Processing—Structure—Property Interrelationships
of Ferroelectric Thin Films with Emphasis on Formation Kinetics

by

Chi Kong Kwok

Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

in
Materials Engineering Science

APPROVED:

S. B. Desu, Chairman

R. S. Gordon

R. W. Hendricks

Aicha Elshabini-Riad

W. T. Reynolds, Jr.

July, 1992

Blacksburg, Virginia
Processing–Structure–Property Interrelationships

of Ferroelectric Thin Films with Emphasis on Formation Kinetics

by

Chi Kong Kwok

S. B. Desu, Chairman

Materials Engineering Science

(ABSTRACT)

Lead zirconate titanate (PZT) is a ferroelectric material which has many interesting properties. Recently, PZT thin films have been considered as one of the most promising materials for the application of nonvolatile electronic memories. In this study, a sol–gel process for PZT film preparation was adopted and greatly modified. PZT films with very desirable electrical properties have been successfully prepared by this modified sol–gel process.

One of the problems of incorporating PZT films into the DRAM devices is the need of high post–deposition annealing temperatures which complicates their integration into the existing semiconductor manufacturing process. In this work, formation kinetics of PZT films were studied and the nucleation was found to be the rate–limiting step in the formation of the perovskite phase. Based on this finding, a seeding process was invented to encourage the nucleation of the perovskite phase. As a result of this seeding process, the transformation temperature has been lowered by as much as 100°C. The seeded PZT films also have good ferroelectric properties.

The ferroelectric domain structures, and the metastable pyrochlore phase including its transformation to the perovskite phase have been investigated by
transmission electron microscopy (TEM). The domain structures of the PZT films had the \( \{110\} <110> \) orientation and most of them were \( 90^\circ \) domains. The TEM study of the pyrochlore to perovskite transformation provides valuable insight on the formation of the perovskite phase.

Among all the processing steps, the drying process of the sol–gel films created the highest growth stress. In addition, the thin film stress study was also used to determine the transformation stress and Curie temperature.

The effects of composition, thermal processing conditions, and film thickness on electrical properties have been studied. Some of the notable results are as follows:

1. PZT films with a Zr/Ti ratio of 53/47, the morphotropic boundary (MPB) composition, have the highest remanent polarization and the lowest coercive field.

2. The optimum annealing temperatures for most of the PZT compositions are found to be about 50°C higher than the completion temperature of the perovskite formation (\( T_{C,\text{per}} \)) of the same composition.

3. PZT films with film thicknesses greater than or equal to 170 nm have electrical properties very close to those of the thicker films and are not susceptible to dielectric breakdown at an applied voltage of 5 V.
Dedication

To my parents

Kam Tong Kwok
and
Lai Kuen Leung
Acknowledgements

I wish to thank my thesis advisor Dr. Seshu B. Desu for the freedom he gave me to venture into different aspects of thin film research, and for the invaluable guidance and support throughout the course of this study. I also appreciate Dr. Desu's enthusiasm in the fundamental understanding of the research problems and his resourcefulness in helping to solve them.

Appreciation is also expressed to Drs. Ronald Gordon, Robert Hendricks, Achia Elshabini-Riad, and William Reynolds, Jr. for their suggestions and reviewing this dissertation. Much indebtedness are due to Dr. Reynolds for providing very helpful suggestions in the area of formation kinetics.

Thanks are due to all members of the thin film laboratory in Virginia Tech for their friendship and enlightening discussions.

Finally, I wish to extend my deepest debt of gratitude to my parents for their love and support, and to a special friend, Mable, for her love, understanding and encouragement.

This research was funded in part by DARPA and Ceram, Inc.
Table of Contents

Chapter 1. Introduction.................................................................1
  1.1 Ferroelectric Memories.........................................................1
  1.2 Ferroelectric Materials.......................................................7
  1.3 Purpose of Research..........................................................12
    1.3.1 Objectives of Research..................................................13

Chapter 2. Preparation Methods..................................................14
  2.1 Introduction.............................................................................14
  2.2 Sol–Gel Processing...............................................................17
  2.3 Sol–Gel Processing of PZT Thin Films......................................19
    2.3.1 Selection of Precursors..................................................21
    2.3.2 Selection of Solvent......................................................26
    2.3.3 Chemical Modification by Carboxylic Acid..........................26
    2.3.4 Film Formation, Drying and Annealing..............................28
      2.3.4.1 The Effect of Molar Concentration and Spin Speed...........28
      2.3.4.2 The Effect of Drying Temperature...............................32
      2.3.4.3 The Effect of Heating Rate and Thermal
        Processing Conditions..................................................34

Chapter 3. Transmission Electron Microscopy Study of PZT Thin Films.........39
  3.1 Background..............................................................................39
  3.2 Domain Structures of PZT Thin Films.....................................42
    3.2.1 Experimental Procedures.................................................42
3.2.2 TEM of Domain Structures ................................................. 43

3.3 Microanalysis of The Grain Boundary Phases .......................... 48

3.4 TEM Study of The Pyrochlore–Perovskite Transformation ....... 52
   3.4.1 TEM Study of The Metastable Pyrochlore Phase ............... 54

3.5 Summary ............................................................................. 63

Chapter 4. Formation Kinetics of PZT Thin Films ....................... 64

4.1 Introduction ......................................................................... 64

4.2 Formation Kinetics of PZT Films ........................................ 65
   4.2.1 Kinetic Study of PZT Films ........................................ 68
   4.2.2 Experimental Procedures ........................................... 69
   4.2.3 Kinetics Studies ......................................................... 69
   4.2.4 X–ray Diffraction Analysis ......................................... 82
   4.2.5 Summary ....................................................................... 82

4.3 Low Temperature Processing .............................................. 84
   4.3.1 High Pressure Transformation .................................... 84
   4.3.2 Experimental Procedures ........................................... 86
   4.3.3 High Pressure Perovskite Formation ........................... 86
   4.3.4 Seeding Process ......................................................... 88
      4.3.4.1 Experimental Procedures ...................................... 89
      4.3.4.2 Low Temperature Transformation by Seeding ........ 91
      4.3.4.3 Electrical Properties of Seeded PZT Films ............ 102
      4.3.4.4 Summary ............................................................ 103
Chapter 5. Stress in PZT Thin Films ................................................................. 104

5.1 Introduction ............................................................................................ 104

5.1.1 Origins of Stress in Thin Films ......................................................... 105

5.1.2 Methods of Stress Measurement ...................................................... 107

5.2 Curvature Method, Assumptions and Limitations ................................. 108

5.3 Stress in PZT Films .............................................................................. 114

5.3.1 Experimental Procedures ................................................................. 115

5.3.2 The Study of Transformation Stress of PZT Films ......................... 117

Chapter 6. Electric Properties of PZT Thin Films ..................................... 132

