evidence of secondary phases at the interface is observed, in support of the hypothesis that the copper oxide phase is thin in comparison with the dielectric and likely discontinuous. The cross-sections show dense microstructures and verify that the equiaxed polycrystalline grain morphology exists throughout the film thickness with no apparent variation in average grain size. The other
firing temperatures used in this study, though not shown, fit within these trends. Additionally, the film thicknesses appear invariant between each firing condition, which allows confidence in associating all variations in dielectric properties to a grain size and crystalline quality effect rather than thickness dependence.

Figure 4.2: 3\(\mu\)m x 3\(\mu\)m topographical AFM scans of barium titanate processed at a) 700°C, b) 800°C, and c) 900°C.

Figure 4.3: Secondary electron images of cross-sections of barium titanate thin films processed at a) 700°C, b) 800°C, and c) 900°C.

Average grain sizes were measured from the AFM topographical images using a linear intercept method. Figure 4.4 shows a plot of the average measured grain size as a function of firing temperature. The error bars represent the 95% confidence interval for the measurement. The effect of processing temperature on the ultimate grain size clearly demonstrates a trend of increasing grain size with increasing thermal budget. For samples fired at 700°C the average grain size is limited to 61 nm while increasing the process temperature by just 200°C results in grains more than a factor of 2 larger at 138 nm.
Figure 4.4: Average grain size as a function process temperature for a series of barium titanate thin films on copper.

The temperature dependence of permittivity and loss tangent for the films of each grain size is shown in Figure 4.5. From this plot effect of grain size on the dielectric properties is clear. Higher processing temperatures has allowed for larger grains, which in turn resulted in increased permittivity. This is demonstrated by comparing the two extremes; sample processed at 900°C with an average grain size of 138 nm has a peak permittivity of 1800 while the sample processed a 700°C with an average grain size of 61 nm has a maximum permittivity of 300.

Figure 4.5: Temperature dependence of permittivity and loss tangent for a grain size series of barium titanate thin films on copper substrates.

By observing the phase transition behavior for each sample, three distinct phenomena can be observed. First it is seen that each exhibits diffuse phase transitions that appear to be
second order in nature. Second, for the largest grain size material the apparent shift of the orthorhombic-tetragonal phase transition is again observed. This is accompanied by a broadening of the permittivity maximum over a large temperature range as was discussed in Chapter 3. Third, the phase transition temperature is invariant with grain size between 76 nm and 138 nm. Quantifying this and plotting the phase transition temperature as a function of grain size verifies this trend as shown in Figure 4.6. Each material with grain size between 76 and 138 nm have Curie points of approximately 120°C, which agrees well with expectations for bulk barium titanate.\textsuperscript{14, 18} Since the phase transition temperature is invariant for the largest grain size material but the permittivity decreases, suggests that the volume associated with grain boundaries may be the most important factor. This has been suggested by Frey \textit{et al.} for fine-grained bulk ceramics with a brick wall model.\textsuperscript{57} One distinct difference between this work and Frey’s work is that Frey was able to show unambiguously that the grain boundary thickness was invariant with grain size reduction through TEM investigations and the permittivity/grain size ratio agreed well with the brick wall model. In this work the permittivity decrease is greater than observed by Frey and may be a byproduct of decreasing processing temperatures that may manifest in materials with thicker grain boundaries, or materials where there are simply more crystallographic defects within each grain. For the finest grained material however, the phase transition appears to occur at approximately 60°C.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.6.png}
\caption{Dependence of the average grain size on the Curie point of barium titanate thin films.}
\end{figure}
It is known for materials derived from chemical solutions that hydroxyl groups can be incorporated. Furthermore, this incorporation of hydroxyl defects is a known extrinsic scaling effect in ferroelectric materials and has been attributed to decreases in the phase transition temperature by other groups.\textsuperscript{117, 119-121} It is possible that the relatively low processing temperature of 700°C used to form the 61 nm material could be insufficient to drive off hydroxyl defects remaining from the organic decomposition and thermolysis. To investigate the existence of hydroxyl groups in the lattice infrared spectroscopy was performed on each of the samples. A Digilab FTS 6000 spectrometer equipped with a liquid nitrogen cooled MCT narrow-band detector was used to collect the spectra at room temperature with a resolution of 2 cm\textsuperscript{-1} and were compiled as an average of 64 scans. A bare copper foil was used a calibration standard. Figure 4.7 shows the FT-IR spectra for each sample.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.7.png}
\caption{FT-IR absorbance spectra of barium titanate thin films processed between 700° and 900°C.}
\end{figure}

From the spectra, several features are evident. The signal below 1500 cm\textsuperscript{-1} could be attributed BaCO\textsubscript{3} however this is unlikely as the highest absorbance occurs at wavenumbers below what would be expected for BaCO\textsubscript{3} and the low level and random nature makes it more likely that this is system noise. The peak at 2350 cm\textsuperscript{-1} can be attributed to atmospheric carbon dioxide and is not due to absorption to film species. A broad peak ranging between 3000 and 3500 cm\textsuperscript{-1} is observed in all samples. This broad peak can be associated with that of the stretching mode of surface hydroxyl groups and not hydroxyls located within the
thickness of the film.\textsuperscript{120} If hydroxyl groups were incorporated in the film, peaks of the lattice hydroxyl stretching modes would appear as narrow peaks 3460 and 3510 cm\textsuperscript{-1} and are not observed in these materials.\textsuperscript{118} That no lattice hydroxyl groups were identified, in particular for the 61 nm sample, is suggestive that they are not responsible for the decrease in phase transition temperature. It is believed then that the decrease in phase transition temperature is associated with a decrease in film crystallinity due to a low processing temperature. While the measured grain size was larger than would be expected for such a $T_c$ shift, the actual crystallite size may be much smaller, of the order where size effects begin to cause shifts in the phase transition.

The room temperature field dependence of permittivity and loss tangent for each sample was measured and is shown in Figure 4.8. As with the temperature dependence, the peak permittivity increases with increasing grain size accompanied by an increase in the dielectric tunability. Each material, including the finest-grained material, shows hysteretic behavior as has been identified in polarization-field loops by Frey et al. for materials with grain sizes as small as 40 nm.\textsuperscript{57} It is interesting to note that the polarization values in the bulk materials decreased substantially with decreasing grain size, similar to the permittivity peaks in the thin films measured in this study. The saturation levels and loss tangents are similar for each grain size material, which suggests that the intrinsic response of the lattice is identical. The extrinsic response, however, is strongly size dependent and diminishes as the grain dimensions decrease.
In chapter 3 it was suggested that the thin films on copper behave more similarly to bulk ceramics than traditional thin films as a result of higher process temperatures. To further illustrate and confirm this point, a plot of the room temperature dielectric constant versus average grain size was adapted from Arlt et al, and the bulk ceramic data of Frey and thin film data of Parker were added. These data are shown in Figure 4.9. The permittivity values from the Parker data were chosen at –80°C to be an equivalent temperature away from the ferroelectric-paraelectric phase transition.
From this plot, we can appreciate both the impact of grain size and ultimate processing temperatures. Consider the data points of Frey, Ihlefeld, and Parker at the comparable grain sizes of 170 nm, 140 nm, and 185 nm respectively. These three examples represent material with comparable crystal dimension along the measurement axis, however, the permittivity values are distinctly different. Frey achieves a permittivity of 3000, Ihlefeld, 1800, and Parker 400. We hypothesize that the processing temperature differences superimposed upon the grain size can account in part for this difference. Frey calcined and sintered his powders at 750°C and between 800 and 1325°C at a pressure of 8 GPa, respectively, Ihlefeld densified at 900°C, and Parker was limited to a 650°C MOCVD deposition. The effect of the increased thermal budgets on permittivity becomes clear from this analysis and suggests that an increase in processing energy minimizes extrinsic contributions to scaling.

For completion, the strain state of these films is considered. The coefficient of thermal expansion for copper is 17.0 ppm/°C while barium titanate is ~9.8 ppm/°C above the transition temperature. With this large thermal expansion disparity a large compressive strain would be expected upon cooling from the firing temperature. The films however, as removed from the furnace are flat and do not curl as the weights holding the ends are removed. This suggests a very low state of strain in the system. One possible reason for this is that the shear modulus of copper is 41.1 GPa, while for cubic perovskites it is generally
greater than 100 GPa. This, coupled with the low yield stress (~68 MPa for annealed oxygen-free copper) may account for the relatively strain-free state of the Cu-BT stack. Typically, we assume that films and substrates do not deform plastically as thermal expansion mismatch accumulates upon cooling. However, give the low moduli of Cu such an assumption is unwise. To illustrate this further, it is interesting to consider the microstructure alteration in the copper substrate during film crystallization. As the samples are fired to 900°C (~0.86 T_melt for copper) the rate of diffusion in copper allows for dramatic grain growth and strain relaxation. A demonstration of the grain growth of copper is shown in the X-ray diffraction patterns collected using the area detector in Figure 4.10. The left half of the image shows the diffraction pattern of the as-deposited film. As expected, only the Cu 111 diffraction peaks is clearly visible with a broad low angle peak associated with the amorphous gel. The diffraction pattern is a solid ring, suggesting a large number of randomly oriented grains were sampled in the scan. Alternatively, the image on the right half of the figure shows the X-ray diffraction pattern of an as-fired sample. Here the perovskite peaks of barium titanate are evident as well as the Cu 111 peak. The copper peak is now discontinuous with several spots on an arc of a ring. This occurs as a fewer number of randomly oriented grains are sampled and results from grain coarsening - each spot represents a single crystal, i.e., a large Cu grain. The solid diffraction arc of the un-fired film suggests sub-micron grain sizes in the copper while the discontinuous arc of the fired film suggests that the grains have grown to a size in excess of approximately 5µm.
Figure 4.10: X-ray diffraction patterns of a) as-deposited and b) as-fired barium titanate thin films on copper. The discontinuous copper diffraction arc in the as-fired sample suggests large-scale grain growth.

Upon cooling, the relatively defect free copper substrate forms dislocations and twin boundaries as a result of the thermal expansion mismatch, low shear modulus, and low yield point. This results in a relatively strain free system as is supported by the phase transition temperatures for the barium titanate films. If the film were under a large compressive strain a substantial $T_c$ shift would be expected. Additionally, the compressive stress would favor a c-axis orientation of the domains in the material, which would lower the ultimate measured permittivity. That the permittivity is high in the material suggests that significant strain is not present.
Chapter 5: Phase Transition Engineering

Pure barium titanate thin films work well as a demonstration vehicle for developing the process and a properties database for the technology of thin films on copper. Unfortunately, the temperature response of the material has too much variation in permittivity over the range from $-55^\circ$ to $125^\circ$C for large value capacitors. In this particular temperature range it is desired to have materials with a variation in permittivity not greater than $\pm 15\%$ from the room temperature value. This specification, called X7R, is an Electronic Industry Association (EIA) standard for the temperature coefficient of capacitance that is commonly used in consumer electronics.\textsuperscript{284} Superimposing the X7R capacitance-temperature space over a permittivity versus temperature plot for pure barium titanate reveals a need to shift the phase transition peak to lower temperatures.

![Figure 5.1: Temperature dependence of permittivity for pure barium titanate on copper. The shaded region represents the X7R EIA specification for capacitance stability.](image)

To shift the phase transition temperature of BaTiO$_3$ several perovskite solid solutions can be considered including strontium titanate, barium zirconate, barium stannate, and barium hafnate. In this chapter the $B$-site alloys of zirconium, hafnium, and tin will be investigated.

5.1: Barium Titanate – Barium Zirconate Solid Solutions

Barium zirconate, a known phase transition pincher was investigated as a possible alloying material to modify the temperature coefficient of capacitance such that it fits the
desired X7R specification. Films were prepared with Ti/Zr ratios of 95/5, 90/10, and 75/25 and stoichiometric Ba/B-site ratios. Solutions were prepared in a similar manner to that of pure barium titanate with minor modifications to add the zirconium precursor. Zirconium propoxide (70 weight% in propanol, Sigma-Aldrich) was chosen as the zirconium source in the study. In a 50 mL Erlenmeyer flask, the desired amount of zirconium precursor was massed to which titanium isopropoxide was added dropwise. The mixture was stirred briefly to allow for mixing and reacting (a slightly exothermic reaction was noticed upon adding the titanium source). Acetylacetone was added to the mixture in a molar ratio of 4:1 chelating agent:B-site cation. The solution was capped and allowed to stir for roughly two hours. Concurrently, barium acetate was dissolved in glacial acetic acid. The barium precursor was added in a stoichiometric ratio, as measured by a digital balance and DEA was added to the solution. After stirring the mixture for approximately 12 hours, methanol was added to bring the concentration to 0.3M. The solution preparation procedure is shown in Figure 5.2.

![Solution preparation procedure for a barium titanate zirconate hybrid-chelate solution chemistry.](image)

Films were prepared in the manner discussed in Chapter 3 with four total spun-on layers for an ultimate as-fired thickness of approximately 600 nm. Films were fired to 900°C for 30 minutes for crystallization and densification. The oxidation free energy for zirconium is similar to that of barium as shown in Figure 5.3, allowing for the use of the same crystallization conditions as used for barium titanate.
Figure 5.3: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides. The shaded region represents the conditions where barium titanium and zirconium oxidize and copper is reduced.\textsuperscript{190}

Phase development was studied with X-ray diffraction for each composition as shown in the diffraction patterns in Figure 5.4. From these plots, clear evidence exists for perovskite formation with no diffraction peaks that could be associated with secondary phases including zirconium. This demonstrates that the processing conditions used were appropriate for crystallization of the material into the perovskite barium titanate zirconate while preserving the copper substrate.

Figure 5.4: X-ray diffraction patterns for $\text{Ba(Ti}_{x-1}\text{Zr}_x\text{)}\text{O}_3$ thin films processed at 900°C on copper.
To verify that zirconium was incorporated into the lattice, the lattice parameter was calculated for composition using the Nelson-Riley extrapolation function and the diffraction peaks for the 001, 002, and 003 planes. The Nelson-Riley function is shown in Equation 5.1 where \( a \) is the measured lattice parameter, \( a_0 \) is the calculated lattice parameter, and \( \theta \) is the Bragg angle. This method is particularly useful for characterizing lattice parameters as it minimizes measurement errors associated with sample height maladjustment and X-ray absorption.

\[
a = a_0 - a_0 k \left[ \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right] \quad \text{Equation (5.1)}
\]

\[
a_{\text{solution}} = n_A a_A + n_B a_B \quad \text{Equation (5.2)}
\]

The expected lattice parameter values were calculated using Vegard’s Law as shown in Equation 5.2 where \( a_{\text{solution}} \) is the lattice parameter of the solid solution, \( a_A \) and \( a_B \), and \( n_A \) and \( n_B \) are the lattice parameters and mole fractions of end-members A and B. The pseudocubic lattice parameter of barium titanate of 4.008Å and cubic parameter of barium zirconate of 4.193Å were used in the calculation. The resulting measured and calculated lattice constants are shown in Figure 5.5.

![Figure 5.5: Measured lattice parameter and lattice parameter calculated from Vegard’s Law for barium titanate zirconate thin films.](image)
From the lattice parameter plot there is a clear trend of increasing unit cell dimensions with increasing barium zirconate content. The measured data points do not coincide with the calculated lattice parameter values, however the parallel trend of the two data sets suggests that the diffractometer used was slightly out of alignment during the measurement. For the system geometry a lattice parameter difference of 0.002 nm corresponds to a 2θ misalignment of ~ 0.2°. A misalignment of this small of an angle is reasonable and from the similar trends of the measured and calculated lattice parameters it is likely that zirconium was fully incorporated into the perovskite lattice.