6.1 Introduction ............................................................................................ 132

6.2 Electrical Property Measurements ....................................................... 136

6.2.1 Sample Preparation for Electrical Measurements ....................... 136

6.2.2 Hysteresis Measurement ................................................................. 140

6.3 The Effect of Composition and Thermal Processing Conditions ......... 144

6.3.1 The Effect of Applied Voltage ......................................................... 144

6.3.2 The Effect of Excess Lead Concentration ....................................... 144

6.3.3 The Effect of Composition .............................................................. 148

6.3.4 The Effect of Annealing Temperature ............................................ 160

6.4 The Effect of Film Thickness ............................................................... 168

Chapter 7. Conclusions and Recommendations ....................................... 176

Appendix A. Sol–Gel Processing of PZT Films: Experimental Procedures .... 180
Appendix B. Experimental Procedures for Film Stress Measurements..............183

Appendix C. Basic Operation of The Hysteresis Measurement.........................187

Bibliography........................................................................................................188

Vita..................................................................................................................200
List of Figures

Figure 1.1 Hysteresis loop of a ferroelectric material........................................3
Figure 1.2 Proposed ferroelectric memory device configuration.........................6
Figure 1.3 PZT perovskite unit cell.................................................................8
Figure 1.4 Phase diagram of lead zirconate titanate..........................................11

Figure 2.1 (a) Flow diagram of the original sol–gel process.............................22
Figure 2.1 (b) Flow diagram of the modified sol–gel process............................23
Figure 2.2 Variation of film thickness with molar concentration.........................30
Figure 2.3 Variation of film thickness with spin speed....................................31
Figure 2.4 TGA of PZT precursor..................................................................33
Figure 2.5 Hysteresis loops of PZT films annealed at different oxygen partial pressure.................................................................36
Figure 2.6 AES depth profile of lead concentration of PZT films
annealed at different P_{02}..................................................................................37

Figure 3.1 Transmission electron micrographs of PZT films (a) pyrochlore
phase, 500°C/1 hr. (b) perovskite phase, 700°C/1.5 hr.................................44
Figure 3.2 (a) Bright field (b) dark field micrographs and (c) SAD of the
domain structure which the dark field shows the orientation of
one variant of twinning.................................................................46
Figure 3.3 (a) Bright field (b) dark field micrograph (c) bright field
similar to (a) but intentionally tilt off the [110] zone axis
and (d) SAD showing the [110] zone axis.............................................47
Figure 3.4 (a) STEM micrograph showing the grain boundary and the thin
area along the grain boundary and (b) lead concentration as
a function of the distance from the grain boundary...............................50
Figure 3.5  XRD of PZT films on sapphire and annealed at (a) 450°C (b) 550°C (c) 600°C (d) 650°C for 15 min. in air........................................53

Figure 3.6  (a) Bright field (b) dark field and (c) SAD of the pyrochlore phase showing very fine grain structure........................................57

Figure 3.7  TEM micrographs of the perovskite particles growing on the pyrochlore phase. (a) bright field (b) perovskite diffraction pattern and (c) pyrochlore diffraction pattern..........................58

Figure 3.8  The microstructural development of the PZT film as a function of annealing temperature........................................60

Figure 4.1  SEM micrographs of PZT film annealed at 550°C for 10 min., (a) secondary electron imaging, (b) backscattered electron imaging. Arrows on both micrographs show the outline of the same feature........................................70

Figure 4.2  The linear dimension of the growing phase as a function of annealing time at different temperatures........................................73

Figure 4.3  SEM micrographs of PZT films annealed at 525°C for (a) 10 min. (b) 25 min. and (c) 45 min........................................77

Figure 4.4  The nucleation rate as a function of annealing time at different temperatures........................................78

Figure 4.5  Avrami plot of volume fraction (ln ln {1/1−X}) as a function of the natural logarithm of annealing times........................................80

Figure 4.6  An Arrhenius plot of reaction constant as a function as a function of the reciprocal of temperature........................................81

Figure 4.7  XRD of the PZT films annealed at 550°C for (a) 2 min. (b) 6 min. and (c) 15 min........................................83

Figure 4.8  XRD of the PZT films annealed at (a) atmospheric pressure and (b) at a pressure of 100 bar........................................87

Figure 4.9  XRD of unseeded 53/47 PZT film annealed at (a) 500°C (b) 550°C (c) 650°C for 15 min. The symbols PE and PY indicate perovskite phase and pyrochlore phase, respectively........92

Figure 4.10 Initial and complete perovskite transformation temperatures as a function of Zr and Ti composition in the PbZrO₃−PbTiO₃ solid solution........................................93

Figure 4.11 Grain size of the perovskite phase as a function of Ti atomic concentration........................................94

-xi-
Figure 4.12  Microstructure of the perovskite phase as a function of compositions.................................................................96

Figure 4.13  XRD of the seeded 53/47 PZT films annealed at (a) 500°C (b) 525°C and (c) 550°C for 15 min.........................................................98

Figure 4.14  XRD of the seeded 53/47 PZT films annealed at 500°C for (a) 15 min. (b) 30 min. and (c) 1 hr.........................................................99

Figure 4.15  Microstructure of (a) unseeded PbTiO₃ film annealed at 650°C (b) unseeded 53/47 film annealed at 650°C and (c) seeded 53/47 film annealed at 650°C.................................................................101

Figure 5.1  Correlation Fatcor (M) at a function of thickness ratio at different elastic constant ratio E₇/E₈ of (a) 0.1 (b) 1 and (c) 10...............................................................111

Figure 5.2  Schematic diagrams of anticipated stress-temperature (S-T) plot..................................................................................112

Figure 5.3  (a) 1st run S-T plot of Pt substrate without film deposition.....119

Figure 5.3  (b) 2nd run S-T plot of Pt substrate.................................................120

Figure 5.4  (a) 1st run S-T plot of PbTiO₃ film..............................................122

Figure 5.4  (b) 2nd run S-T plot of PbTiO₃ film.............................................123

Figure 5.5  (a) 1st run S-T plot of 53/47 PZT film........................................124

Figure 5.5  (b) 2nd run S-T plot of 53/47 PZT film......................................125

Figure 5.6  (a) 1st run S-T plot of 75/25 PZT film........................................126

Figure 5.6  (b) 2nd run S-T plot of 75/25 PZT film......................................127

Figure 6.1  Cross-section of the test capacitor..................................................137

Figure 6.2  Schematic diagram of Sawyer-Tower circuit.................................138

Figure 6.3  A typical hysteresis loop of the PZT film.......................................139

Figure 6.4  Block diagram of the RT66A tester..............................................141

Figure 6.5  Polarization as a function of applied voltage............................142

Figure 6.6  Coercive field as a function of applied voltage...........................143

Figure 6.7  Polarization as a function of excess lead concentration.............146
Figure 6.8  Coercive field as a function of excess lead concentration............147
Figure 6.9  Variation of polarization with composition, 600°C annealing temperature.................................................................150
Figure 6.10 Variation of polarization with composition, 650°C annealing temperature.................................................................151
Figure 6.11 Variation of Coercive field with composition, 600°C annealing temperature.................................................................153
Figure 6.12 Variation of Coercive field with composition, 650°C annealing temperature.................................................................154
Figure 6.13 Comparison of two hysteresis loops, well-defined loop from the perovskite phase, near-linear loop from the pyrochlore phase.................................................................156
Figure 6.14 Capacitance–voltage (C–V) plot of a good PZT capacitor........157
Figure 6.15 Variation of dielectric constant with frequency......................158
Figure 6.16 Leakage current of PZT films of different compositions...........159
Figure 6.17 Polarization of PbTiO₃ film as a function of annealing temperature..................................................................................162
Figure 6.18 Polarization of 30/70 PZT film as a function of annealing temperature..................................................................................163
Figure 6.19 Polarization of 40/60 PZT film as a function of annealing temperature..................................................................................164
Figure 6.20 Polarization of 53/47 PZT film as a function of annealing temperature..................................................................................165
Figure 6.21 Polarization of 65/35 PZT film as a function of annealing temperature..................................................................................166
Figure 6.22 Polarization of 75/25 PZT film as a function of annealing temperature..................................................................................167
Figure 6.23 Polarization as a function of film thickness..............................169
Figure 6.24 Coercive field as a function of film thickness............................170
Figure 6.25 Log–log plot of coercive field as function of film thickness.........174
List of Tables

Table 1.1  The comparisons of 3 different types of electronic memories..............5
Table 2.1  Selected properties of lead, zirconium and titanium precursors.........25
Table 3.1  The peak positions and peak intensities of the perovskite and
            the pyrochlore phase.................................................................59
Table 4.1  Volume fractions obtained from experiments and from
            theoretical calculations...................................................................76
Table 4.2  Electrical properties of seeded and unseeded PZT films...............103
Table 5.1  Mechanical stress and Curie Temperature as a function
            of composition...............................................................................130
Table 6.1  Comparisons of electrical properties of PZT thin films.................152
Chapter 1. Introduction

In the first section of this chapter, the current status of electronic memories and how ferroelectric thin films can radically impact this technology are discussed in the first section. The selection of ferroelectric materials is discussed in the second section and the basic background information of the ferroelectric materials is also introduced. In the third section, problems associated with the processing of ferroelectric thin films are assessed. Finally, the objectives of this dissertation will be outlined in the last section.

1.1 FERROELECTRIC MEMORIES

The DRAM (dynamic random access memory) is one of the critical memory components that is in use in all types of computers today. Continuing efforts have been made to increase both the switching speed and the memory density, while decreasing the cost of these DRAM devices. Each generation of DRAM production, for example, from 16 kbit in 1980 to 1 Mbit in 1988, only spans an average of three years [1].

With the increasing desire to pack more capacitor cells in the same die size, the use of SiO₂ (dielectric constant around 4.0) as a dielectric layer becomes impractical. For instance, for a 1 Mbit device, the dielectric layer has to be smaller
than 6 nm; for the higher capacity memories, the dielectric thickness is so thin that process control becomes extremely difficult and electron tunneling becomes a major concern. The three dimensional capacitor designs such as using a 'stack' capacitors or 'trench' capacitors, which undoubtedly will make the processing uncomfortably complex, and thus not be able to satisfy the 256 Mbit DRAM requirements [2]. This prospect has revived and intensified the search for appropriate dielectric materials with substantially higher dielectric constants. Also, their physical properties and processing has to be compatible with current ULSI circuit fabrication.

The logical choice for the new dielectric is the ferroelectric—based material since some of the commonly used ferroelectrics have dielectric constants at least two orders of magnitude higher than that of SiO₂. In addition to their high dielectric constant, more importantly, the characteristic polarization response of the ferroelectrics to an electric field makes it a perfect candidate to use as a nonvolatile memory device. On the contrary, DRAM is volatile and needs to be recharged by a refresh circuitry hundreds of times every second. Stored information in the DRAM is lost when the power is turned off.

A basic characteristic of all ferroelectric materials is their hysteretic behavior relating polarization, \( P \), and electric field, \( E \), as shown in Figure 1.1. There is a threshold electric field, \( E_c \), above which the polarization switches. However, the polarization at zero applied field (remanent polarization, \( P_r \)) is stable and no applied field is required to maintain the stored charge. Hence, ferroelectric materials can be modeled as bistable capacitors with two distinct polarization values and thus can be used as a true nonvolatile electronic memory.
Memory applications

Figure 1.1  Hysteresis loop of a ferroelectric material
Electrical Erasable Programmable Read Only Memories (EEPROM) and flash memories are the two common nonvolatile memory devices available in the market today. But strictly speaking, the EEPROM and flash memory are "read–mostly" memories because of their very slow write/erase speed and very limited number of write/erase cycles before these memory elements fail. A comparison of DRAM, EEPROM, flash memory and ferroelectric memory (FRAM) is given in Table 1.1.

The distinct advantages of FRAM over other nonvolatile memories are: (1) fast write and erase access times on the order of nanoseconds, (2) low operating voltage, 5 V or less can be used compared with 12–15 V for the other nonvolatile memory devices, (3) long write/erase lifetime (10⁶ times higher than the EEPROM and flash memories), (4) wide operating temperature range (−180°C to 350°C), and (5) high radiation hardness which is very attractive to military and space applications.

Furthermore, ferroelectric films can be built directly over or merged into active devices as shown in Figure 1.2. Also, the ferroelectric films, electrodes and passivation layers can be deposited in separated small facilities; thus any possible contamination of Si production lines by metal ions from the ferroelectric materials is eliminated. From the standpoint of ULSI production, the insertion of ferroelectric materials into the existing devices is less complicated and more cost effective than developing a completely new processing scheme.

In principle, FRAM could eventually replace the SRAM in cache memory, DRAM in the main system memory and EEPROM in the lookup tables. If the cost of FRAM can be reduced to the level comparable to magnetic storage, it could most certainly replace the hard disk as the mass storage devices since FRAM has much faster access speed and does not have mechanical wear problems.
Table 1.1 The comparison of 3 different electronic memories

<table>
<thead>
<tr>
<th></th>
<th>FRAM</th>
<th>EEPROM</th>
<th>DRAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Write/erase voltage</td>
<td>5</td>
<td>16</td>
<td>5</td>
</tr>
<tr>
<td>Typ. Access time (nsec)</td>
<td>100</td>
<td>110</td>
<td>1000</td>
</tr>
<tr>
<td>Write Speed (usec/byte)</td>
<td>.2</td>
<td>2000</td>
<td>1</td>
</tr>
<tr>
<td>Erase Speed (usec/byte)</td>
<td>0.1</td>
<td>2000</td>
<td>10</td>
</tr>
<tr>
<td>Max write/erase cycle</td>
<td>$10^{12}$</td>
<td>$10^4$</td>
<td>inf.</td>
</tr>
<tr>
<td>Radiation Tolerance (Rad)</td>
<td>$10^8$</td>
<td>$10^5$</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 1.2  Proposed ferroelectric memory device configuration
In summary, if ferroelectric materials can be successfully incorporated into the existing ULSI technology, they have the potential of replacing most of the memory elements found in the computer today. In fact, in addition to the computer applications, any application that requires inexpensive and nonvolatile memory can be benefited from the FRAM technology. Such examples include the memory chip in automobiles, kitchen and household appliances, mobile phones, and laptop/palmtop computers.