The temperature dependence of permittivity was measured for each composition as shown in Figure 5.6. From the plot, three distinct trends can be identified. First, increasing the zirconium content decreased the phase transition temperature, $T_{\text{max}}$. Second, with increasing zirconium level the maximum permittivity (the permittivity at $T_{\text{max}}$) decreased. Third, the phase transitions became more diffuse with increasing barium zirconate concentration.

![Figure 5.6: Temperature dependence of permittivity and loss tangent for Ba(Ti$_{1-x}$Zr$_x$)O$_3$ thin films on copper substrates.](image)

A decrease in the phase transition temperature and an increase in phase transition diffuseness were expected and have been discussed in section 2.4.2. Figure 5.7 plots the phase transition temperature versus zirconium content for the films on copper and two studies on bulk ceramics from Verbitskaia et al. and Kell et al.\textsuperscript{134, 135} The transition temperatures of the films
are slightly lower than the bulk ceramics for all compositions, however the effects of chemical purity and grain sizes can account for this disparity.

![Figure 5.7](image)

**Figure 5.7:** Phase transition temperature versus composition of barium titanate zirconate thin films and bulk ceramics.\textsuperscript{134, 135}

Permittivity at $T_{\text{max}}$ was plotted versus composition for the thin films on copper in Figure 5.8. A clear decrease in permittivity with increasing zirconium composition was revealed. As no quality single crystal data exists in the literature and the bulk ceramic work is of unknown grain size, this trend could not be verified as intrinsic or extrinsic.

![Figure 5.8](image)

**Figure 5.8:** Permittivity at $T_{\text{max}}$ versus composition for barium titanate zirconate thin films.

Figure 5.9 shows 3 $\mu$m x 3 $\mu$m AFM topographical scans of the barium titanate zirconate thin films. Average grain sizes were measured using the linear intercept method and plotted versus composition as shown in Figure 5.10 with error bars indicating a 95% confidence interval for the measurement.\textsuperscript{267} There is a clear trend of decreasing grain size
with increasing barium zirconate content. The reasons for this are unknown, however it is speculated that the zirconium addition may alter the nucleation behavior of the films or that its refractoriness may inhibit grain growth during the crystallization anneal.

**Figure 5.9:** 3µm x 3µm topographical AFM scans of a series of barium titanate zirconate thin films with compositions of a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Zr$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Zr$_{0.10}$)O$_3$, d) Ba(Ti$_{0.75}$Zr$_{0.25}$)O$_3$.

**Figure 5.10:** Average grain size versus composition for barium titanate zirconate thin films.
Since Zr additions produce a concomitant reduction in grain size, an additional grain size series of pure barium titanate samples was prepared with a methanol-diluted solution to isolate whether the decrease in permittivity was an intrinsic effect of zirconium additions or due to a grain size reduction. The temperature dependence of permittivity was measured for the new grain size series of the pure barium titanate as shown in Figure 5.11. AFM topographical scans were taken of the samples and the average grain size was measured. The permittivity at the phase transition values for both the pure BaTiO$_3$ and Ba(Ti,Zr)O$_3$ samples were plotted versus average grain size as shown in Figure 5.12.

**Figure 5.11:** Temperature dependence of permittivity for a reference set of pure barium titanate thin films of varying grain size.

**Figure 5.12:** Grain size dependence of permittivity at $T_{\text{max}}$ for barium titanate zirconate and barium titanate thin films.

The permittivity at the phase transition versus grain size follows the same trend for both zirconium substituted and pure samples. Therefore, it is possible to conclude that the reduction in average grain diameter is responsible for the decrease in permittivity and is not
an intrinsic effect due to zirconium incorporation for materials containing up to 25 mole % BaZrO₃. Both the effect of grain size and zirconium on the dielectric properties of barium titanate zirconate have been discussed in the literature, however this is the first study to decouple the effects of zirconium and grain size on the dielectric properties of these materials and to show that zirconium additions do not intrinsically diminish the dielectric properties.

**Figure 5.13:** *Field dependence of permittivity and loss tangent for a composition series of barium titanate zirconate thin films at room temperature.*

The field dependence of room temperature permittivity and loss tangent was measured for each composition as shown in Figure 5.13. The effect of zirconium on the maximum permittivity is evident as the peak value decreases with increasing concentration of substituent. This decrease can again be attributed to the decrease in grain size with Zr addition. It should be highlighted that the permittivity values at saturation are the same for each composition showing that the intrinsic response of the lattice is identical. From the temperature dependent measurements, it is known that large shifts in $T_{max}$ occur with increasing mole fraction of Zr. Consequently, the room temperature tunability comparisons are of limited value for comparing the dielectric properties. Comparing each composition’s field dependence of permittivity at a common reference point, for instance $T_{max}$, provides a more meaningful assessment. This data is shown in Figure 5.14. It is observed that the value of the maximum permittivity is increased for all compositions and that the hysteresis of the 0,
5 and 10% BaZrO$_3$ compositions is decreased since dipoles become less stable as the measurement temperature approaches the Curie point. From the plot it appears that the tunability of all compositions is increased slightly as would be expected given an increase in permittivity at the phase transition.

![Field dependence of permittivity and loss tangent for a composition series of barium titanate zirconate thin films at each composition’s respective $T_{\text{max}}$.](image)

**Figure 5.14:** Field dependence of permittivity and loss tangent for a composition series of barium titanate zirconate thin films at each composition’s respective $T_{\text{max}}$.

C-V curves were taken over a range of -123°C to 123°C for fields of 0 to 130 kV/cm. The tunabilities were calculated from Equation 2.10 and are plotted as a function of temperature in Figure 5.15. From this plot the generalization that higher permittivity results in higher tunability can be appreciated and the transition temperatures are evident as peaks in tunabilities.\textsuperscript{37}
Figure 5.15: Tunability as a function of temperature for a field strength of 130 kV/cm for Ba(Ti$_{1-x}$Zr$_x$)O$_3$ thin films.

It is known in bulk ceramics that BTZ compositions with 25 mole % or greater zirconium show the relaxor characteristics of phase transition dispersion and increased transition diffuseness. Since the BTZ films show an increasing diffuseness as the zirconium level increases, the temperature dependent dielectric properties were characterized with oscillator frequencies of 1, 10 and 100 kHz to investigate dielectric relaxation, as shown in Figure 5.16.
Figure 5.16: Temperature dependence of permittivity at 1, 10, and 100 kHz for a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Zr$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Zr$_{0.10}$)O$_3$, and d) Ba(Ti$_{0.75}$Zr$_{0.25}$)O$_3$ thin films.

For compositions containing up to 10% barium zirconate dispersion is identified in the permittivity while none is identified in the phase transition, however for the composition containing 25% BaZrO$_3$ some dispersion is seen. Specifically, we observe a frequency dependent permittivity below $T_{max}$, with this dependency diminishing at higher temperatures. This is the classic signature of a relaxor ferroelectric and is consistent with bulk ceramic data.

The goal of this study was to determine if and how much barium zirconate is necessary to shift the Curie point of barium titanate such that X7R characteristics could be achieved. Figure 5.17 plots the temperature response of permittivity of each for the BTZ series with their corresponding X7R regions mapped.
While none of the compositions measured fulfilled the X7R requirement, from inspection it appears that a composition containing between 5 and 10 mole percent zirconium will provide the desired temperature response.

### 5.2 Barium Titanate – Barium Hafnate Solid Solutions

Barium titanate hafnate (BTH) thin films were deposited and the properties measured to elucidate any similarities to the barium titanate zirconate system. Hafnium, like zirconium, is a known phase transition pincher in BaTiO$_3$. Films were prepared with compositions containing 5, 10 and 25 mole percent barium hafnate. Solution preparation methods were...
similar to that of barium titanate zirconate with the exception that the solutions were prepared using the acetic acid dilution chemistry. Tetrakis(1-methoxy-2-methyl-2-propoxy)hafnium (Hf(TMMP)_4 Sigma-Aldrich 99.99%) was used as the hafnium source due to unavailability of hafnium butoxide at the time of solution preparation. Hf(TMMP)_4 was massed into an Erlenmeyer flask and the appropriate stoichiometric amount of titanium-isopropoxide was added. Acetylacetone was reacted with the B-site precursors in a 4:1 ratio. The solutions were capped and allowed to room at stir at room temperature for 2 hours. The barium precursor was prepared by dissolving barium acetate in glacial acetic acid in a capped Erlenmeyer flask. The two precursors were combined by adding the barium source to the B-site source in a 1:1 A to B-site ratio. DEA was slowly added to the solution, which was then allowed to stir for approximately 12 hours prior to spin casting. Resulting solutions had a molarity of 0.3. The preparation procedure for the barium titanate hafnate hybrid-chelate solutions is shown in Figure 5.18.

\[ \text{Figure 5.18: Solution preparation procedure for a barium titanate hafnate hybrid-chelate solution chemistry.} \]

The optimized spin casting procedure of 7:30 minute 250°C dry steps was used for the films with a total of 6 layers. The oxygen partial pressure versus temperature phase diagram for the four constituents of the system, barium, titanium, hafnium, and copper shows a large process region where barium titanate hafnate is stable in equilibrium with copper metal and oxygen as shown in Figure 5.19.
Figure 5.19: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides. The shaded region represents the conditions where barium titanium and zirconium oxidize and copper is reduced.\textsuperscript{190}

Given the similarities in phase equilibria between BTZ and BTH, the identical processing conditions were used: 900°C and a $pO_2$ of $10^{-13}$ atm. Films were reoxidized at 550°C and $10^{-5}$ Torr O$_2$ for 30 minutes prior to platinum electrode deposition.

To verify that the perovskite structure formed for each composition, X-ray diffraction patterns for each film were collected as shown in Figure 5.20. For each composition there are peaks consistent with a perovskite crystal structure and no peaks associated with secondary phases. This is with the exception of a possible Cu$_2$O peak in for the composition containing 25 mole percent barium hafnate.
Figure 5.20: X-ray diffraction patterns for Ba(Ti$_{1-x}$Hf$_x$)$_3$O$_5$ thin films processed at 900°C on copper.

As each of these films was fired during the same run, the existence of the copper oxide phase in one sample is unlikely to be caused by an anomaly in the processing conditions. A more probable cause for the formation of copper oxide in the sample with the highest level of hafnium is trapped organics from the precursor gel. Similar phenomena have been identified in the lead zirconate titanate system by Losego and coworkers where a processing condition that should result in reduction of copper has copper oxide peaks present in the X-ray diffraction patterns. The copper oxide phase was attributed to residual organics in the gel that upon firing become trapped near the interface and can oxidize the substrate. As the hafnium source used has a much higher organic content than a typical alkoxide precursor (for example (OC(CH$_3$)$_2$CH$_2$OCH$_3$)$_4$ for Hf(TMMP)$_4$ versus (OCH$_2$CH$_2$CH$_3$)$_4$ for Zr propoxide) it is possible that these organics become trapped and the oxygen associated with them can oxidize the substrate. Alternatively, it is possible that hafnium alters the formation of an oxycarbonate phase upon crystallization either by not forming and leaving its associated organic ligands trapped in the film or by creating a more tenacious phase that requires higher temperatures to decompose. In either case, the existence of the copper oxide phase should not be ignored in analysis of the dielectric data.

To verify that hafnium was substituting for titanium, lattice parameters were measured using X-ray diffraction measurements of the 001, 002, and 003 reflections and extrapolating the lattice constant using the Nelson-Riley function. For each composition
pseudocubic unit cells were assumed due to the resolution of the X-ray instrument that does not allow peak splitting associated with tetragonal or orthorhombic structures to be identified. Lattice parameters are plotted versus composition for both the measured values and those calculated using Vegard’s Law and the accepted lattice parameters from the Powder Diffraction File of 4.008Å and 4.171Å for barium titanate and barium hafnate respectively in Figure 5.21.

Figure 5.21: Measured lattice parameter and lattice parameter calculated from Vegard’s Law for barium titanate hafnate thin films.

The measured and calculated lattice parameters coincide reasonably well with increasing lattice constant corresponding with increasing substituent level. There is a slight discrepancy in the 10 and 25 mole percent samples, however the difference occurs in the fourth decimal place and may represent a resolution limit of the instrument. The increasing lattice constant combined with the lack of secondary phases in the X-ray diffraction patterns suggests that hafnium was incorporated into the perovskite lattice at the B-Site.

The temperature dependence of permittivity and loss tangent was measured for each of the barium titanate hafnate films as shown in Figure 5.22. As the level of barium hafnate increases three phenomena are observed. First there is a shift of the phase transition to lower temperatures. Second, the value of the permittivity maximum decreases. Third, the phase transition appears to become increasingly diffuse. It is important to note that the loss tangents are low for each film composition. Each of these phenomena was observed in the
BTZ films suggesting similarities in the two systems and is expected given the similarities between Zr and Hf chemistry.

Figure 5.22: Temperature dependence of permittivity and loss tangent for $\text{Ba(Ti}_{1-x}\text{Hf}_x\text{)O}_3$ thin films on copper substrates.

The phase transition temperature was plotted as a function of composition for both the films on copper and for bulk ceramics from the literature as shown in Figure 5.23. $T_{\text{max}}$ for the thin film materials shows a much stronger effect of hafnium on the transition in comparison with the bulk ceramics. While the reason is unclear, the purity of the bulk material was unknown, and the fine thin film grain sizes (which are most likely smaller than the bulk material) may accelerate $T_c$ shifting.

Figure 5.23: Phase transition temperature versus composition of barium titanate hafnate thin films and bulk ceramics.$^{164}$
The maximum permittivity was plotted versus BaHfO$_3$ concentration in Figure 5.24. A similar trend to the barium titanate zirconate system is observed with a slightly greater decrease in permittivity at the 25% level. To decouple the effects of intrinsic dielectric property change and grain size, AFM topographical scans were collected for the various barium titanate hafnate compositions over a 3 µm x 3 µm scan area and the average grain size measured using a linear intercept method as shown in Figures 5.25 and 5.26. The error bars represent the 95% confidence level.

**Figure 5.24:** Permittivity at $T_{\text{max}}$ versus composition for barium titanate hafnate thin films.
Figure 5.25: 3µm x 3µm topographical AFM scans of a series of barium titanate hafnate thin films with compositions of a) BaTiO₃, b) Ba(TiₐHfₐ0.ₐ)O₃, c) Ba(Ti₀.₃Hf₀.₃)O₃, d) Ba(Ti₀.₇5Hf₀.₇5)O₃.

Figure 5.26: Average grain size versus composition for barium titanate hafnate thin films.

From the AFM scans and subsequent measurements, a clear trend of decreasing grain size with increasing level of barium hafnate is observed. This is a similar trend to that observed in the barium titanate zirconate system. To establish if the trend in decreasing peak
permittivity is associated with the decrease in grain size or an intrinsic hafnium incorporation effect, a plot of permittivity at $T_{\text{max}}$ versus average grain size was developed for both barium titanate hafnate and the pure barium titanate scaling series from Chapter 4 as shown in Figure 5.27.

![Figure 5.27: Grain size dependence of permittivity at $T_{\text{max}}$ for barium titanate hafnate and barium titanate thin films.](image)

The trend of maximum permittivity versus grain size scales similarly for both pure barium titanate and the barium titanate hafnate compositions. This trend is identical to that observed in the chemically similar barium titanate zirconate system and allows the conclusion to be drawn that hafnium incorporation onto the $B$-site does not intrinsically decrease the dielectric response. Rather, the decrease observed in permittivity results from a reduction in grain size. The phenomenon responsible for the grain size reduction is unclear, however the nucleation behavior may have been altered or the refractoriness of hafnium oxide may have impeded diffusion thereby limiting grain growth.