1.2 FERROELECTRIC MATERIALS

The characteristics of ferroelectric materials are generally defined by their reversible spontaneous polarization $P_s$ in the absence of an applied electric field [3]. This spontaneous polarization arises from a noncentrosymmetric arrangement of ions in the unit cell which produces an electric dipole moment associated with the distorted unit cell. Adjacent unit cells tend to deform in the same direction and form a region called a ferroelectric domain. In polycrystalline ferroelectrics, multiple domain formation is commonly found in single grains. The most common ferroelectrics have the $ABO_3$ perovskite structure as shown in Figure 1.3. At temperatures above the Curie temperature, the material has centrosymmetric structure and thus does not have $P_s$. As the temperature is lowered through the Curie temperature (for instances, 120°C for BaTiO$_3$ and about 350°C for PbTiO$_3$), the center $B$ ion is displaced from its body-centered position. The cubic unit cell deforms and becomes one of the noncentrosymmetric structures such as the tetragonal, rhombohedral or monoclinic structure.
Figure 1.3  PZT perovskite unit cell
When an electric field with increasing field strength is applied to the ferroelectric, domains orient favorably with respect to the field direction grow in size at the expense of the other domains. Also, some of the domains reorient along the direction of the applied field. This will continue until all of the domain growth and reorientation have occurred. At this stage, the material has reached saturation polarization $P_{\text{sat}}$. If the electric field is then removed, some of the domains do not return to their random configurations and orientations. The polarization at this stage is called remanent polarization $P_r$. Figure 1.1 shows the characteristic hysteresis behavior between the polarization and the electric field.

To fully utilize these ferroelectric properties for memory applications, the materials chosen must not only have excellent figures of merit, but also have to satisfy the very stringent ULSI fabrication requirements. For example, potassium, sodium or cadmium—containing materials would not be a good choice because of their highly contaminating nature and/or high toxicity. Some of the major requirements for good ferroelectric candidates for the 64 Mbit DRAMs are suggested by Parker and Tasch [4] and are listed as follows:

1. The lower limit of charge capacity, which is governed by the soft error threshold, should be from 5–10 $\mu$C/cm$^2$.
2. Desirable dielectric constant around 1000 or higher.
3. Leakage current smaller than 0.1–0.5 pA.
4. Fatigue cycles up to $10^{12}$ cycles, the ideal lifetime is $10^{15}$ cycles.
5. Wide operating temperature range: $-55^\circ\text{C}$ to $120^\circ\text{C}$.
6. Compatible to ULSI fabrication operations.
7. A large knowledge base, so some of the thin film properties can be inferred from their bulk ceramic values.
This list is far from comprehensive but can be used as a guideline for the search of an optimum candidate. Triglycerine sulphate (TGS) and KNO₃ are some of earlier ferroelectric materials which have been studied, but they are very unstable in the presence of moisture. The perovskite titanate and niobate families have been studied since the 1950s. BaTiO₃ and PbZrₓTi₁₋ₓO₃ (PZT), in particular, have been studied extensively because of their excellent piezoelectric and dielectric properties. BaTiO₃ has 4 phase transitions: cubic — tetragonal — orthorhombic — rhombohedral transitions at transition temperatures of 130°C, 0°C and −90°C, respectively.

On the contrary, PZT has only one transition. When x > 0.53, there is a cubic to rhombohedral transition with transition temperatures ranging from 370°C to 230°C depending on the composition. When x < 0.53, PZT transforms from cubic structure to tetragonal structure at temperature ranged from 370°C to 490°C. These phase transition of the PZT material can be found in the phase diagram as shown in Figure 1.4 [5]. It is imperative for the ferroelectric memory to have a wide range of operating temperatures within which the electrical properties are relatively consistent, and in this respect, the PZT is superior to BaTiO₃.

In short, PZT has a combination of good ferroelectric properties, a large knowledge base, a wide operating temperature range and stability in a wide range of ambient conditions; hence, it is one of the promising materials for ferroelectric memory applications.
Figure 1.4  Phase diagram of lead zirconate titanate [5]
1.3 PURPOSE OF RESEARCH

In the previous sections, the need for and the advantages of ferroelectric memories were described and the most promising material for such a FRAM device has been identified. However, progress in preparing these PZT films has been slow. Persistent problems associated with film preparation via a chemical route, include film cracking, nonuniform microstructure and poor electrical properties. These processing issues have to be addressed and a systematic approach to tackle these problems can be found in Section 2.3.

The behavior and properties of ferroelectric films can be quite different from those of bulk ferroelectric ceramics. Metastable phase formation and transformation kinetics of these thin films are very much different from their ceramic counterparts. But, until now, very little work has been done on both the study of phase transformation and transformation kinetics in these ferroelectric films. The study of transformation kinetics does not only serve academic interest, but more importantly, can be used to improve the processing of the ferroelectric films. One critical problem with the incorporation of ferroelectric films to the ULSI process is the high annealing temperature required to transform the non–ferroelectric phase to the ferroelectric perovskite phase. By understanding the transformation kinetics of these films, we can modify the thin film process to produce PZT films at temperatures compatible to the ULSI processing. Chapters 3 and 4 are devoted to investigating the phase transformations in perovskite film formation.

The kinetics of transformation and electrical properties of the ferroelectric films can be greatly influenced by the mechanical stress which is present in the films.
The origins of these mechanical stresses are the combination of intrinsic stress during and after film growth, extrinsic stress due to phase transformation, and thermal stress due to temperature change. The intention of Chapter 5 is to investigate the thin film stress in the PZT films.

Although extensive information regarding electrical properties exist for bulk ferroelectric materials, very limited data exist for thin films less than 1 \( \mu \text{m} \). Ferroelectric properties, breakdown field and leakage current, which are very important in the design of ferroelectric memories, are not readily available. Also, there is little understanding regarding the dependence of electrical properties on film thickness, composition and processing parameters. Chapter 6 presents results of electrical properties which address some of the above issues.

1.3.1 Objectives of Research

The purpose of this research, can be summarized as follows:

1. To optimize the fabrication of PZT thin films using a modified sol–gel process.

2. To understand the transformation and kinetics of the PZT perovskite phase.

3. To devise processing procedures for low temperature formation of the PZT films based on the understanding of the transformation kinetics.

4. To determine and study the mechanical stress present in the PZT films.

5. To understand the effect of process parameters on the electrical properties of the PZT thin film devices.
Chapter 2. Preparation methods

This chapter will be divided into three sections. The first section is an overall comparison of the common PZT thin film deposition techniques. A detailed description of the sol–gel process is given in section 2.2. Section 2.3 discusses the sol–gel process of PZT thin films, the problems associated with precursor and film preparation at the start of this study and the modification required to improve the sol–gel process.

2.1 INTRODUCTION

A wide variety of preparation techniques have been employed to produce PZT thin films. Sputtering, sol–gel, chemical vapor deposition (CVD), electron–beam evaporation, and laser ablation are some of the techniques used [6–20]. The choice of an appropriate preparation technique depends on the final applications of these ferroelectric films. In our work, the objective is to incorporate the PZT films into the existing electronic memory fabrication process. The requirements for a compatible process are very stringent and some of the major requirements are:

1. Strict control of stoichiometry.

2. Uniform deposition over a large area (diameter around 100 mm –200 mm).
3. High deposition rate, high throughput.

4. Low setup cost.

There are pros and cons for all the above mentioned processes used for producing PZT films. Vacuum and electron beam evaporation provide high deposition rates and relatively uniform films but control of stoichiometry of multi-component films is difficult because of the different vapor pressures from the different source materials. The other problem of the evaporation technique is the undesirable interactions between the deposited films and the substrate of interest, for example, silicon substrates and platinum coated silicon substrates.

Laser ablation is a newly developed thin film deposition technique and has found some success in depositing high temperature superconducting films. There are only a few reported works on laser deposition of PZT films [20–22]. The major drawbacks of this technique are the nonuniformity of the deposited films and the limited ability to scale up the process for industrial applications.

Sputtering, CVD, and sol–gel are three of the most promising deposition techniques which are capable of producing good quality ferroelectric films and can be modified and scaled up to industrial applications. Two types of sputtering can be used for oxide film deposition; one is reactive sputtering where metal targets are sputtered in the presence of oxygen gas, and the other is radio frequency (RF) sputtering of an appropriate oxide target. Nonetheless, there are problems associated with the reactive sputtering of complex oxide film such as the PZT films. Different sputtering yields from different metal targets and the oxidation of the metal targets are some of the problems that discourage the use of reactive sputtering. Sputtering of an oxide target avoids these problems. However, in order
to implement sputtering into large scale productions, some of the technical problems still have to be solved. They are:

(1) inflexibility to modify or change the stoichiometry of the deposited film (since one target can only produce one film composition and the PZT targets are very expensive to manufacture).

(2) inherently slow deposition rates.

(3) a gradually changing target composition over a period of time due to preferred sputtering.

(4) step coverage over small steps is not good since sputtering is a line-of-sight deposition process.

Because of these disadvantages, further improvements in sputtering are needed before it can be adopted by the semiconductor industry for the large scale complex oxide deposition.

Chemical vapor deposition (CVD) has many advantages which include very good uniformity over large areas, good control of stoichiometry, easy accommodation of extra dopant deposition and excellent step coverage. Step coverage is a very important issue in Ultra Large Scale Integrated—circuits (ULSI) applications. As the linewidth of individual devices decreases to submicron level, a uniform thin film coverage by physical vapor deposition (PVD) or spin coating deposition becomes difficult. Hence, in the ULSI applications, CVD should be considered as the most favorable thin film deposition process.

Nevertheless, CVD for multi—component oxides is a very complex process. The selection of precursors is very critical. The criteria for precursors are not only that
each precursor should decompose and form good quality films of its oxide component but also that each must react and form the final complex oxide at the same deposition temperature and same total pressure. Process parameters such as bubbler temperature and carrier gas flow rate of precursors, total pressure, and deposition temperature have to be optimized to obtain good quality films with the desired composition and uniformity. So far, there are only a few reports of successful fabrication of PZT films by CVD [15,16,23,24]. More efforts on the CVD of ferroelectric films are needed before this process can be put into large scale production.

2.2 SOL–GEL PROCESSING

The sol–gel process is a method of preparing inorganic materials via chemical routes. This process involves the following steps: (1) precursor (sol) formation, (2) hydrolysis, (3) polycondensation, (4) film or gel formation, and (5) sintering.

The initial stage of the sol–gel process involves preparation of a solution of the oxide materials of interest. A variety of materials can be used to prepare the precursor solution. Metal alkoxides, symbolized M(OR)_x where R is an alkyl group, are very suitable components for sol gel preparation and have been widely used in SiO_2 and Si–containing glass depositions [25]. Film formation from metal alkoxides (M(OR)_x) is a two step process. The metal alkoxide is first hydrolyzed to form monomers as shown below:

\[ M(OR)_x + H_2O \rightarrow M(OR)_{x-1}(OH) + ROH \] (2.1)
These monomers can be subsequently polymerized to form three-dimensional networks through the two reactions as shown below:

\[ 2M(OR)_{x-1}(OH) \rightarrow (OR)_{x-1}M-O-M(OR)_{x-1} + H_2O \quad (2.2) \]

and

\[ M(OR)_{x-1}(OH) + M(OR)_x \rightarrow (OR)_{x-1}M-O-M(OR)_{x-1} + ROH \quad (2.3) \]

Polycondensation reactions (2.2) and (2.3) produce the expected M-O-M networks but also produce water and alcohol as by-products. At this stage, the sol precursor is ready for film deposition. Dipping, spraying or spinning are some of the common methods for thin film deposition using sol-gel process.

After film deposition, in most cases, annealing or sintering is needed to remove the alcohol, water and volatile organics in the film and transform an amorphous as-deposited film to a crystalline structure.

The advantages of sol-gel process are:

1. molecular homogeneity.
2. high deposition rate and high throughput.
3. excellent composition control.
4. easy introduction of dopants.
5. deposition can be done in ambient condition, no vacuum processing is needed, low capital cost.
6. materials can be produced in a variety of forms such as very fine powders, thin films, monoliths and fibers.
And some of the disadvantages of the sol–gel process are:

1. Excessive shrinkage during film formation and may lead to crackings.
2. Limited selection of some of the precursor materials.
3. The high cost of some of the precursor materials.

In addition to the advantages of sol–gel processing mentioned previously, transformation mechanisms and structure–property relationships can be thoroughly explored because of the short processing cycles and consistent results.