The field dependence of permittivity and loss tangent was measured for each composition at room temperature as shown in Figure 5.28. Each composition shows dielectric tunability and saturation of the dielectric constant and is consistent with a ferroelectric material. As was observed for BTZ, a decrease in tunability and maximum permittivity with increasing hafnium level is demonstrated and can likely be attributed to the grain size reduction resulting from the hafnium incorporation.
As no known studies exist in the literature investigating relaxor behavior in barium titanate hafnate, the frequency dispersion of the phase transition was investigated in the thin film materials as shown in Figure 5.29. As hafnium and zirconium are chemically similar and both systems show diffuse phase transitions, it was anticipated that relaxor characteristics at the 25% level would be observed. In this experiment, no evidence of frequency dependence of $T_{\text{max}}$ is observed. However, a deviation from Curie-Weiss behavior is noted and suggests that relaxor ferroelectric behavior is starting to occur at this level. Knowing that relaxor behavior does not start until the 25% level in barium titanate zirconate, it is hypothesized that 25% hafnium may be at the limit of relaxor behavior and that increasing the level would result in the observation of a frequency dispersive transition temperature.

**Figure 5.28:** Field dependence of permittivity and loss tangent for a composition series of barium titanate hafnate thin films at room temperature.
To investigate the films for X7R compliance, the temperature dependence of permittivity at 10 kHz was plotted with each respective X7R region superimposed as shown in Figure 5.30. As was identified in the barium titanate zirconate films, none of the compositions deposited satisfied the X7R standard. However, it appears that a composition containing between 5 and 10 mole percent barium hafnate may sufficiently pinch the transitions such that the desired temperature stability is achieved.
Figure 5.30: Temperature dependence of permittivity with EIA specification X7R regions mapped for a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Hf$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Hf$_{0.10}$)O$_3$, and d) Ba(Ti$_{0.75}$Hf$_{0.25}$)O$_3$ thin films.

5.3 Barium Titanate – Barium Stannate Solid Solutions

For both barium titanate zirconate and barium titanate hafnate a decrease in the grain size and a subsequent decrease in permittivity was identified as the substituent level increased. It would be useful then to develop a material set where the phase transition temperature could be tailored without sacrificing the grain size and permittivity that makes the barium titanate on foil embodiment attractive for capacitor applications. It is known that fluxing agents, such as PbO, can improve diffusion and provide a vehicle for grain growth.$^{287}$ With an industry effort to eliminate lead containing materials from consumer products,
another $p$-block oxide, SnO$_2$, was considered in the form of barium stannate. Barium stannate is a known phase transition pincher and behaves similarly to both barium zirconate and barium hafnate in its effects on the dielectric properties of barium titanate. Inspection of the thermodynamics of metal oxidation however reveals a key difference from the previously studied systems. The phase field for oxidation of tin and reduction of copper is much smaller than that for BT, BTZ, or BTH as shown in Figure 5.31. Given the reduced processing phase field, a precise knowledge and control of the oxygen partial pressure is necessary.

![Figure 5.31: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides. The shaded region represents the conditions where barium, titanium, and tin oxidize and copper is reduced.](image)

Films were prepared with compositions containing ratios of Ti/Sn of 100/0, 95/5, 90/10, and 75/25. The chemical precursor was prepared in a manner similar to that of barium titanate hafnate. The tin source used was tin tert-butoxide (Sigma Aldrich, 99.99+%). Attempts were made to use the less expensive tin acetate source, however the powder was difficult to dissolve in any reasonable solvent including acetic acid and methanol with DEA and nitric acid added to adjust the solution pH. Tin tert-butoxide is chemically similar to titanium isopropoxide and presented no difficulties in solution preparation or stability. The solution was prepared by reacting titanium isopropoxide with tin tert-butoxide in a 50 mL Erlenmeyer flask. Acetylacetone was reacted with the $B$-site precursors to chelate and stabilize the chemicals and the solution was allowed to stir for approximately 2 hours. Barium acetate was dissolved in glacial acetic acid in a 50 mL Erlenmeyer flask. After dissolution of the barium acetate powder, an equimolar amount of barium was added to the $B$-site precursor. The solution was allowed to stir for approximately 1 hour at which point
DEA was added and the solution was capped and stirred for approximately 12 hours. The solution preparation procedure is outlined in Figure 5.32.

**Figure 5.32:** Solution preparation procedure for a barium titanate stannate hybrid-chelate solution chemistry.

Films were prepared using the optimized spin casting methods. The solutions were deposited and spun at 3000 RPM for 30 seconds followed by a 250°C, 7:30 minute dry step. The process was repeated 5 times for a total of 6 layers. The films were crystallized under the standard conditions of a 30°/minute ramp to 900°C with a 30 minute dwell and cooling controlled by Newtonian cooling. The atmosphere used consisted of 410 sccm of N\textsubscript{2}, 55 sccm of 1% H\textsubscript{2} in an N\textsubscript{2} carrier flowed through a 25°C water bubbler. The $p$O\textsubscript{2} at 900°C was 5x10\textsuperscript{-13} atm and is plotted on the pressure – temperature phase diagram in Figure 5.33. From the plot, it is apparent that the condition used is sufficient to oxidize the tin while reducing copper if equilibrium is achieved. Closer observation of the Figure reveals that the partial pressure of oxygen used is in the phase field that should favor the 2+ oxidation state of tin. This is attractive as a reduction in the melting temperature with decreased valence may help to flux the system. While it may be possible to stabilize the 2+ state during high temperature processing, it was hypothesized that the stoichiometry of the system with tin substituted for titanium would force tin onto the octahedral site of the perovskite cell and could help to stabilize the 4+ state. Additionally, a reoxidation anneal at a higher $p$O\textsubscript{2} should be sufficient to oxidize Sn\textsuperscript{2+} to Sn\textsuperscript{4+}. Films were then annealed at 550°C and 10\textsuperscript{-5} Torr O\textsubscript{2} prior to platinium electrode deposition and dielectric characterization.
Figure 5.33: Oxygen pressure-temperature phase diagram for the reactions of metals, oxygen and metal oxides with the actual firing conditions plotted.  

X-ray diffraction was used to study phase assemblage in the materials after the crystallization anneal as shown in Figure 5.34. From the plot, clear evidence of perovskite phase formation is observed. No peaks associated with secondary tin phases can be identified, in particular SnO as would be represented by its most intense reflection at 26.26° or 34.06° depending on phase. This indicates that tin has been incorporated into the lattice.

Figure 5.34: X-ray diffraction patterns for $Ba(Ti_{1-x}Sn_x)O_3$ thin films processed at 900°C on copper.

To verify the incorporation of tin onto the $B$-site, lattice parameter measurements were made using the 001, 002, and 003 diffraction peaks and the Nelson-Riley extrapolation
Theoretical lattice constants were calculated using the two end member lattice parameters and Vegard’s Law with barium titanate having a pseudocubic lattice parameter of 4.008 Å and cubic barium stannate having 4.116 Å as shown in Figure 5.35. The trend of increasing lattice parameter with increasing concentration of tin suggests that tin is incorporated into the lattice. For this system there is a similar discrepancy between the measured and calculated lattice parameters in comparison with the zirconium data. The difference between the measured and calculated values for the pure barium titanate composition suggests minor instrument misalignment. This coupled with the measurement error can account for some of the discrepancy.

The temperature dependence of permittivity and loss tangent was measured for each composition as shown in Figure 5.36. Similar trends to the previous solid solution examples are observed, including a shift in the phase transition to lower temperatures, an increase in the broadness of the transition, and a decrease in the peak permittivity with increasing concentration of barium stannate.

![Figure 5.35: Measured lattice parameter and lattice parameter calculated from Vegard’s Law for barium titanate stannate thin films.](image)
Figure 5.36: Temperature dependence of permittivity and loss tangent for Ba(Ti$_{1-x}$Sn$_x$)O$_3$ thin films processed at 900°C on copper.

Phase transition temperatures were plotted as a function of composition for both the films on copper and bulk ceramics from the literature as shown in Figure 5.37. A favorable comparison is made between the two studies with nearly equivalent $T_{max}$ values for each composition. This provides further evidence that the tin was incorporated into the lattice at the B-site.

Figure 5.37: Phase transition temperature versus composition of barium titanate stannate thin films and bulk ceramics.$^{154}$

Plotting the permittivity at $T_{max}$ reveals a similar trend to that observed in both BTZ and BTH thin films with decreasing permittivity with increasing tin content as shown in Figure 5.38.
Topographical AFM scans were collected for the BTS samples to decouple the effect of composition and grain size on the dielectric response as shown in Figure 5.39. The average grain sizes were measured using the linear intercept method and are plotted as a function of composition in Figure 5.40. The error bars indicate the 95% confidence level for the measured values. From this plot, the fluxing effect can be appreciated, as the degree of grain size reduction with composition is not as high as for the hafnium and zirconium substituted materials. This is evident in the 25 mole percent samples where barium stannate and barium zirconate alloys resulted in grain sizes of approximately 94 and 74 nm, respectively. This suggests that processing in the SnO region of the phase diagram has allowed for fluxing and grain growth.
Figure 5.39: 3µm x 3µm topographical AFM scans of a series of barium titanate stannate thin films with compositions of a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Sn$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Sn$_{0.10}$)O$_3$, d) Ba(Ti$_{0.75}$Sn$_{0.25}$)O$_3$.

Figure 5.40: Average grain size versus composition for barium titanate stannate thin films.

Comparing the peak permittivity as a function of grain size for both pure barium titanate and barium titanate stannate reveals a different trend than that observed for zirconium and hafnium as shown in Figure 5.41. For compositions containing 0 to 5 mole percent tin, the grain size-permittivity trend tracks well for pure and tin substituted films.
Upon increasing the level to 10 mole percent, however there is an increase in grain size with a decrease in permittivity. For the 25 percent level, it is observed that there is a dramatic decrease in permittivity with a slight reduction in grain diameter, which does not scale with the pure material. As no secondary phases were identified through X-ray diffraction, it is unlikely that a composite material is dampening the response.

**Figure 5.41:** Grain size dependence of permittivity at $T_{\text{max}}$ for barium titanate stannate and barium titanate thin films.

**Figure 5.42:** Field dependence of permittivity and loss tangent for a composition series of barium titanate stannate thin films at room temperature.
The electric field response was measured for each composition as shown in Figure 5.42. Consistent with the temperature dependent data, a decrease in the peak permittivity is observed as the substituent level increases. It is important to note that the high-field permittivity saturates at the same level. This indicates that the intrinsic response of the lattice for each composition is identical. This, combined with the decrease in tunability, suggests that the extrinsic response is diminished with additional barium stannate. A possible explanation is that defects are impeding the domain wall motion. As the films were fired in a processing regime where Sn\(^{2+}\) is favored over Sn\(^{4+}\), it is possible that the reoxidation anneal did not completely convert all 2-valent ions to 4-valent. Shown in Equation 5.3 is a defect equilibrium reaction of Sn\(^{2+}\) located on a titanium site. If ionically compensated, each Sn\(^{2+}\) would be balanced by an oxygen vacancy.

\[
\text{BaO} + \text{SnO} \xrightarrow{\text{BaTiO}_3} \text{Ba}^{\text{Ba}} + \text{Sn}^{\text{T}_1} + 2\text{O}^{\text{O}} + \text{V}^{\text{O}}
\]

Equation (5.3)

Consequently, the oxygen vacancies could pin domain walls, and therefore quench the extrinsic ferroelectric response.

It has been observed in bulk BTS that the phase transitions become increasingly diffuse as the substitution level of barium stannate increases up to 25 mole percent where relaxor behavior is recorded. To determine if this behavior scales to thin films, temperature dependent permittivity and loss tangent measurements were taken for each composition at frequencies of 1, 10 and 100 kHz. The results are shown in Figure 5.43. Unlike barium titanate zirconate, no evidence of relaxor behavior is observed, even at the 25 mole percent level. There are multiple explanations for a lack of frequency dependent dispersion of the phase transition. First, the 25% level is the minimum concentration necessary to observe dispersion in the bulk, and it is possible that a higher level is necessary. Second, the possibility of Sn\(^{2+}\) remaining in the lattice may alter the response of the material, in particular the existence of polar-microregions.
Figure 5.43: Temperature dependence of permittivity at 1, 10, and 100 kHz for a) BaTiO$_3$, b) Ba(Ti$_{0.95}$Sn$_{0.05}$)O$_3$, c) Ba(Ti$_{0.90}$Sn$_{0.10}$)O$_3$, and d) Ba(Ti$_{0.75}$Sn$_{0.25}$)O$_3$ thin films.

Each composition’s response at 10 kHz was plotted against its respective X7R permittivity-temperature space as shown in Figure 5.44. Similar to the previous studies, the X7R requirement was not met by any of the compositions. However, from inspection it appears that a composition between 5 and 10 mole % BaSnO$_3$ may be sufficient to shift $T_{max}$ to a lower temperature and maintain a high enough permittivity at the 125°C boundary condition to meet the X7R specification.
Figure 5.44: Temperature dependence of permittivity with EIA specification X7R regions mapped for a) $\text{BaTiO}_3$, b) $\text{Ba(Ti}_{0.95}\text{Sn}_{0.05})\text{O}_3$, c) $\text{Ba(Ti}_{0.90}\text{Sn}_{0.10})\text{O}_3$, and d) $\text{Ba(Ti}_{0.75}\text{Sn}_{0.25})\text{O}_3$ thin films.
Chapter 6: Defect Equilibria

This chapter is divided into two sections. The first section discusses intrinsic defect equilibria in barium titanate including vacancies formed from processing and those from stoichiometry considerations. The second discusses the methods of preparation and properties of doped barium titanate thin films. This section will focus on acceptor doping in an effort to eliminate the necessity of the reoxidation anneal.

6.1: Intrinsic Equilibria

All barium titanate thin films presented thus far have been processed in low $pO_2$ atmospheres to facilitate compatibility with the metallic copper substrate. As was discussed in Chapter 3, such processing can result in the formation of oxygen vacancies as the material is slightly reduced. Calculations predict the oxygen vacancy concentration in pure barium titanate processed at 900°C and 10^{-13} atm O_2 to be ~340 ppb from Equation 6.1. These defects are intrinsic to the atmospheric equilibration process and likely are electronically compensated in the lattice by electrons by Equation 6.2.

\[
[V_{O}^{\ddagger}] = \left[ \frac{1}{4} pO_2^{1/2} \exp\left(\frac{-\Delta H}{RT}\right) \right]^{1/3} \quad \text{Equation (6.1)}
\]

\[
\begin{align*}
\text{BaTiO}_3 & \leftrightarrow \text{Ba}^{x}_{\text{Ba}} + \text{Ti}^{x}_{\text{Ti}} + 2\text{O}^{x} + \frac{1}{2}O_2(g) \uparrow + V_{O}^{\ddagger} + 2e' \\
& \quad \text{Equation (6.2)}
\end{align*}
\]

The vacancy concentration predicted above assumes a perfectly stoichiometric material. Considering, however the effect of non-stoichiometry (i.e. A:B-site ratio) on the oxygen vacancy concentration reveals a strong dependence. For barium titanate with excess titanium or barium an anion vacancy generating reaction, Equations 6.3 and 6.4 respectively would be expected. Each case considers only ionic compensation as opposed to electronic compensation, and both teach that stoichiometry alone can control the oxygen vacancy concentration.
\[ \text{TiO}_2 \xrightarrow{\text{BaTiO}_3} V_{\text{Ba}}^n + \text{Ti}^{4+}_{\text{Ti}} + 2\text{O}^x_{\text{O}} + V_{\text{O}}^{**} \]  
Equation (6.3)

\[ \text{BaO} \xrightarrow{\text{BaTiO}_3} \text{Ba}_{\text{Ba}}^n + \text{V}^{4+}_{\text{Ti}} + \text{O}^x_{\text{O}} + 2V_{\text{O}}^{**} \]  
Equation (6.4)

In this model the limits of vacancy formation are controlled by the solubility of excess barium or titanium. From the BaO-TiO\(_2\) phase diagram, a limited solubility range would be expected given that for the temperatures of interest BaTiO\(_3\) is a line compound as shown in Figure 6.1.