2.3 SOL–GEL PROCESSING OF LEAD ZIRCONATE TITANATE THIN FILMS

The sol–gel method for ferroelectric films is a recent development; PZT film deposition by this chemical method was first reported by Fukushima et al. in 1984 [26]. Fukushima formed 50/50 PZT films from a precursor composed of lead 2-ethylhexanoate, zirconium acetyl–acetonate, titanium tetrabutoxide, and butanol. A dielectric constant of 300, $P_s$ of 36μC/cm$^2$, and $E_c$ of 45 kV/cm were reported for 2 μm films on Pt–coated Si substrates. Blum and Gurkovich (1985) fabricated PbTiO$_3$ monolithic gels from a precursor consisting of lead acetate and titanium isopropanoxide dissolved in methoxyethanol (C$_3$H$_8$O$_2$) [27]. The crystallization temperature was observed to be 470°C but no electrical properties were reported. Lead 2-ethylhexanoate, zirconium n–propanoxide, and titanium n–butoxide and isopropanol were used by Lipeles and Coleman (1986) to form 50/50 PZT films. They used Fourier transform infrared spectroscopy (FTIR) to study the consolidation of PZT films at 275°C and 400°C and found that even at 400°C, ethylhexanoate was not completely removed from the films. The dielectric
constant, $P_r$, and $E_c$ were found to be 500, 12 $\mu$C/cm$^2$, and 60 kV/cm, respectively [28]. K. Budd et al. studied PbTiO$_3$, PZT and PLZT and reported that the tendency of film cracking and the crystallization temperature can both be related to the water concentration and the type of substrate used [29]. A new approach by Yi, Wu and Sayer to form PZT films which used acetic acid as an stabilizing agent in the precursors of lead acetate, Ti isopropoxide and Zr n-propoxide. The purpose of the acetic acid addition was to stabilize the precursors. Film cracking was observed in some conditions; $P_r$ ranged from 1–7 $\mu$C/cm$^2$, and $E_c$ was between 26–80 kV/cm.

In summary, little work has been done in the sol–gel processing of PZT thin films and most of the works I have cited above have some common problems. They are: (1) nonuniform morphology and microstructure, (2) film cracking (3) short shelf life resulting in premature precipitation and gelation and (4) relatively poor electrical properties. In order to remedy these shortcomings and to improve upon the electrical properties of the PZT films, a systematic study of the whole process is needed. Processing parameters such as precursors, stabilizing agents, hydrolysis water concentration, heating rate, drying and annealing temperatures and many other factors have to be investigated. The final goals of the study of the sol–gel processing are:

(1) to understand how a precursor solution can be prepared such that it is stable in ambient conditions during preparation and has a long shelf life (2–3 months).

(2) to understand how to produce consistent microstructure and good electrical properties.
At the start of the study, the procedures suggested by Yi, Wu and Sayer were adopted, and these sol–gel procedures are shown as a flow diagram in Figure 2.1 (a). Many problems were encountered by following this procedure. They included frequent precipitation or gelation during sol preparation, sporadic shelf life (from a few hours to a few weeks), film cracking, nonuniform microstructure (second phase formation) and poor electrical properties. In order to solve these problems, major modification has to be made and each important process parameter has to be reconsidered. The modified preparation procedure is presented in Figure 2.1 (b). The key modification is the order of precursor mixing and the details of this modification are discussed below.

2.3.1 Selection of Precursors

The choice of precursors is dictated by many factors, which include: availability, cost, metal content, sensitivity to moisture, decomposition temperature, and reactivity. The availability of Pb, Zr and Ti metalorganic compounds is quite limited, and some of the commercially available precursors are listed in Table 2.1 for comparison. Metal content and reactivity is intimately related, and the proper choice would be a compound with high metal content and low reactivity. Precursors with high metal content and low organic content have less tendency to crack because less organics are being removed and thus, there is less volumetric shrinkage occurs during drying and annealing. In other words, thicker films can be deposited in each spinning; this becomes important when the film thickness becomes greater than several μm.
Flow chart for PZT film preparation by a Sol-gel process

Sayer's method

A: Pb acetate

B: Acetic acid

Dissolve A in B at 80°C
A:B = 2g:1mL

Add Zr n-propoxide

Add Ti isopropoxide

Mix in ultrasonic cleaner

Add water and ethylene glycol

Spin-coat at 8500 rpm, 20s

Prepare thicker film

Fire at 300°C - 500°C

Anneal at 600°C, 6 hr.

PZT film

Figure 2.1 (a) Flow diagram of the original sol-gel process
Flow chart for PZT film preparation by a Sol-gel process

Modified method

A: Pb acetate  B: Acetic acid  Tl isopropoxide  Zr n-propoxide

Dissolve A in B at 95°C  A:B = 2g:1mL  Mix in ultrasonic cleaner for 5 min.

Add acetic acid  Add n-propanol

Mix in ultrasonic cleaner

Add distilled water

Add acetic acid and n-propanol

Spin-coat at 1500 rpm, 30s

Dry at 150°C, 5 min.

Prepare thicker film  Anneal at 650°C, 15 min.

PZT film

Figure 2.1  (b) Flow diagram of the modified sol–gel process
On the other hand, precursors with high metal content usually are much more reactive and may be difficult to form a stable solution. For example, for the alkoxides with different alkyl groups, the reactivity usually increases in the order of methyl > ethyl > propyl > butyl > higher order alkyl groups [31]. Ti and Zr methoxides and ethoxides are very reactive and thus, are not suitable for sol preparation. Ti and Zr propoxides and butoxides are still quite reactive but some chemical modifications can be made to retard their reactivities and subsequently, they can be effectively used in sol preparation. This aspect of chemical modification will be discussed in Section 2.3.3. Pb alkoxides are generally very reactive and are not suitable for preparing precursors. Pb 2-ethylhexanoate has been used in some studies and shows some promise. Pb acetate is another metalorganic compound which has been gradually accepted for Pb precursor preparation. Pb acetate is compatible with the acetic acid modification since it readily dissolves in acetic acid at 85-90°C. Also, all the precursor components should have decomposition temperatures similar to each other which in each case should be less than the crystallization temperature. In the case of PZT, the decomposition temperature should be around 350°C or lower. Furthermore, since the cost of precursor (per 100 gram) can range from a few dollars to more than a thousand dollars, the cost at times may become a practical concern. In all, the selection of Pb acetate, Ti isopropoxide and Zr n-propoxide in this study is based on the aforementioned discussion, and later results have shown that this selection is a sound choice.
Table 2.1 Selected properties of lead, zirconium and titanium precursors

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Wt.% of M</th>
<th>m.p./b.p. (°C)</th>
<th>$/100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead acetate trihydrate Pb(C₂H₃O₂)₂·3H₂O</td>
<td>64</td>
<td>75/280</td>
<td>4</td>
</tr>
<tr>
<td>Lead acetylactonate Pb(C₆H₇O₂)₂</td>
<td>51</td>
<td>—</td>
<td>175</td>
</tr>
<tr>
<td>Lead 2-ethylhexanoate Pb(C₁₀H₁₇O₂)₂</td>
<td>24</td>
<td>—</td>
<td>4</td>
</tr>
<tr>
<td>Tetraphenyllead Pb(C₅H₅)₄</td>
<td>40</td>
<td>229/325</td>
<td>600</td>
</tr>
<tr>
<td>Bis 2,2,6,6-tetramethyl-3,5-heptanedionato lead</td>
<td>36</td>
<td>125/320</td>
<td>1200</td>
</tr>
<tr>
<td>Zirconium ethoxide Zr(O₂C₂H₅)₄</td>
<td>34</td>
<td>171/ —</td>
<td>275</td>
</tr>
<tr>
<td>Zirconium n-propoxide Zr(O₂C₃H₇)₄ in 30% propanol</td>
<td>28</td>
<td>—</td>
<td>9</td>
</tr>
<tr>
<td>Zirconium n-butoxide Zr(O₂C₄H₉)₄ in 20% butanol</td>
<td>24</td>
<td>—</td>
<td>5</td>
</tr>
<tr>
<td>Zirconium 2-ethylhexanoate Zr(C₁₀H₁₇O₂)₄ in 20% mineral spirit</td>
<td>13</td>
<td>—</td>
<td>10</td>
</tr>
<tr>
<td>Titanium ethoxide Ti(O₂C₂H₅)₄</td>
<td>21</td>
<td>122/ —</td>
<td>26</td>
</tr>
<tr>
<td>Titanium 2-ethylhexoxide Ti(C₆H₁₇O₂)₄</td>
<td>8.5</td>
<td>-25/194</td>
<td>5</td>
</tr>
<tr>
<td>Titanium isoproxide Ti(O₂C₃H₇)₄</td>
<td>17</td>
<td>20/58</td>
<td>4</td>
</tr>
<tr>
<td>Titanium n-butoxide Ti(O₂C₄H₉)₄</td>
<td>14</td>
<td>-55/312</td>
<td>4</td>
</tr>
</tbody>
</table>
2.3.2 Selection of Solvent

The selection of solvent is relatively straightforward. Alcohol is generally used as a solvent. In order to avoid alcoholysis, which can be shown by reaction (2.4), the parent alcohol should be used.

\[
M(OR)_n + xR'OH \leftrightarrow M(OR)_{n-x}(OR')_x + xROH
\]  \hspace{1cm} (2.4)

where \( R' \) = alkyl group or the group attached to hydroxyl in carboxylic acids [32]. Propanol, the parent alcohol of the Ti and Zr propoxides, is used as the solvent in our study.

2.3.3 Chemical Modification by Carboxylic Acid

Zr and Ti propoxides used in the precursor preparation are very reactive to water; precipitation starts to occur within a few minutes if they are exposed to moisture in the ambient condition. However, Doeuff et al. have shown that precipitation does not occur when acetic acid is added to the alkoxide prior to water, even in small amounts [33]. This result indicates that acetic acid can be used to slow down the hydrolysis of the alkoxides, and subsequently, results in a more homogeneous microstructure. When the ratio of acetic acid/titanium alkoxide (\([\text{Ac}]/[\text{Ti}]\)) increased from 0.3 to 7.5, the gelation time increased from 30 seconds to 4 months. For thin film deposition, the gelation time should be fairly long. The acetic acid reacts with the alkoxide to form \( M(OR)_x(\text{Ac})_y \) and the acetate anions can coordinate in one or more of the following modes:
Monodentate: \[ M-O-C-CH_3 \] (chelating I)

Bidentate: \[ M_2\{O\}_2C-CH_3 \] (chelating II)

Bidentate: \[ M_2\{O\}_2C\cdot CH_3 \] (bridging III)

Schwartz used FTIR to study this acetate reaction and found that most of the acetate groups are bridging in nature [34]. The chelating acetates are more difficult to hydrolyze than the OR group, thus, the addition of acetic acid to the PZT precursor stabilizes the precursor solution and encourages polycondensation. This, in turn, produces a more homogeneous microstructure.

The sequence of precursor mixing greatly affects the properties of the PZT films, and one of the major modifications of sol preparation in this work is to propose the proper sequence of precursor mixing. The original sol preparation procedures adopted from Sayer's method [30] require adding Zr alkoxide to Pb acetate in acetic acid solution; Ti alkoxide is then added to the mixed solution of Zr and Pb precursors. This mixing sequence produces an inhomogeneous microstructure and poor electrical properties. In general, for the multicomponent oxide system, a homogeneous microstructure can be obtained by controlling the reaction rates of the precursors. The basic principle is to slow down the reaction rate of the two most reactive components before adding the third less reactive component. In this case, the reaction rates of the two most reactive components are the Zr and the Ti alkoxides. Therefore, they should be mixed first in the presence of the chelating agent, namely acetic acid. Subsequently, the Pb acetate which dissolved in acetic acid is added to the Zr–Ti complex alkoxide solution.
The mixing of Zr and Ti alkoxides in acetic acid solution has demonstrably minimized the reaction between these two alkoxides and water, eliminating the precipitation due to their reactions with the moisture. The shelf life of this modified precursor solution has been extended to more than two months because of the proper sequence of precursor mixing used. Likewise, the electrical properties are vastly improved because of this modification. The discussion of the electrical properties of these PZT films is deferred until Chapter 7 where they will be discussed in more details.

2.3.4 Film Formation, Drying and Annealing

In order to prepare thin films from the precursor solution, the solution is deposited onto an appropriate substrate to form a wet film. This wet film is then dried and annealed to form the desired crystalline film. In the following sections, the processing variables such as (1) the molar concentration of the precursor solution, (2) the spin speed and the spinning time, (3) the drying temperature and time, (4) the heating rate of the annealing process, and (5) annealing time, temperature and annealing ambient condition, will be studied.

2.3.4.1 The Effect of Molar Concentration and Spin Speed

In this study, thin films are deposited by spin-coating. The film thickness is mainly controlled by the viscosity of the solution and the spin speed (in rpm). The viscosity of the solution is generally directly related to the molar concentration of the solution [35]. Figure 2.2 shows a linear relationship between the film thickness
and the molar concentration. The film thickness increases in proportion to the increase in molar concentration of the solution as expected.

Empirically, film cracking is directly related to the film thickness as well as the heating rate. Film cracking occurs when the thickness in a single spin is larger than a certain value but this thickness limit is substrate dependent. For the PZT system in this study, the two commonly used substrates are the platinum coated silicon wafers and single crystal sapphire wafers. The tendency of film cracking on these two substrates increases sharply when the molar concentration of the PZT solution is larger than 0.5 M; therefore, the molar concentration of most of the PZT solutions used in this study is 0.4 M. Thicker films, if needed, can be obtained by repeating the spin-dry cycle.