**Figure 6.1:** Equilibrium phase diagrams for the BaO-TiO\(_2\) system (adapted from a) Rase et al.\(^{288}\) and b) Kirby et al.\(^{289}\)).

Hu et al. and Sharma et al. investigated the solubility of BaO and TiO\(_2\) in BaTiO\(_3\) respectively.\(^{290, 291}\) Through extensive X-ray, SEM, TEM, and electrical conductivity studies, it was concluded that the solubility of BaO was less than 100 ppm at which point a second phase of Ba\(_2\)TiO\(_4\) precipitated at the grain boundaries. Likewise, TiO\(_2\) solubility was limited to approximately 100 ppm prior to Ba\(_6\)Ti\(_{17}\)O\(_{40}\) precipitation. To explore the solubility limits in thin film BaTiO\(_3\), a series with compositions containing excess barium and titanium was prepared. Films were processed at the standard conditions of 900°C and a \(p\text{O}_2\) of \(\sim 10^{-13}\) atm for 30 minutes. To investigate the phase development X-ray diffraction patterns for the composition series were collected and are shown in Figures 6.2 and 6.3.
Figure 6.2: X-ray diffraction patterns of Ba$_{1+x}$TiO$_3$ thin films with x ranging from 0 to 0.05 fired at 900°C for 30 minutes.

Figure 6.3: X-ray diffraction patterns of BaTi$_{1+x}$O$_3$ thin films with x ranging from 0 to 0.05 fired for 30 minutes at 900°C.

For the barium excess films, a second phase of Ba$_2$TiO$_4$ is observed at the 5 mole percent excess level, while for the titanium excess films no secondary phases can be identified. This is unexpected from the BaO-TiO$_2$ phase diagram and the work of Hu and Sharma and suggests that equilibrium is not achieved at 900°C for firing times of 30 minutes. To verify
this and to check if equilibrium can be reached at 900°C, an equivalent set of films were fired at 900°C for 14 hours with the X-ray diffraction patterns shown in Figures 6.4 and 6.5.

**Figure 6.4:** X-ray diffraction patterns of Ba\textsubscript{1+x}TiO\textsubscript{3} thin films with x ranging from 0 to 0.05 fired at 900°C for 14 hours.

**Figure 6.5:** X-ray diffraction patterns of BaTi\textsubscript{1+x}O\textsubscript{3} thin films with x ranging from 0 to 0.05 fired at 900°C for 14 hours.

As with the samples fired for 30 minutes, the samples processed at 900°C for 14 hours reveal no second phase formation for the titanium excess films and possible formation of Ba\textsubscript{2}TiO\textsubscript{4}
in the 5 mole percent excess barium film. This implies that either equilibrium was not reached, or the solubility limit at 900°C and at low $pO_2$ values is significantly larger than that achieved under typical processing conditions of 1200°C and air atmospheres.

The implication of this expanded solubility is that the oxygen vacancy concentration in pure BaTiO$_3$ thin films may be strongly dependent on the stoichiometry given the experimental challenges associated with achieving Ba:Ti ratios very close to unity. In contrast, the bulk systems fired at significantly higher temperatures will ‘self-correct’ by forming a second phase resulting in $0.998 < \text{Ba/Ti} < 1.001$, thus maximum oxygen vacancy concentrations of 100 ppm and 200 ppm for Ti excess and Ba excess respectively. This demonstrates a necessity for stoichiometry control in thin film oxide systems – especially considering that most films are grown at more modest temperatures where the meta-stable phase field may be even broader.$^{292}$

In sections 3.3.3 the necessity of a reoxidation anneal to obtain reasonable dielectric properties for processing in reductive conditions was discussed. Interestingly, films have been prepared without doping or reoxidation that show equivalent dielectric properties. Figures 6.6 and 6.7 are plots of the field dependence of permittivity and loss tangent of a barium titanate thin film processed at 900°C and $10^{13}$ atm O$_2$ without a reoxidation anneal. This data (specifically the loss tangent at large fields) demonstrates that if stoichiometry is well controlled, films that are highly insulating in the as-fired state can be prepared. We attribute this high insulation resistance to ionic compensation of cation non-stoichiometry by atmosphere-induced oxygen vacancies. Unfortunately, films with high-quality dielectric properties ‘as-fired’ are the exception and more often reoxidation anneals are necessary to improve the high-field loss behavior.
6.2: Extrinisic Equilibria – Acceptor Doping

High-quality thin films can be prepared either in the as-deposited state or with a reoxidation anneal. The limited reproducibility of the as-fired films, and the additional processing step required for reoxidation are unattractive from an industrial standpoint. For this reason, acceptor doping was investigated to determine the concentrations necessary and what effect, if any, the dopants had on the properties. Three dopants were chosen for the study: Mn, Mg, and Ca. Each of these elements, when ionized, is of an appropriate size to replace titanium in the perovskite lattice. The ionic radius of Ti$^{4+}$ is 0.745 Å while the studied dopants have ionic radii in 6-fold coordination of: 0.81 Å for Mn$^{2+}$ and 0.785 Å for Mn$^{3+}$, both in the low spin state, 0.67 Å for Mn$^{4+}$, 0.86 Å for Mg$^{2+}$, and 1.14 Å for Ca$^{2+}$. For completeness and comparison, the ionic radius in 12-fold coordination of barium and calcium is 1.75 Å and 1.48 Å respectively. Under normal pressures, Mn and Mg do not occupy 12-coordinated anion polyhedra. From this comparison, it is clear that both Mn and Mg substitute for titanium in the lattice. From ionic radius arguments, it may appear that calcium is too large to occupy the 6-coordinated site in the barium titanate lattice, however there is extensive evidence in the literature of calcium localizing on the B-site. The relatively large radius of calcium in 6-fold coordination would generate lattice strain that could be minimized by calcium substituting for barium, where it has a limited substitution solubility.

Figure 6.6: Field dependence of permittivity and loss tangent for a 680 nm thick, 140 nm grain-sized barium titanate thin film on copper fired at 900°C and 10$^{-13}$ atm O$_2$ without reoxidation.
As shown in Equation 6.2 oxygen vacancies due to low $pO_2$ conditions can be compensated electronically. To minimize this electronic carrier concentration acceptor doping can be used as shown in Equations 6.3 through 6.6. Equations 6.3 and 6.5 show ionic compensation by anion vacancies of divalent and trivalent acceptors respectively. Equations 6.4 and 6.6 show electronic compensation for divalent and trivalent acceptors through formation of holes in the valance band. This allows for electrons created during the high temperature processing to recombine and neutralize. Additional dopants can be compensated ionically by oxygen vacancies.

$$\text{AO} \xrightarrow{T_{TiO_2}} A'_\text{Ti}^n + O'_\text{O}^+ + V''_O$$  \hspace{1cm} \text{Equation (6.3)}

$$\text{AO} + \frac{1}{2}O_2 \xrightarrow{T_{TiO_2}} A'^{n}_\text{Ti} + 2O'_\text{O}^+ + 2h^+$$  \hspace{1cm} \text{Equation (6.4)}

$$A_2O_3 \xrightarrow{2T_{TiO_2}} 2A'^{n}_\text{Ti} + 3O'_\text{O}^+ + V''_O$$  \hspace{1cm} \text{Equation (6.5)}

$$A_2O_3 + \frac{1}{2}O_2 \xrightarrow{2T_{TiO_2}} 2A'^{n}_\text{Ti} + 4O'_\text{O}^+ + 2h^+$$  \hspace{1cm} \text{Equation (6.6)}

Modifying these equations specifically for the dopants used in this study results in Equations 6.7 to 6.14 with the odd numbered equations representing ionic compensation and even equations representing electronic compensation.

$$\text{MnO} \xrightarrow{T_{TiO_2}} Mn'^{n}_{\text{Ti}} + O'_\text{O}^+ + V''_O$$  \hspace{1cm} \text{Equation (6.7)}

$$\text{MnO} + \frac{1}{2}O_2 \xrightarrow{T_{TiO_2}} Mn'^{n}_{\text{Ti}} + 2O'_\text{O}^+ + 2h^+$$  \hspace{1cm} \text{Equation (6.8)}

$$\text{Mn}_2O_3 \xrightarrow{2T_{TiO_2}} 2Mn'^{n}_{\text{Ti}} + 3O'_\text{O}^+ + V''_O$$  \hspace{1cm} \text{Equation (6.9)}

$$\text{Mn}_2O_3 + \frac{1}{2}O_2 \xrightarrow{2T_{TiO_2}} 2Mn'^{n}_{\text{Ti}} + 4O'_\text{O}^+ + 2h^+$$  \hspace{1cm} \text{Equation (6.10)}

$$\text{MgO} \xrightarrow{T_{TiO_2}} Mg'^{n}_{\text{Ti}} + O'_\text{O}^+ + V''_O$$  \hspace{1cm} \text{Equation (6.11)}

$$\text{MgO} + \frac{1}{2}O_2 \xrightarrow{T_{TiO_2}} Mg'^{n}_{\text{Ti}} + 2O'_\text{O}^+ + 2h^+$$  \hspace{1cm} \text{Equation (6.12)}
These equations teach that to compensate for the intrinsic 340 ppb oxygen vacancies, approximately 340 ppb of a doubly ionized acceptor and approximately 680 ppb of a triply ionized acceptor are needed. Practically achieving that level of control with solutions containing less than 0.005 moles of each cation species is extremely difficult. For this reason, solutions were prepared with 100, 1000, and 10,000 ppm (1 mol%) of dopants. These levels are reasonable when considering the bulk ceramic literature where doping levels of tenths of a mole percent are common.

All solutions formed were based on acetic acid dilutions. The three dopant precursors were prepared such that their molecular mass of gram solution per mole dopant was on the order of 25,000 g/mol. This high mass allowed for higher precision in adding the dopants to the stock barium titanate solutions. To prepare the manganese precursor, manganese acetate tetrahydrate (99.99%, Sigma-Aldrich) was the Mn source. The tetrahydrate form was chosen as the amount of water was known and magnesium acetate is hygroscopic thus its molecular mass depends on relative humidity. 0.285 g Mn-acetate was massed on a 5 decimal balance on a weighing paper and then poured into a 50 mL Erlenmeyer flask. The weighing paper was massed after pouring to account for powder electrostatically attracted to the paper during the massing and subsequent transfer. 29.75 g of glacial acetic acid was then added to the flask while on the balance to dissolve the manganese precursor and to provide for a highly dilute solution with a ‘molecular mass’ of 25,990 g/mol Mn. For the magnesium precursor, magnesium acetate tetrahydrate (99.999%, Sigma-Aldrich) was used for the same reasons as above for the manganese source. 0.249 g Mg-acetate tetrahydrate was massed in the same manner as the Mn source. 29.75 g of glacial acetic acid was added to the flask to dissolve and dilute the solution. The final ‘molecular mass’ of the solution was 25,970 g/mol Mg. Calcium precursor solution preparation proved substantially more complex. Calcium acetate monohydrate (Fisher Scientific) was chosen as the calcium source to minimize uncertainties due to the hygroscopicity. Calcium acetate monohydrated was insoluble in acetic acid;
cloudy solutions indicative of undissolved powder remained after several hours of stirring at room temperature. The method of calcium dissolution described by Losego in preparing calcium copper titanate was employed. A methanol-based solution was formed by mixing 2 mL of triethanolamine (TEA) (98%, Sigma-Aldrich) with 30 mL of methanol (99.9%, Fisher Chemical) and adding 10 drops of nitric acid (99.999+%, Sigma-Aldrich) to maintain a neutral pH. 0.200 g of Ca-acetate monohydrate was then added to the liquid in a 50 mL Erlenmeyer flask. The powder source dissolved within 3 minutes. It was discovered that it is important to have the pH of the dopant solutions be similar to the pH of the parent barium titanate solution to prevent precipitation. The parent solution has a pH of 6 and the as-prepared calcium precursor had a pH of 7, so it was necessary to add a few more drops of nitric acid. The final solution has a ‘molecular mass’ of 25,860 g/mol Ca.

The titanium precursor was prepared as shown previously for pure barium titanate. Titanium isopropoxide was massed in a capped 50 mL Erlenmeyer flask to which acetylacetone was added to chelate and stabilize the solution. Barium acetate was dissolved in glacial acetic acid a capped 50 mL Erlenmeyer flask. The ‘molecular mass’ of the barium precursor was approximately 2430 g/mol Ba – approximately an order of magnitude more concentrated than the dopant precursors. The barium source was added drop-wise to the titanium precursor to a level in excess of the number of moles of titanium. The excess was measured and the number of moles calculated based upon the molecular mass of the precursors. For example, in a solution that requires 100 ppm dopant to be forced onto the B-site, ~100 ppm excess barium was added. With the specific amount excess calculated, the stoichiometric balance was made by adding the appropriate number of moles of the dopant, in this case 100 ppm. It is at this step where the highly dilute dopant solutions are useful allow for higher precision in adding the dopants to compensate for the excess Ba. The final stoichiometry and formula of the barium titanate is \( \text{BaTi}_{1-x}\text{A}_x\text{O}_3 \) with \( x \) ranging between \( 10^{-4} \) and \( 10^{-2} \). Typical solutions are made to a precision of 0.005% in Ba to Ti ratio. At this level of precision, the purity of the components and accuracy of the scale become significant sources of error.
The solutions were spin cast in 6 layers with a 250°C x 7:30 minute dry following each spin step. The films were then crystallized by ramping the furnace at 30°/min to 900°C and holding for 30 minutes in an atmosphere similar to those used before with a $pO_2$ of $5 \times 10^{-13}$ at the holding temperature. To verify perovskite phase formation and phase purity, X-ray diffraction patterns were collected as shown in Figures 6.7 to 6.9 below.

**Figure 6.7:** X-ray diffraction patterns for pure and Mn-doped barium titanate thin films on copper. Film stoichiometry is $BaTi_{1-x}Mn_xO_3$ where the levels indicated represent $x$.

**Figure 6.8:** X-ray diffraction patterns for pure and Mg-doped barium titanate thin films on copper. Film stoichiometry is $BaTi_{1-x}Mg_xO_3$ where the levels indicated represent $x$. 
Figure 6.9: X-ray diffraction patterns for pure and Ca-doped barium titanate thin films on copper. Film stoichiometry is $\text{BaTi}_x\text{Ca}_x\text{O}_3$ where the levels indicated represent $x$.

For each condition clear evidence exists for the formation of the perovskite phase of barium titanate with sharp and intense diffraction lines. The lack of secondary phases suggests that each dopant element was incorporated for each doping level. One distinct feature is present in both the Mn and Ca-doped materials at the 1 mol% doping level. In each of these films there is a secondary peak that can be attributed to copper oxide formation. These films were processed under conditions that under equilibrium would ensure reduction of copper oxide, so the presence of these peaks cannot be explained from an anomaly in the processing. The copper oxide existence must be due to a kinetic limitation in reduction, however the reason is not well understood.

Dopants and impurities are well known to limit grain growth in ceramic materials. In particular, in Mg-doped barium titanate with mol% Mg greater than 1, grain sizes were reduced. In light of this possibility, FE-SEM images were taken for each composition to study the effects of the dopants on the microstructure as shown in Figures 6.10 to 6.12 below.
Figure 6.10: SEM secondary electron topographical images of manganese-doped barium titanate (BaTi$_{1-x}$Mn$_x$O$_3$) thin films with compositions of a) pure BaTiO$_3$, b) 100 ppm Mn, c) 1000 ppm Mn, and d) 1 mol% Mn.

Figure 6.11: SEM secondary electron topographical images of magnesium-doped barium titanate (BaTi$_{1-x}$Mg$_x$O$_3$) thin films with compositions of a) pure BaTiO$_3$, b) 100 ppm Mg, c) 1000 ppm Mg, and d) 1 mol% Mg.
Qualitatively there appears to be a trend of decreasing grain size with increasing dopant level. To quantify the grain size for each composition and verify the trend, the linear intercept method was used on the topographical images and the results are shown in Figures 6.13 to 6.15.

Figure 6.13: Average grain diameter plotted versus dopant level of manganese-doped barium titanate (BaTi$_{1-x}$Mn$_x$O$_3$). Error bars indicate a 95% confidence interval for each composition.
Figure 6.14: Average grain diameter plotted versus dopant level of magnesium-doped barium titanate (BaTi$_{1-x}$Mg$_x$O$_3$). Error bars indicate a 95% confidence interval for each composition.

Figure 6.15: Average grain diameter plotted versus dopant level of calcium-doped barium titanate (BaTi$_{1-x}$Ca$_x$O$_3$). Error bars indicate a 95% confidence interval for each composition.

For calcium and manganese doped there is an apparent decrease in grain size with dopant level, in particular at the 1 mol% concentration. The manganese-doped samples, however, show an increase in grain size from the 100 to 1000 ppm level with a decrease at the 1 mol% concentration. This may be the result of an increased oxygen vacancy concentration from the 100 to 1000 ppm level, which facilitates increased diffusion and coarsening. While the trends are identified, the broad distribution of grain sizes in each sample has resulted in large confidence intervals with a high degree of overlap. With this in mind, it can be assumed that at least between the 100 and 1000 ppm level, the error of the measurement effectively results in materials with an invariant grain size. It is interesting to note that the pure sample had an
average grain diameter of 135 nm, a value larger than that measured for any of the doped films. This may indicate a decrease in coarsening rate due to impurity solute drag.

The dielectric properties of the doped films were characterized using two criteria. The first characterization technique was to conduct capacitance versus voltage sweeps to investigate the permittivity and loss response. This was done with an oscillator frequency of 10 kHz and level of 0.05 V. The second was a capacitance versus frequency sweep to investigate the existence of space charges that result from the doping, processing, or both. As the compensation mechanism is expected to be dependent upon the $pO_2$, three firing conditions were used, $5 \times 10^{-13}$, $5 \times 10^{-12}$, and $5 \times 10^{-11}$ atm O$_2$. Figures 6.16 through 6.33 show the field and frequency dependent permittivity and loss tangent values for 100, 1000, 10,000 ppm Ca, Mg, and Mn doped samples respectively.
100 ppm Ca

Figure 6.16: Electric field dependence of permittivity and loss tangent for 100 ppm Ca-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$.

Figure 6.17: Frequency dependence of permittivity and loss tangent for 100 ppm Ca-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$. 
100 ppm Mg

**Figure 6.18:** Electric field dependence of permittivity and loss tangent for 100 ppm Mg-doped barium titanate processed at a) $5 \times 10^{-13}$ atm O$_2$ b) $5 \times 10^{-12}$ atm O$_2$ and c) $5 \times 10^{-11}$ atm O$_2$.

**Figure 6.19:** Frequency dependence of permittivity and loss tangent for 100 ppm Mg-doped barium titanate processed at a) $5 \times 10^{-13}$ atm O$_2$ b) $5 \times 10^{-12}$ atm O$_2$ and c) $5 \times 10^{-11}$ atm O$_2$. 
100 ppm Mn

Figure 6.20: Electric field dependence of permittivity and loss tangent for 100 ppm Mn-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$.

Figure 6.21: Frequency dependence of permittivity and loss tangent for 100 ppm Mn-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$. 
1000 ppm Ca

**Figure 6.22:** Electric field dependence of permittivity and loss tangent for 1000 ppm Ca-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$.

**Figure 6.23:** Frequency dependence of permittivity and loss tangent for 1000 ppm Ca-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$. 

1000 ppm Mg

Figure 6.24: Electric field dependence of permittivity and loss tangent for 1000 ppm Mg-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$.

Figure 6.25: Frequency dependence of permittivity and loss tangent for 1000 ppm Mg-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$. 
1000 ppm Mn

Figure 6.26: Electric field dependence of permittivity and loss tangent for 1000 ppm Mn-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$.

Figure 6.27: Frequency dependence of permittivity and loss tangent for 1000 ppm Mn-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$. 
1 mol% Ca

Figure 6.28: Electric field dependence of permittivity and loss tangent for 1 mol% Ca-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$.

Figure 6.29: Frequency dependence of permittivity and loss tangent for 1 mol% Ca-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$. 
1 mol% Mg

**Figure 6.30:** Electric field dependence of permittivity and loss tangent for 1mol% Mg-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$.

**Figure 6.31:** Frequency dependence of permittivity and loss tangent for 1 mol% Mg-doped barium titanate processed at a) $5 \times 10^{-13}$ atm $O_2$ b) $5 \times 10^{-12}$ atm $O_2$ and c) $5 \times 10^{-11}$ atm $O_2$. 
Several trends should be highlighted from the electrical data:

(1) For each dopant, firing conditions could be established at levels of 1000 ppm or less, which were free from space charge, highly tunable, and low-loss. For example, a $pO_2$ of $5 \times 10^{11}$ atm at a doping level of 1000 ppm resulted in reasonable dielectric properties regardless of dopant. Additionally, 100 ppm of Ca or Mg at a $pO_2$ of $5 \times 10^{13}$ atm behaved similarly.
(2) Altering the firing atmosphere changed the space charge characteristics. This was particularly evident in the 100 ppm Mg samples where no space charge signature could be identified in films processed at the lowest $pO_2$. Increasing the oxygen level, however, increased the amount of frequency dispersion, which is a signature of a space charge contribution to permittivity. The mechanism causing this response is unclear, but is almost certainly associated with changing the defect compensation mechanism. Probing the exact compensation mechanism is difficult and would require further investigation using other instrumentation and techniques such as electron paramagnetic resonance (EPR).\textsuperscript{299}

(3) Doping levels of 1 mole % greatly reduced the extrinsic contribution to permittivity as the tunabilities decreased substantially. This is indicative of a highly defective material where the energy barriers to domain wall motion are sufficiently high to limit the response. From Equations 6.3 and 6.5 it is established that ionic compensation of acceptor dopants results in the formation of oxygen vacancies. If ionic compensation dominates, it would be expected in the 1 mole % doped films that 1/100 oxygen sites would be vacant. This would result in a concentration of one vacancy approximately every 3 unit cells (which interestingly is approximately the width of a domain wall), which could effectively pin a domain wall (at least temporarily) and quench the extrinsic response. While this represents an extreme condition and there is most likely a mixture of ionic and electronic charge compensation, this demonstrates the effect that dopants can have on the crystal defect density and its relation to the ferroelectric response. It is interesting that both Mn and Ca doped samples show large loss tangent peaks indicative of space charge at the 1 mole % level, while Mg shows none. It is possible that this could be a contribution of the copper oxide phase identified in the X-ray patterns.

Two obstacles encumber comparison of the results with the literature. First, most doping work has been done in bulk materials and thus very little, if any, high field or frequency dependent data exists. The majority of studies measure conductivity as a function of $pO_2$ and temperature, which is difficult to do on a thin film. Second, this is the first known study on the effects of dopants in a ferroelectric film fired under reducing atmospheres. This study however, does demonstrate that dopants can be used to eliminate the reoxidation anneal
for the processing of barium titanate thin films on copper and that several different dopants can be used with similar results.

**6.3: Reduction and Compensation**

In comparing the doping results with expected intrinsic oxygen vacancy concentration, it is noticed that the doping levels that resulted in reasonable dielectric properties were several orders of magnitude higher than would be necessary as predicted by thermodynamics. For example, for 1000 ppm of divalent dopant, which gives reasonable dielectric properties, 1000 ppm of extrinsic oxygen vacancies would be expected. However the processing conditions used should stabilize only 340 ppb intrinsic oxygen vacancies. The excess extrinsic oxygen vacancies, in equilibrium, should be filled by the oxygen from the firing atmosphere and the charge compensation mechanism should become electronic, with the material becoming $p$-type. This would result in a less insulating material and likely higher loss tangents. Clearly does not occur suggesting that another mechanism is responsible for the phenomena encountered

The situation is further complicated by considering films with reasonable dielectric properties in the as-fired state. Leakage current data was gathered from a barium titanate film in the as-fired state as shown in Figure 6.34.

![Figure 6.34: DC leakage current density versus applied bias for a 780 nm thick barium titanate thin film processed at 900°C and 10^{-13} atm O_2 without reoxidation.](image)

181
Calculating the conductivity for the un-reoxidized film at 10 volts bias gives a value of approximately \(10^{-11} \text{ (Ω-cm)}\). Assuming an intrinsic oxygen vacancy concentration of 340 ppm and using a simple Boltzmann distribution for ionization of the electrons associated with the oxygen vacancies predicts a material with a conductivity of \(\sim 3.6 \times 10^{-5} \text{ (Ω-cm)}\) – a value that 6 orders of magnitude greater than that measured (see Appendix). Three possible explanations for the insulating properties include: (1) the impurities present in the chemical precursors are able to compensate for the oxygen vacancies created during firing, (2) the dopants segregate and do not incorporate into the lattice, and (3) the stoichiometry of the solution was such that cation vacancies could ionically compensate for intrinsic oxygen vacancies, minimizing electronic compensation.

Table 6.1: Typical impurity levels in barium titanate solution precursor chemicals.

<table>
<thead>
<tr>
<th>Source</th>
<th>Impurity</th>
<th>Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium</td>
<td>Ca</td>
<td>50 ppm</td>
</tr>
<tr>
<td>Barium</td>
<td>Fe</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Barium</td>
<td>K</td>
<td>3 ppm</td>
</tr>
<tr>
<td>Barium</td>
<td>Na</td>
<td>5 ppm</td>
</tr>
</tbody>
</table>

Investigation of the impurity levels in the cation sources reveals a relatively high level of acceptors as shown in Table 6.1. Assuming these acceptors sit on the appropriate site, the extrinsic oxygen vacancy concentration is greater than 2 orders of magnitude higher than the ‘intrinsic’ level from the processing conditions. This could certainly account for the ability to process materials without additional doping or reoxidation. However, it was shown in Equations 6.3 and 6.5 that non-stoichiometry should also enhance the oxygen vacancy concentration through ionic compensation. The addition of these two factors, intrinsic impurities and a limited ability to control stoichiometry suggests a similar situation as the extrinsic material where it should be \(p\)-type and conductive given the processing conditions. Two phenomena that could explain this are: (1) equilibrium is not reached or (2) there are more intrinsic oxygen vacancies than expected from the calculation. It was already shown in section 6.1 that at 900°C equilibrium may not be reached from the phase development of films with excess barium and titanium. This gives plausibility to situation (1). Considering situation (2), we investigate the enthalpy of reduction used to calculate the intrinsic vacancy concentration.
For the calculations of the intrinsic oxygen vacancy concentration, the enthalpy of reduction used ($\Delta H = 568$ kJ/mol) was from the literature and was found empirically on bulk barium titanate ceramics with an average grain size of 100 $\mu$m. The films used in the study had average grain sizes on the order of 100 nm – 3 orders smaller in magnitude. As grain size decreases the volume fraction of grain boundaries increases. Therefore, it is expected that the thin films have a greater grain boundary volume than the bulk samples from which the enthalpy data was collected. It is well known that many material properties differ at surfaces and interfaces than in the bulk and it is possible that the enthalpy of reduction is such a material property and may decrease at interfaces. Using this reasoning, the enthalpy of reduction was calculated based on the results of this study. Assuming that the 100 ppm acceptor doped samples are completely ionically compensated, it would be expected that 100 ppm of vacancies are formed due to the processing conditions. Inserting the processing parameters of $900^\circ$C and $10^{13}$ atm $O_2$ into Equation 6.1 reveals that the necessary enthalpy of reduction to form 100 ppm intrinsic vacancies is 402 kJ/mol. This is only a 30% reduction from the bulk value therefore seems reasonable. A more complete calculation by assuming two enthalpy’s of reduction, one for the bulk of the grain and one for the grain boundary, suggests that the enthalpy of reduction of the grain boundary region is ~330 kJ/mol. This was calculated assuming spherical grains with grain boundaries that are 2 unit cells in thickness. That this value is only 40% less than was found for bulk ceramics suggests plausibility.
Chapter 7: Liquid Phase Sintering of BaTiO$_3$ Thin Films

The previous chapters illustrated a method to form high-quality barium titanate thin films on copper substrates. While successful, several barriers remain prior to commercialization of an embedded capacitor technology. One issue is to improve and control the microstructure to allow for a consistent and reliable product. The current process can result in films with a small amount of residual porosity, which could act as defect sites that ultimately lead to dielectric breakdown. Figure 7.1 is a typical cross-section of a barium titanate thin film processed on copper from chemical solution deposition, which shows a typical level of residual porosity.

![SEM image of fractured cross section of a barium titanate thin film on copper.](image)

The proposed method of modifying the microstructure involves flux-assisted or liquid phase sintering to improve mass transport and better densify the material. In addition to improved density, one potential outcome is an increase in grain size – and potentially an increase in permittivity. Several liquid phase systems were considered to perform this experiment. In bulk barium titanate, zinc-borate has been used to develop a dielectric compatible with copper electrodes for multilayer ceramic capacitors. Inspection of the phase diagram for zinc oxide and boron oxide reveals that the lowest melting temperature eutectic is at 961°C. This is in excess of the desired processing temperature of 900°C, so other systems were considered. A similar system was found in the barium oxide – boron oxide phase diagram. Here, several eutectics exist with melting temperatures of 869, 878,
and 899°C – all lower than the desired process temperature.\textsuperscript{301} Another system with a low melting temperature eutectic at 850°C was found in the barium oxide – phosphorus oxide system.\textsuperscript{302} To maintain a reasonable experimental array, this study was limited to these two systems.

### 7.1: Barium-Borate Flux Modified Barium Titanate

Figure 7.2 shows the phase diagram for BaO-B\textsubscript{2}O\textsubscript{3}. Highlighted on the diagram are the compositions studied in this experiment. The two eutectic compositions chosen have melting temperatures slightly below the standard annealing temperature, while the line compound has a slightly higher melting point. Our furnace routinely overshoots by a small amount thus a liquid phase would be expected for all compositions. The two end members, BaO and B\textsubscript{2}O\textsubscript{3}, were also studied.

![Equilibrium phase diagram for the system BaO-B\textsubscript{2}O\textsubscript{3} (adapted from Levin et al.)](image)

\textbf{Figure 7.2:} Equilibrium phase diagram for the system BaO-B\textsubscript{2}O\textsubscript{3} (adapted from Levin et al.\textsuperscript{301})
Films were made with nominal compositions containing $\text{BaTiO}_3 + x\text{B}_2\text{O}_3 + y\text{BaO}$ as shown in Table 7.1. For convenience, the compositions containing 0.76%, 1.38%, 2.76%, 4.14%, and 6.9 mole% $\text{B}_2\text{O}_3$ will be described as 0.5%, 1%, 2%, 3%, and 5% respectively.

**Table 7.1: Compositions of the thin films in the barium borate liquid phase sintering study.**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Moles BaTiO$_3$</th>
<th>Moles BaO</th>
<th>Moles B$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% $\text{B}_2\text{O}_3$</td>
<td>1</td>
<td>0</td>
<td>0.0000</td>
</tr>
<tr>
<td>0.5% $\text{B}_2\text{O}_3$</td>
<td>1</td>
<td>0</td>
<td>0.0069</td>
</tr>
<tr>
<td>1% $\text{B}_2\text{O}_3$</td>
<td>1</td>
<td>0</td>
<td>0.0138</td>
</tr>
<tr>
<td>2% $\text{B}_2\text{O}_3$</td>
<td>1</td>
<td>0</td>
<td>0.0276</td>
</tr>
<tr>
<td>3% $\text{B}_2\text{O}_3$</td>
<td>1</td>
<td>0</td>
<td>0.0414</td>
</tr>
<tr>
<td>4% $\text{B}_2\text{O}_3$</td>
<td>1</td>
<td>0</td>
<td>0.0520</td>
</tr>
<tr>
<td>5% $\text{B}_2\text{O}_3$</td>
<td>1</td>
<td>0</td>
<td>0.0690</td>
</tr>
</tbody>
</table>

869°C Eutectic (Eut 1)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Moles BaO</th>
<th>Moles $\text{B}_2\text{O}_3$</th>
<th>Moles $\text{B}_2\text{O}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% BaO</td>
<td>1</td>
<td>0.0023</td>
<td>0.0069</td>
</tr>
<tr>
<td>1% BaO</td>
<td>1</td>
<td>0.0045</td>
<td>0.0138</td>
</tr>
<tr>
<td>2% BaO</td>
<td>1</td>
<td>0.0090</td>
<td>0.0276</td>
</tr>
<tr>
<td>3% BaO</td>
<td>1</td>
<td>0.0135</td>
<td>0.0414</td>
</tr>
<tr>
<td>4% BaO</td>
<td>1</td>
<td>0.0190</td>
<td>0.0520</td>
</tr>
<tr>
<td>5% BaO</td>
<td>1</td>
<td>0.0225</td>
<td>0.0690</td>
</tr>
</tbody>
</table>

899°C Eutectic (Eut 2)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Moles BaO</th>
<th>Moles $\text{B}_2\text{O}_3$</th>
<th>Moles $\text{B}_2\text{O}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% BaO</td>
<td>1</td>
<td>0.0040</td>
<td>0.0069</td>
</tr>
<tr>
<td>1% BaO</td>
<td>1</td>
<td>0.0081</td>
<td>0.0138</td>
</tr>
<tr>
<td>2% BaO</td>
<td>1</td>
<td>0.0163</td>
<td>0.0276</td>
</tr>
<tr>
<td>3% BaO</td>
<td>1</td>
<td>0.0244</td>
<td>0.0414</td>
</tr>
<tr>
<td>4% BaO</td>
<td>1</td>
<td>0.0326</td>
<td>0.0520</td>
</tr>
<tr>
<td>5% BaO</td>
<td>1</td>
<td>0.0407</td>
<td>0.0690</td>
</tr>
</tbody>
</table>

Barium Oxide

<table>
<thead>
<tr>
<th>Composition</th>
<th>Moles BaO</th>
<th>Moles BaO</th>
<th>Moles BaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5% BaO</td>
<td>1</td>
<td>0.0050</td>
<td>0</td>
</tr>
<tr>
<td>1% BaO</td>
<td>1</td>
<td>0.0100</td>
<td>0</td>
</tr>
<tr>
<td>2% BaO</td>
<td>1</td>
<td>0.0200</td>
<td>0</td>
</tr>
<tr>
<td>3% BaO</td>
<td>1</td>
<td>0.0300</td>
<td>0</td>
</tr>
<tr>
<td>4% BaO</td>
<td>1</td>
<td>0.0400</td>
<td>0</td>
</tr>
<tr>
<td>5% BaO</td>
<td>1</td>
<td>0.0500</td>
<td>0</td>
</tr>
</tbody>
</table>

Solutions were made using an acetic acid diluted procedure as outlined in Chapter 3 with excess barium precursor being made and the stoichiometric ratio added to titanium precursor. After stirring for 1 hour DEA was added and the solution capped and allowed to stir an addition hour. The glass precursor was prepared by adding triethyl borate (99%, Sigma-Aldrich) to the remaining barium precursor at a level such that the final solution had a molecular mass of approximately 500 g/mol B. For the BaO excess solutions, an appropriate
excess of the barium precursor was added to the titanium precursor. For the B₂O₃ excess compositions, triethyl borate was added directly to glacial acetic acid to obtain a solution with a molecular mass of 500 g/mol B. The glass precursors were added to the barium titanate solution dropwise on a digital balance to determine the quantity. Solutions were capped and allowed to stir for approximately 12 hours prior to deposition.

Films were spin cast onto copper foils as described in Chapter 3 with a total of 6 layers. The films were crystallized at 900°C and 5x10⁻¹³ atm O₂ for 30 minutes prior to a reoxidation anneal at 450°C and 1x10⁻⁷ atm O₂. For each glass/flux system X-ray diffraction patterns were collected as shown in Figures 7.3 through 7.7 below.

![X-ray diffraction patterns](image)

**Figure 7.3:** X-ray diffraction patterns for BaTiO₃-B₂O₃ thin films on copper.
Figure 7.4: X-ray diffraction patterns for BaTiO$_3$ – 869°C eutectic BaO-B$_2$O$_3$ thin films.

Figure 7.5: X-ray diffraction patterns for BaTiO$_3$ – BaO-2B$_2$O$_3$ thin films.
For each boron containing composition no peaks consistent with crystalline secondary phases could be identified. This indicates that either full solid solutions were made of the fluxing agents and the barium titanate, or the fluxing agents remain as an amorphous phase. As discussed in Chapter 6, for the barium-excess films at the 5% level there was a minority peak consistent with a barium metatitanate phase Ba$_2$TiO$_4$, and is again observed in this series. There was also some evidence of a small amount of copper oxide for compositions containing greater than 1 mol% excess barium.
While gathering the X-ray diffraction patterns, an interesting feature was identified, in the films modified with high concentrations of the two eutectic and BaO-2B₂O₃ compositions, individual diffraction points could be observed along the χ axis of the perovskite peaks as shown in Figure 7.7 for a characteristic sample set from the 899°C eutectic composition. The discontinuous arcs suggest that significant grain growth has occurred such that the beam is only sampling as many grains as spots on the χ arc. Since the beam is approximately 1 mm in diameter, this suggests very large grains.

**Figure 7.8:** X-ray diffraction patterns of a) pure BaTiO₃ b) BaTiO₃ – 2% 899°C eutectic BaO-B₂O₃ and c) BaTiO₃ – 5% 899°C eutectic BaO-B₂O₃ The discontinuous BaTiO₃ diffraction arcs in the 5% sample suggests large-scale grain growth as indicated by the arrows.
Figure 7.9: SEM topographical micrographs of $\text{BaTiO}_3 - \text{B}_2\text{O}_3$ with compositions ranging from a) Pure $\text{BaTiO}_3$ to f) 6.9 mole % $\text{B}_2\text{O}_3$.

Figure 7.10: SEM topographical micrographs of $\text{BaTiO}_3 - 869^\circ\text{C}$ eutectic $\text{BaO-B}_2\text{O}_3$ with compositions ranging from a) 0.5% glass to f) 5% glass.
Figure 7.11: SEM topographical micrographs of BaTiO$_3$ – BaO-2B$_2$O$_3$ with compositions ranging from a) 0.5% glass to f) 5% glass.

Figure 7.12: SEM topographical micrographs of BaTiO$_3$ – 899°C eutectic BaO-B$_2$O$_3$ with compositions ranging from a) 0.5% glass to f) 5% glass.
To quantify grain growth topographical SEM micrographs were gathered as shown in Figures 7.9 through 7.13. The individual figures correspond to a specific BaTiO$_3$-flux composition series. Several trends could be identified from the micrographs: (1) For each composition, the grain size appears to increase with increasing glass/flux level, (2) anomalous grain growth could be observed in films with a barium borate additions at the 3% level, and (3) neither pure boron or barium excess resulted in anomalous grain growth with the exception of some large grains in the 5% B$_2$O$_3$ sample.

To simplify the discussion of the microstructures, it will be divided into 2 sections. First will be flux compositions containing only barium excess or only B$_2$O$_3$. Second will be flux compositions that contain both BaO and B$_2$O$_3$.

**7.1.1: Boron Oxide Flux Modified Barium Titanate**

For the boron oxide samples, the average grain size was measured using the linear intercept method with the results shown in Figure 7.14.
Figure 7.14: *Average grain diameter versus percent flux phase for barium titanate thin films with B$_2$O$_3$ additions.*

The average grain size increases as the boron level is increased from 0 to 2%, at which point a decrease is observed. At the 5% level the grain size increases again as some 0.5 to 1µm diameter exaggerated grains begin to develop. The decrease in grain size is not well understood, and was unexpected. The mechanism of grain growth in this system could be either a defect reaction allowing for an increase in vacancies to improve mass transport, or is related to the low melting temperature of B$_2$O$_3$ and its contribution of liquid phase transport. To investigate this further, the lattice parameter was measured by collecting X-ray diffraction patterns of the 001, 002, and 003 planes of a representative set of the films and the lattice constant was calculated using the Nelson-Riley extrapolation function. No significant variation in lattice parameter could be resolved. This can be representative of two scenarios. The first is that the boron does not incorporate into the lattice and remains at the grain boundaries. The second is that it does incorporate, however the site occupancy is such that the unit cell volume essentially does not change. For example, this could occur if boron sits on the titanium site where a lattice parameter reduction might be favored and concurrently sits on an interstitial site where a lattice expansion might be favored. The lack of lattice constant change is consistent with some of the literature studies on boron added to bulk barium titanate where no unit cell dimension changes have been observed and is in contradiction with other literature that suggests that boron occupies an interstitial site alone and expands the lattice.\(^{252,254}\)
Figure 7.15: Measured lattice parameter as a function of flux content for barium titanate thin films with $B_2O_3$ added.

7.1.2: Barium Oxide Modified Barium Titanate

For BaO excess films, as shown in Figure 7.16, the grain size increases with increasing barium level before decreasing at the 3% level. This decrease corresponds with the observation of the secondary $Ba_2TiO_4$ phase in the X-ray diffraction patterns and it is likely that its presence inhibits grain growth. Because no low melting temperature phases exist in this system, it is hypothesized that the grain growth mechanism is related to very large vacancy concentrations, which result from the barium excess allowed by the solubility windows.

Figure 7.16: Average grain diameter versus mole percent excess BaO for barium titanate thin films.
Lattice parameter measurements were made for the barium excess films with the results shown in Figure 7.17. No clear trend could be identified from the lattice constant variation observed.

![Figure 7.17: Measured lattice parameter as a function excess BaO for barium titanate thin films.](image)

### 7.1.3: Barium Borate Flux Modified Barium Titanate

Average grain size as a function of glass content was measured for the barium borate containing films as shown in Figure 7.18. Only films containing less than 3% glass were considered as the anomalous grain growth at higher concentrations makes the value of average grain diameter misleading. It is clear from the plot that the grain growth scales similarly regardless of the barium borate composition as at each flux level equivalent average grain sizes are measured.

![Figure 7.18: Average grain diameter versus percent flux phase for barium titanate thin films with barium borate additions.](image)
Lattice parameter measurements were conducted on the barium borate-barium titanate compositions to investigate possible solid solution formation. Figures 7.19 through 7.21 show the lattice parameter as a function of flux content for each composition of barium borate.

**Figure 7.19:** Measured lattice parameter as a function of flux content for barium titanate-869°C eutectic BaO-B₂O₃ thin films.

**Figure 7.20:** Measured lattice parameter as a function of flux content for BaTiO₃-BaO-2B₂O₃ thin films.
For the compositions showing exaggerated grain growth and grains with diameters in excess of 1µm, clear evidence of tetragonal splitting is observed and indicated by $a$ and $c$ lattice constants in plots 7.19 to 7.21. To demonstrate the splitting, a higher-resolution scan of the $\{002\}$ family of planes was conducted on the 899°C eutectic series by increasing the focusing circle of the Bruker diffractometer from 15 cm to 30 cm to decrease the solid angle sampled and increase resolution with the results shown in Figure 7.22. Here the peak splitting and increase in tetragonality that occurs can be appreciated in the 3% through 5% concentrations. The peak shoulders at lower concentration still indicate a non-centrosymmetric structure, but the spontaneous strain is not large enough to be fully resolved on our instrument. In the pure barium titanate there is a shoulder at higher angles, which we interpret as an indication of the orthorhombic phase. This has been previously proposed in the literature for small particle BaTiO$_3$. The existence of a non-centrosymmetric crystal structure for grain sizes larger than 500 nm is consistent with that observed in bulk ceramics. This is the first known observation of peak splitting in a polycrystalline barium titanate film.

**Figure 7.21:** *Measured lattice parameter as a function of flux content for barium titanate-899°C eutectic BaO-B$_2$O$_3$ thin films.*
Figure 7.22: X-ray diffraction pattern of the \{002\} family of planes for 899°C eutectic fluxed barium titanate.

For the barium borate compositions it is difficult to determine whether a liquid phase was present during firing, particularly for samples containing less than 3% of the additive phase. For the 5% BaO-2B₂O₃ composition, however there is clear evidence of a secondary phase wetting the grain boundaries as is evident in Figure 7.11(f). As no secondary crystalline phases could be identified in the X-ray patterns, the observed phase is likely amorphous. Several interesting microstructural features are present in the exaggerated-grained materials. In Figure 7.11(e) clear evidence of an equilibrium grain morphology is present with the cubic grains and 90° grain boundaries. The abnormal grains also have terraced surfaces, which may be indicative of a liquid phase being present during crystallization and sintering. At the onset of exaggerated grain growth, there is an apparent bimodal distribution of grain sizes with submicron grains making up a matrix surrounding the larger several micron wide grains. That no readily observable liquid phases are present in the compositions with normal grain growth suggests a solubility limit of the glass in the barium titanate to a level of approximately 2 to 2.5%. As the solubility limit as surpassed, the additional liquid phase improves mass transport resulting in anomalous grain growth. Though all modifications enabled grain growth when compared to pure BaTiO₃, only additions combining Ba and B yielded exaggerated grains and SEM evidence of a liquid phase. As the barium level in the glass increases, the concentration of glass necessary for exaggerated grain growth decreases. This is apparent in comparing the two eutectic systems. The 869°C eutectic has a normal, equiaxed grain morphology at the 3% level. The 899°C eutectic, with a higher barium level, shows the onset of abnormal grain growth at between
the 2 and 3% level. It should be noted that the actual number of moles of the second phase increases as the barium level increases in the glass compositions. For example, the 3% 869°C eutectic has 0.0135 moles of BaO while the 899°C eutectic has 0.0244 moles of BaO and both have 0.0414 moles of B₂O₃. This increase in the quantity of flux phase may account for the observed change in the onset of abnormal grain growth, but the actual dependency remains to be determined.

One of the goals of this work was to improve the density of the films through the use of a flux/liquid phase. SEM micrographs of fractured cross sections were gathered for the films without abnormal grain growth as shown in Figures 7.23 through 7.27. From the micrographs clear trends of improved densification with increasing level of additive can be observed. This is with the exception of the barium oxide excess compositions, which appear to have similar porosity levels for each of the observed compositions. The improved densification may best be shown in Figure 7.18, where a porosity-free film can be observed at the 2.5% level.

**Figure 7.23:** SEM micrographs of fractured cross sections of barium titanate films containing a) 0% B₂O₃, b) 0.5% B₂O₃, and c) 1% B₂O₃.

**Figure 7.24:** SEM micrographs of fractured cross sections of barium titanate-869°C eutectic BaO- B₂O₃ films with concentrations of a) 0.5%, b) 1%, and c) 2%. 200
Figure 7.25: SEM micrographs of fractured cross sections of barium titanate-$\text{BaO-2B}_2\text{O}_3$ films with concentrations of a) 0.5%, b) 1%, and c) 2.5%.

Figure 7.26: SEM micrographs of fractured cross sections of barium titanate-899°C eutectic $\text{BaO-B}_2\text{O}_3$ films with concentrations of a) 0.5%, b) 1%, and c) 2%.

Figure 7.27: SEM micrographs of fractured cross sections of barium titanate films containing a) 0.5 mol% $\text{BaO}$, b) 1 mol% $\text{BaO}$, and c) 2 mol% $\text{BaO}$.

### 7.1.4: Dielectric Properties of Barium Borate Fluxed $\text{BaTiO}_3$

With the observed grain growth in each of the compositions with increasing level of glass phase, it is anticipated that a concomitant increase in permittivity will occur. Temperature dependence of permittivity and loss tangent was measured for films without anomalous grain growth as shown in Figures 7.28 through 7.32. Films with exaggerated
grains showed a dewetting behavior from the substrate and resulted in short-circuited capacitors upon electrode deposition.

**Figure 7.28:** Temperature dependence of permittivity and loss tangent for BaTiO$_3$-B$_2$O$_3$. Average grain sizes are shown with 147 nm representing 0%, 179 nm representing 0.5%, and 184 nm representing 1%.

**Figure 7.29:** Temperature dependence of permittivity and loss tangent for BaTiO$_3$-869°C eutectic BaO-B$_2$O$_3$. Average grain sizes are shown with 107 nm representing 0%, 127 nm representing 0.5%, 138 nm representing 1%, and 157 nm representing 2%.
Figure 7.30: Temperature dependence of permittivity and loss tangent for BaTiO$_3$-BaO-2B$_2$O$_3$. Average grain sizes are shown with 107 nm representing 0%, 132 nm representing 0.5%, and 144 nm representing 1%.

Figure 7.31: Temperature dependence of permittivity and loss tangent for BaTiO$_3$-899°C eutectic BaO-B$_2$O$_3$. Average grain sizes are shown with 107 nm representing 0%, 127 nm representing 0.5%, and 147 nm representing 1%.
Figure 7.32: Temperature dependence of permittivity and loss tangent for BaTiO₃-BaO. Average grain sizes are shown with 147 nm representing 0%, 158 nm representing 0.5 mol%, and 164 nm representing 1 mol%.

From these plots, the effect of fluxing agents on the dielectric response is clear. Higher levels of the fluxes increase the peak permittivity values. To demonstrate the effect of the increased grain size due to the flux on the permittivity, the dielectric constant at $T_{\text{max}}$ was plotted versus the measured grain size as shown in Figure 7.33.

Figure 7.33: Maximum relative permittivity as a function of grain size for barium borate-based fluxed barium titanate thin films of varying compositions.

A trend is identified in the permittivity versus grain size plot for the varying compositions of fluxes where the barium borate flux values appear to fall along a line, while the barium oxide and boron oxide fluxed materials have equivalent permittivity peaks at larger grain sizes.
One possible explanation for this phenomenon is the increased densification of the barium borate containing films. Increased density minimizes the dilution effect that porosity can have on the permittivity and allows for higher values at finer grain sizes. In addition, the presence of the liquid phase may help improve overall crystalline quality, thus extrinsic contribution to permittivity.

![Figure 7.34: Relative permittivity at 20°C as a function of average grain size from several barium titanate scaling effects studies (adapted from Arlt\textsuperscript{54}, Frey\textsuperscript{63}, Parker\textsuperscript{64}, and Ihlefeld).](image)

With the exceptionally high permittivity values obtained from the barium borate fluxed films, it is of interest to see how the trend scales with materials from the literature. Figure 7.34 shows a plot of the room temperature permittivity as a function of average grain diameter for several barium titanate and barium strontium titanate bulk and thin film materials from the literature, including the size scaling study presented in Chapter 4.\textsuperscript{54, 57, 63, 64} The permittivities of the barium strontium titanate thin films of Parker were measured at -80°C to ensure an equal temperature difference from the phase transition as the barium titanate samples. Two features of interest stand out from the plot. First, for an equivalent physical grain size, the fluxed films on copper have higher permittivities than the pure barium titanate from the scaling study. Second, for the first time a polycrystalline thin film has a room temperature permittivity equivalent to or in excess of well-prepared bulk ceramics of equivalent grain dimensions. This is evident at ~160 nm where the fluxed film has surpassed the well-prepared (and previously unequaled) material of Frey, which has been
the gold standard for fine-grained ceramic BaTiO$_3$ since 1996.$^{57, 63}$ Two possible explanations for the enhanced permittivity in the fluxed material over the pure thin film examples include the increased density of the fluxed materials and also increased sub-grain crystallite size as a result of improved transport. This improved transport builds upon the hypothesis presented in Chapter 3 of higher thermal budgets allowing for improved crystallinity and chemical homogeneity in the films on copper in comparison with typical thin films processed at lower temperatures.

To demonstrate the dielectric improvements in the fluxed films, field dependence of permittivity and loss tangent was measured for an exceptional pure barium titanate thin film and two fluxed with B$_2$O$_3$ as shown in Figure 7.35. All measurements were made at 10 kHz with an oscillator level of approximately 0.6 kV/cm. All samples display clear hysteresis in permittivity with equivalent saturation values. Additionally, loss tangents at fields of 125 kV/cm are less than 0.005 (< 0.5%). For an applied field of 190 kV/cm the pure barium titanate displayed a tunability of $\sim$89% while the film fluxed with 1% B$_2$O$_3$ exhibited a tunability of $\sim$93%. This difference may seem marginal, however in comparing the ratio of the peak to saturation permittivity, the pure sample exhibits approximately 10:1 while the fluxed sample improves to 14:1. While increased grain size likely contributes to this enhancement, the improved crystallinity as a result of the flux also will minimize barriers to domain wall motion allowing for improved tunability and permittivity.
Figure 7.35: Field dependence of permittivity and loss tangent for $B_2O_3$-fluxed barium titanate thin films on copper.

As very little field dependent dielectric data exists in the literature for bulk ceramic samples, perhaps the best metric for comparison is the temperature dependence of permittivity. Figure 7.36 shows permittivity versus temperature plots for bulk ceramic and thin film materials of similar crystallite size. In so far as possible, materials were chosen with average crystal dimensions similar to those in the fluxed sample in the measurement axis. The effect of the fluxing agent on the permittivity response can be appreciated as the bulk ceramic data of Arlt has been surpassed by a thin film with a grain size ~120 nm smaller. Additionally, in comparison with the bulk material of Frey, while not displaying the sharp peak at the phase transition, matches or exceeds the permittivity at temperatures less than or equal to room temperature.
It was previously shown, and again demonstrated in Figure 7.36, that films processed at 900°C have properties far exceeding materials processed at 700°C and approaching, but not quite equaling, bulk ceramics processed in temperatures well in excess of 1000°C. Increasing mass transport with the aid of a liquid phase has allowed for further enhancement of crystallinity and homogeneity and allows for properties previously only achieved with advanced high-pressure and high temperature processing – at temperatures 300° less than those employed in typical bulk ceramic sintering. This is a dramatic and important breakthrough in ferroelectric thin film technology and demonstrates that for films of thicknesses of approximately 600 nm the dominant suppressor of dielectric properties is the result of extrinsic defects consequential from limited thermal budgets and mass transport.

7.2: Barium-Phosphate Flux Modified Barium Titanate

With the success of the barium borate system in growing the grains and densifying the microstructure, a liquid phase composition of low melting temperature was considered in the barium phosphate system. Figure 7.37 shows the partial barium phosphate phase diagram with the investigate composition highlighted. A eutectic composition of \((\text{BaO})_{52.5}-(\text{P}_2\text{O}_5)_{47.5}\) with an 850°C melting temperature was chosen as the liquid phase for this investigation.
Films were deposited with nominal compositions of BaTiO$_3$-$x$(BaO)$_{32.5-y}$(P$_2$O$_5$)$_{47.5}$ with $x$ ranging from 1 to 5 mol percent as shown in Table 7.2.

![Equilibrium phase diagram for the system BaO-P$_2$O$_5$](image)

**Figure 7.37:** *Equilibrium phase diagram for the system BaO-P$_2$O$_5$* (adapted from McCauley and Hummel)

**Table 7.2:** *Compositions of the thin films in the barium phosphate liquid phase sintering study.*

<table>
<thead>
<tr>
<th>Composition</th>
<th>Moles BaTiO$_3$</th>
<th>Moles BaO</th>
<th>Moles P$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>850°C Eutectic</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0% P$_2$O$_5$</td>
<td>1</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>1% P$_2$O$_5$</td>
<td>1</td>
<td>0.0100</td>
<td>0.0090</td>
</tr>
<tr>
<td>1.5% P$_2$O$_5$</td>
<td>1</td>
<td>0.0150</td>
<td>0.0136</td>
</tr>
<tr>
<td>2.5% P$_2$O$_5$</td>
<td>1</td>
<td>0.0250</td>
<td>0.0226</td>
</tr>
<tr>
<td>5% P$_2$O$_5$</td>
<td>1</td>
<td>0.0500</td>
<td>0.0452</td>
</tr>
</tbody>
</table>

Chemical solutions were prepared using the acetic acid diluted formulation. Titanium isopropoxide was reacted with acetylacetone in a capped Erlenmeyer flask and allowed to stir for approximately 2 hours. Excess barium acetate was dissolved in glacial acetic acid and allowed to stir for at room temperature. After approximately 2 hours, an equimolar ratio of the barium precursor was added dropwise to the titanium precursor and allowed to stir for 1
hour prior to the addition of diethanolamine. While the bulk barium titanate solution stirred, di(2-ethylhexyl)phosphoric acid (Alfa Aesar) was added to the remaining barium precursor with the stoichiometry measured and controlled by the masses of the constituents such that the proper ratio of barium (0.311 moles) to phosphorous (0.689 moles) for the eutectic composition was achieved. The resulting glass precursor had a molecular mass of approximately 3100 g/mol Ba. The eutectic composition was added dropwise to the barium titanate solution with the mass recorded on a digital balance to control the stoichiometry and allowed to stir for approximately 12 hours prior to deposition.

The spin casting and hotplate drying procedure described in Chapter 3 with 6 deposition layers and 250°C, 7.5 minute drying events following each layer. The films were then crystallized at 900°C and a $pO_2$ of $\sim 10^{-13}$ atm for 30 minutes. Each BaTiO$_3$-glass composition was studied using X-ray diffraction to identify phase assemblage in the films as shown in Figure 7.38.

![Figure 7.38: X-ray diffraction patterns for BaTiO$_3$ - 850°C eutectic BaO-P$_2$O$_5$ thin films with compositions ranging from 1 to 5 mol% eutectic composition.](image)

Clear evidence of second phase formation is identified by diffraction peaks consistent with Ba(PO$_3$)$_2$ at levels greater than 1.5%. Secondary phase formation has been observed in
bulk materials with P$_2$O$_5$ containing compositions, however the phase observed was Ba$_3$(PO$_4$)$_4$.\textsuperscript{248,249}

To investigate solubility of the phosphate glass into barium titanate, lattice parameter measurements were made for each composition using the 001, 002, and 003 peaks and the Nelson-Riley extrapolation function with the results shown in Figure 7.39. An apparent decrease in the lattice parameter occurs at the 2.5% level. This may be indicative of the Ba(PO$_3$)$_2$ phase stripping barium from the perovskite lattice to achieve its preferred stoichiometry.

![Figure 7.39: Measured lattice parameter as a function of flux content for BaTiO$_3$-850°C eutectic BaO-P$_2$O$_5$ thin films.](image)

In bulk ceramics containing phosphate impurities, it was observed that grain growth was suppressed.\textsuperscript{248,249,266} To investigate if this phenomenon scales to the lower temperatures used for thin film processing, SEM topographical micrographs were captured for each of the compositions as shown in Figure 7.40. Clear evidence of the secondary phase is present in the 2.5 and 5% glass compositions as large precipitates. In comparison with the barium borate fluxes the grain sizes in the barium phosphate system appear to be substantially smaller. This has been quantified by measuring the average grain size for each composition using the linear intercept method as shown in Figure 7.41 where the error bars indicate the 95% confidence interval. A clear decrease in average grain size with barium phosphate addition is evident in the plot. This may be due to the second phase formation inhibiting grain growth and/or may be a demonstration of limited solubility of barium titanate in the
barium phosphate liquid phase, which limits transport. It is interesting to note that the average grain size does not further decrease with increasing glass level.

![SEM topographical micrographs of BaTiO₃ – 850°C eutectic BaO-P₂O₅ with compositions ranging from a) 1% glass, b) 1.5% glass, c) 2.5% glass, and d) 5% glass.](image)

**Figure 7.40:** SEM topographical micrographs of BaTiO₃ – 850°C eutectic BaO-P₂O₅ with compositions ranging from a) 1% glass, b) 1.5% glass, c) 2.5% glass, and d) 5% glass.

![Average grain diameter versus percent flux phase for barium titanate thin films with barium phosphate additions.](image)

**Figure 7.41:** Average grain diameter versus percent flux phase for barium titanate thin films with barium phosphate additions.

Cross-sectional SEM micrographs of fractured cross sections were gathered for 1 and 1.5% barium phosphate samples as shown in Figure 7.42. Clear evidence of densification is observed in comparison with the pure barium titanate sample, most notably for the 1.5% composition.
Figure 7.4: SEM micrographs of fractured cross sections of barium titanate-850°C eutectic BaO- P₂O₅ films with concentrations of a) 0%, b) 1%, and c) 1.5%.

Field dependence of the permittivity and loss tangent was measured for each composition as shown in Figure 7.43 to characterize the dielectric properties. It is observed that the peak permittivity at room temperature peaks at approximately 750. This is greater than a 2-fold decrease from that observed in pure barium titanate. This is most likely the result of a grain size reduction. From the plots a distinct decrease in the tunability with increasing phosphorus content is observed. While this is consistent with a decrease in grain size reduction, the average grain size is relatively constant with glass level. This suggests an increase in the point defect density may contribute to the diminished dielectric response. The precipitate phase has a ratio of barium oxide to phosphorus oxide of 1:1 while the glass composition added has a ratio less than unity and suggests that barium has been stripped from the lattice leaving it titanium rich. As discussed in Chapter 6, in titanium rich barium titanate the excess titanium leads to the formation of barium vacancies, which can be ionically compensated by oxygen vacancies. This defect equilibria combined with the similar saturation levels of the permittivity suggests that the likely the likely cause of the permittivity reduction an increase in the defect density, with a minor contribution from the secondary phase.
Figure 7.43: Field dependence of permittivity and loss tangent for a) 1% barium phosphate, b) 1.5% barium phosphate, c) 2.5% barium phosphate, and d) 5% barium phosphate.
Chapter 8: Conclusions and Future Work

This thesis sought to develop a robust solution-deposition process to deposit barium titanate solid solution thin films on copper substrates, and to use this process to prepare sample sets where variables including grain size, doping, thickness, and composition could be systematically controlled, and through analysis, fundamental issues associated with BaTiO$_3$ could be addressed. The first section of this chapter highlights the innovations and technical accomplishments, while the second section discusses several areas that require more in-depth study to gain a more complete understanding of the observed phenomena.

8.1: Conclusions

Below is a brief summary of the outcomes of this thesis:

- A metalorganic chemical solution containing barium and titanium ions of relatively low toxicity and suitable for large area deposition was developed.
- Barium titanate thin films were deposited on copper foil substrates and processed in a reductive atmosphere such that the film constituents were oxidized and the copper substrate remained metallic. This research demonstrated for the first time the compatibility of a complex oxide film with a copper substrate.
- This research developed the ability to control grain size by approximately a factor of 3 while still maintaining a suitably dense film microstructure. Using this approach, the grain size dependence of the dielectric response was explored. The results suggest that $T_c$ shifts occur below 70 nm, while permittivity scales inversely with grain size over the entire range. These observations are consistent with findings for bulk BaTiO$_3$.
- $B$-site substituents of zirconium, hafnium, and tin were successfully used to shift the phase transition and flatten the overall dielectric response with temperature to achieve X7R temperature coefficient of capacitance characteristics.
- A reduction in maximum permittivity in barium titanate zirconate and barium titanate hafnate films was identified. For the first time, this was decoupled from scaling
effects and was attributed to grain size reduction and not to an intrinsic effect of substituents in the lattice.

- For the first time Mg, Mn, and Ca dopants were used in a thin film to compensate for oxygen point defects resulting from low \( pO_2 \) processing conditions. The successful use of these dopants allows for a reduction of processing steps and is favorable for commercialization.

- Barium borate fluxes were successfully incorporated into the solution chemistry. These fluxes aided in growing the grains and improving film densification resulting in materials with ultra-high permittivities in excess of any ever reported for a thin film and consistent with the best fine-grained bulk ceramics. An increase in permittivity over pure BaTiO\(_3\) for a given grain size was observed. This suggested that the fluxes improve crystallinity and that this is a key parameter in obtaining bulk properties.

- X-ray peak splitting consistent with tetragonal symmetry was observed in fluxed films with exaggerated grains in excess of 500 nm in diameter consistent with findings for bulk BaTiO\(_3\). This is the first known report of tetragonal splitting in a polycrystalline BaTiO\(_3\) thin film.

### 8.2: Future Work

Barium zirconate and barium hafnate could be alloyed with barium titanate to tailor the temperature response of permittivity. While successful in reducing the temperature coefficient of capacitance, both hafnium and zirconium caused a reduction in grain size and a subsequent reduction in peak permittivity. The permittivity reduction was the direct result of the grain size reduction and was not intrinsically due to the solid solution formation. For the barium titanate stannate system however, the addition of tin and the use of high temperature anneal conditions favoring Sn\(^{2+}\) mitigated the grain size reduction. Unlike previous systems, however, there was a drop in the peak permittivity independent of a grain size reduction. This reduction in permittivity is believed to result from \( Sn_{\ell}^+ \) and their complexing with \( V_o^{\prime\prime} \) to form domain pinning dipoles. Further experimentation is necessary to verify this hypothesis by firing a series of BTS films in differing atmospheres with a series of more aggressive reoxidation anneals. This could be tested with a Rayleigh Law experiment to
determine the degree of domain wall pinning and comparing to pure materials of similar grain dimensions. As the valence of tin is altered the oxygen vacancy concentration should decrease and the degree of domain wall pinning may also decrease providing a metric by which the reoxidation level could be analyzed.

A study on defect equilibria was conducted concerning intrinsic defects resulting from non-stoichiometry. X-ray diffraction analysis showed that BaO and TiO$_2$ solubility in BaTiO$_3$ was much greater than reported for bulk ceramics. A series of samples should be developed where the stoichiometry is similarly varied, however they should be deposited on a more refractory substrate such as platinum. A series of experiments varying the firing temperature, time, and $pO_2$ can be conducted such that equilibrium can be achieved in reasonable time scales, and the effects of processing temperature and oxygen partial pressure on the width of the BaTiO$_3$ phase field can be determined.

Doping experiments suggest that the apparent intrinsic oxygen vacancy concentration due to low $pO_2$ processing was several of orders greater than that predicted from theory. It is hypothesized that this results from an altered enthalpy of reduction for materials with fine grain sizes, thus increased grain boundary volume. Equilibrium temperature and oxygen pressure dependent conductivity measurements should be conducted to determine empirically an enthalpy of reduction for BaTiO$_3$ as a function of grain size. This would be of great use to the bulk and thin film communities in determining optimum doping levels especially considering scaling trends to lower film thicknesses and grain diameters.

A series of fluxes and firing conditions that could dramatically enhance grain growth in BaTiO$_3$ were identified. While successful in improving densification and permittivity, substantially more work is needed to achieve appropriate levels of reproducibility. A complete study on the effect of crystallization temperature on phase formation and grain size could provide information on the mechanism of grain growth and densification, separating solid state from liquid phase mass transport. This could best be accompanied by TEM investigations of the microstructure to determine when liquid phases are present at the grain boundaries especially for the lowest levels of additives. A high-resolution study of crystallite
size versus measured grain size would be necessary to fully decouple the crystallinity/dielectric properties hypothesis outlined in the thesis. The zero bias dielectric properties of the materials were extraordinary and probably the best ever measured in fine-grained BaTiO$_3$. However, some compositions displayed higher than desirable losses at high fields. A study on the mechanism of loss in the samples would be important to improving insulation resistance and overall device reliability.

No studies of reliability were conducted in this thesis. Controlling and improving the microstructure prior to any reliability studies to the point of reproducibility where statistical analysis is sensible was the primary concern. A thorough investigation of breakdown mechanisms, conditions, and device lifetimes is necessary prior to commercialization of the technology.

Some recent work toward the end of the thesis research focused on developing large area electrodes to demonstrate feasibility. Our sponsor’s technological goal was a functional 1”x1” capacitor. This was demonstrated on sputtered BST on copper foils by Daniels et al. by using a co-firing process where the electrodes were deposited on the green film and the entire metal-insulator-insulator metal stack was fired at 900°C for densification and grain growth.$^{303}$ The non-wetting nature of the top electrode metal was the key to eliminating short-circuits resulting from flaws in the thin dielectric films. A similar approach was attempted on chemical solution deposited barium titanate films. Here, a 1 cm$^2$ platinum electrode was deposited through a shadow mask onto an as-dried CSD film and the stack was co-fired under the typical conditions of 900°C and a $pO_2$ of $10^{13}$ atm. Observing the electrode through an optical microscope revealed top electrode bubbling and some metallization loss during the anneal and subsequent handling as shown in Figure 8.1.
In spite of the poor top electrode adhesion, electrical characterization revealed a functional capacitor as shown in Figure 8.2. The loss tangents were generally higher than acceptable, however it must be emphasized that this was on a capacitor that was 10,000X larger than any ever measured on a solution derived material in the laboratory at NCSU.

We speculate that metal bubbling, which was not observed on the sputtered dielectrics, resulted from thermalizing organic constituents from the gel during heating. To circumvent this, samples were pre-fired to a temperature above the highest known decomposition temperature of all organic precursor constituents prior to metallization. The temperature of 650°C was chosen as the Ba$_2$Ti$_5$O$_8$CO$_3$ phase was found to decompose below this temperature. This anneal was conducted under atmospheres consistent with reduction of copper. Platinum was deposited as an array of 16 electrodes with diameters of 3 mm. The
films were then fired at 900°C and a $pO_2$ of $\sim 10^{-13}$ atm. Figure 9.3 shows a representative electrode after the co-firing process. No evidence of metallization bubbling was observed. Electrical measurements on the samples revealed that 15 out of 16 of the 3 mm electrodes functioned with no short circuits. It is interesting to note that in many cases large cracks occurred in the co-fired films, and often times these cracks intersected the electrodes. Figure 8.3b shows one such intersection. This capacitor is fully functional and suggests that dewetting metal is critical to this large electrode process.

Figure 8.3: a) Optical micrograph of a 3mm electrode co-fired after a burnout anneal and b) an optical micrograph of a crack in a BaTiO$_3$ film with a co-fired electrode.

While the above work proved to be a useful demonstration of the co-firing process with a necessary burnout anneal, no optimizations were made. Therefore, a future project optimizing the process to find the burnout conditions that give the optimal dielectric properties is critical. Additionally, the demonstration of less expensive and more commercially representative metallization is important.
9. Bibliography:


253. Rhim, S. M., Hong, S., Bak, H. & Kim, O. K. Effects of B$_2$O$_3$ Addition on the Dielectric and Ferroelectric Properties of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ Ceramics. Journal of the American Ceramic Society 83, 1145-1148 (2000).


10. Appendix

10.1 Defect Density Calculation for Barium Titanate

This section of the appendix shows the step-by-step calculations necessary to determine the oxygen vacancy concentration in stoichiometric barium titanate. There are two properties that must be maintained in order for the arguments to be valid. The first is a mass balance of the defect reaction. The second is a condition of electroneutrality in forming a defect. The base equation for the formation of an oxygen vacancy in barium titanate is shown in Equation 10.1 as an oxygen atom from the bulk is driven off into the surrounding environment forming a vacant oxygen site and two electrons to compensate for the charge on the vacancy.

\[ O_0 \leftrightarrow \frac{1}{2}O_2(g) \uparrow + V_o^{**} + 2e' \]  
Equation (10.1)

The mass balance has been achieved in the previous equation by having the oxygen site and oxygen atom accounted for on both sides of the equation. A defect reaction, like that in 10.1, will have an equilibrium constant that is the ratio of the activities of products and reactants as shown in Equation 10.2 below, which can be simplified by assuming the activity of oxygen on the oxygen site to be 1 as in Equation 10.3.

\[ K = \frac{pO_2^{1/2}[V_o^{**}]n^2}{[O_o]} \]  
Equation (10.2)

\[ K = pO_2^{1/2}[V_o^{**}]n^2 \]  
Equation (10.3)

The electroneutrality condition for the defect formation reaction requires each ionized oxygen vacancy to be charge balanced. In the case of electronic compensation, two electrons will be localized with the vacancy such that their concentration is twice that of vacancies as shown in Equation 10.4.
Through rearrangement of and substitution of 10.4 into 10.3, the oxygen vacancy concentration can be written in terms of the $pO_2$ and the equilibrium constant as shown in Equations 9.5 to 9.7.

\[
2[V_o^{\cdot\cdot\cdot}] = [n] \quad \text{Equation (10.4)}
\]

\[
[V_o^{\cdot\cdot\cdot}] = K n^2 pO_2^{-1/2} \quad \text{Equation (10.5)}
\]

\[
[V_o^{\cdot\cdot\cdot}] = K \left(2[V_o^{\cdot\cdot\cdot}]^2\right) pO_2^{-1/2} \quad \text{Equation (10.6)}
\]

\[
[V_o^{\cdot\cdot\cdot}]^3 = \frac{1}{4} K pO_2^{-1/2} \quad \text{Equation (10.7)}
\]

The reaction of oxygen in the lattice to form a vacancy and gaseous oxygen can has an enthalpy associated with it, such that that defect reaction can be written in terms of free energy of formation.

\[
\Delta G = -RT \ln K = -\Delta H + T\Delta S \quad \text{Equation (10.8)}
\]

The change in entropy of the reaction is negligible in comparison with the enthalpy, and for this reason can be ignored and the equation simplified such that the equilibrium coefficient can be written in terms of the enthalpy and temperature as in Equation 10.9.

\[
K = \exp\left(-\frac{\Delta H}{RT}\right) \quad \text{Equation (10.9)}
\]

Substitution of 10.9 into 10.7 results in an expression for the concentration of oxygen vacancies as a function of temperature and $pO_2$ as shown in Equation 10.10.

\[
[V_o^{\cdot\cdot\cdot}] = \left[\frac{1}{4} pO_2^{1/2} \exp\left(-\frac{\Delta H}{RT}\right)\right]^{1/3} \quad \text{Equation (10.10)}
\]
10.2 Conductivity of Pure Barium Titanate

Through calculating the equilibrium oxygen vacancy concentration using 10.10, the carrier density at a given temperature can be found by using the Boltzmann distribution and the ionization energies of each electron associated with the vacancy. To calculate the vacancy density, the concentration from 10.10 must be multiplied by the total number of oxygen sites per cm$^3$. For barium titanate, the number of sites is $\sim 4.7 \times 10^{22}$ cm$^3$.

Processing at 900°C and 5 x $10^{13}$ atm O$_2$ gives a vacancy concentration of approximately $3.1 \times 10^7$. This gives a total vacancy density of $\sim 1.5 \times 10^{16}$ cm$^3$. To calculate the total carrier density, the number of electrons ionized must be calculated. Because there are two electrons with differing ionization energies, they will be calculated in two stages. The carrier density resulting from the first ionization event is calculated as shown in Equations 10.11 and 10.12.

$$n_1 = V_0^* = V_0^3 \exp \left( - \frac{E_d'}{k_B T} \right)$$  \hspace{1cm} \text{Equation (10.11)}

$$n_1 = V_0^* = 1.45 \times 10^{16} \text{ cm}^3 \exp \left( - \frac{0.10 \text{eV}}{8.616 \times 10^{-5} \text{eV/K} \cdot 300 \text{K}} \right) \approx 3 \times 10^{14} \text{ cm}^{-3} \hspace{1cm} \text{Equation (10.12)}$$

The second ionization event can only occur if one of the electrons is delocalized from the vacancy, thus the number of doubly ionized vacancies is dependent upon the fraction of those singly ionized as in Equations 10.13 and 10.14.

$$n_2 = V_0^{**} = V_0^* \exp \left( - \frac{E_d''}{k_B T} \right)$$  \hspace{1cm} \text{Equation (10.13)}

$$n_2 = V_0^{**} = 3 \times 10^{14} \text{ cm}^3 \exp \left( - \frac{1.30 \text{eV}}{8.616 \times 10^{-5} \text{eV/K} \cdot 300 \text{K}} \right) \approx 4.4 \times 10^{-8} \text{ cm}^{-3} \hspace{1cm} \text{Equation (10.14)}$$
From these calculations it is clear that at room temperature only the first ionization effectively contributes to the carrier density.

The conductivity can be calculated from Equation 9.15 assuming only electrons contribute to conduction.

\[ \sigma = n \cdot e \cdot \mu \]  
\[ \text{Equation (10.15)} \]

The mobility was calculated from the empirical equation for electron mobility in barium titanate by Ihrig.

\[ \mu = 8080 T^{-3/2} \exp\left(-\frac{0.021eV}{kT}\right) \frac{cm^2}{V \cdot s} \]  
\[ \text{Equation (10.16)} \]

Using 300 K for the temperature results in a mobility of 0.69.

Inserting the mobility, effective electron charge, and carrier density into 10.15 gives a conductivity of barium titanate at room temperature to be \( \sim 3.6 \times 10^{-5} (\Omega \cdot \text{cm})^{-1} \).

### 10.3 Temperature Dependent Measurements

Figure 10.1 shows a schematic of the modified MMR Technologies Inc. cold stage with the 10” bell jar and Quater Research manipulators that allow for temperature dependent measurements of the dielectric properties.
Figure 10.1: Schematic of the temperature dependent measurement apparatus used in this thesis.