The film thickness can also be controlled by the spin speed; its relationship is shown in Figure 2.3. This relationship can be expressed in the following equation:

\[ t = k \omega^n \]  \hspace{1cm} (2.5)

where \( t \) is final film thickness, \( k \) is a constant dependent on the evaporation rate, the viscosity, the diffusivity and the molecular weight of the solvent; \( \omega \) is the spin speed, and \( n \) is the coefficient. By plotting Figure 2.3 in the form of a log-log plot, the coefficient \( n \) is found to be 0.72. From theoretical modeling of spin coating by Bornside et al. [35], the film thickness of a diluted solution depends inversely on the square root of the spin speed and thus, the coefficient \( n \) has a value of 0.5. The small discrepancy between the experimental result and the theoretical prediction can be attributed to the relatively concentrated solution used in these experiments.
Figure 2.2  Variation of film thickness with molar concentration
Figure 2.3  Variation of film thickness with spin speed
The spin coater used in these experiments has a spin speed ranging from 0 to 9500 rpm. Since spin speeds lower than 1500 rpm tend to produce nonuniform films, a spin speed of 1500 rpm was normally used in most of the experiments in this work, and a film thickness of about 200 nm can be obtained by a single coating. Thinner samples can be obtained by using a higher spin speed and/or a lower molar concentrations. Spin time is another parameter that can affect the film thickness. But in our experiments, equilibrium film thickness, which can be visually observed by the change of the film's interference color, can be obtained within 10 seconds. Therefore, a spin time of 30 seconds was used in all of the spin coating experiments.

2.3.4.2 The Effect of Drying Temperature

The requirement for the drying temperature is that it should be high enough to drive off the free alcohol, the volatile organics, and water from the film, but low enough to minimize the thermal gradient generated during drying. The boiling points for n-propanol, water, and acetic acid are 97°C, 100°C and 118°C, respectively. Thermal–gravimetric analysis (TGA) was used to study the weight change of the sol as a function of annealing temperature. The heating rate of this experiment was 10°C/min. and the experiment was performed in air. From the TGA result as shown in Figure 2.4, weight loss was observed at three different rates. Firstly, there was a very rapid weight decrease (72.3 weight % of the PZT precursor solution ) when the solution is heated from 30°C to 68°C, and this weight loss represents the evaporation of most of the alcohol, water, and acetic acid in the solution. There was another slower linear weight decrease occurring at temperatures from 68°C to 322°C, which showed another weight loss of 9.7 wt. %.
Figure 2.4 TGA of PZT precursor
This weight change can be attributed to the continual evaporation of the remaining alcohol, water, and acetic acid, and the removal of the ligands from the complex oxide networks. The last weight decrease was a very slow process which resulting in a very small weight loss of about 0.7 weight % at temperatures from 322°C to 525°C. This weight loss represents the removal of all of the ligands in the sample. Finally, when the sample was heated beyond 525°C, no weight change was observed, which indicated that all the easily decomposable species had been removed from the sample. No further weight change due to increase in temperature was observed in the sample.

Based on the TGA results, the drying temperature of 150°C was chosen since at this temperature most of the alcohol, acetic acid, and water can be removed from the sample. The drying time can also be determined by visually observing the change of interference colors. The change of interference colors of the drying film stops within two minutes of drying under most processing conditions. This indicates that the film thickness remains unchanged and the shrinkage due to organic evaporation ceases. Hence, a drying time of five minutes is adequate for complete removal of the low boiling point organics.

2.3.4.3 The Effect of Heating Rate and Thermal Processing Conditions

Heating rate is another important processing parameter which greatly affects the mechanical integrity and electrical properties of the PZT films. Recently, there are two studies on the effect of the heating rate of the sol gel derived PZT films [36,37]. Tuttle et al. have reported that the 53/47 PZT films annealed at different heating rates of 15°C/min and 50°C/min have very different microstructures and
properties [36]. They observed that the film annealed at 15°C/min was 40% perovskite by volume whereas, the film annealed at 50°C/min was 85% perovskite. They suggested that rapid heating minimized the nucleation and inhibited the crystallization of pyrochlore resulting in better electrical properties. Higher heating rates up to 8400°C/min by rapid thermal annealing (RTA) were used and the rapidly annealed samples showed improved properties compared to the samples annealed with a heating rate of 50°C/min.

A similar study by Spierings et al. also showed that the slow heating rate annealing process (0.5°C/min) produced a two phase microstructure: a rosette phase and an inter-rosette phase which were identified as the polycrystalline perovskite phase and the pyrochlore phase, respectively. On the contrary, the high heating rate annealing process (2000°C/min) produced only a homogeneous perovskite phase. The electrical properties also improved with the higher heating rate annealing process.

In this study, post-deposition annealings were performed in a horizontal tube furnace, and samples at room temperature were introduced into the heating zone (nominal annealing temperature from 500°C to 750°C) within a couple of seconds. The heating rate is estimated to be higher than 1000°C/min. Even at such a high heating rate, no film cracking was observed, neither on sapphire nor on Pt-coated Si substrates. The microstructures, in general, were quite homogeneous and good electrical properties were obtained with these high heating rate annealings.

The final processing parameter to be considered in this chapter is the atmosphere used during the annealing of PZT films. Experiments have been performed to evaluate the role of oxygen partial pressure (P_\text{O}_2) on the electrical properties of the PZT films during annealing. Five different values of P_\text{O}_2 were used.
Figure 2.5  
Hysteresis loops of PZT films annealed at different oxygen partial pressure
Figure 2.6 AES depth profile of lead concentration of PZT films annealed at different P₀₂
in the annealing experiments. They are 1.0 atm. (pure O₂), 0.2 atm. (in air), 10⁻³ atm., 10⁻⁴ atm., and 2×10⁻⁵ atm. of oxygen. The results of these experiments indicate that the electrical properties of the samples annealed in pure O₂ and in air behaved similarly while the electrical properties deteriorate at lower value of P₀₂. This result is shown in Figure 2.5 which shows the comparison of the hysteretic responses of samples annealed at different P₀₂. This difference in hysteretic responses can be explained by the magnitude of lead depletion from the samples' surfaces. Figure 2.6 is a Auger electron spectroscopy (AES) depth profile of lead concentration with respect to titanium concentration. Lead enrichment was found at thin near-surface regions in the samples annealed in air or in pure oxygen, but the lead concentration in the bulk is stoichiometric. On the contrary, the sample annealed at 2×10⁻⁵ atm. does not show any lead enrichment at the surface but the lead concentration of the bulk was only 50% of the stoichiometric value. This through-thickness lead depletion may contribute to the poor hysteretic properties observed. More detailed discussion of the role of oxygen partial pressure can be found in Reference [38].

In summary, in this study, the precursor solution has been modified to produce better quality PZT films. Empirical processing parameters, such as molar concentration of the precursor, the spin speed and time of spin coating, the drying time and temperature, the heating rate, and annealing atmosphere have been studied. Based on this study, a sol gel film processing technique is suggested in the flow diagram of Figure 2.1 (b) and the experimental procedures are listed in Appendix A. By following these procedures, good quality PZT films can be consistently obtained.
Chapter 3 Transmission Electron Microscopy Study of PZT Thin Films

This chapter has five sections. In the first section, a survey of transmission electron microscopy (TEM) studies of PZT materials is given. The study of domain structures of PZT thin film, the comparison between the domain structures found in thin film and those in PZT bulk ceramics are described in Section 3.2. The investigation of grain boundary segregation by microanalysis is the topic for the Section 3.3. In Section 3.4, the crystal structure of the intermediate pyrochlore phase, and the study of the pyrochlore to perovskite transformation by TEM are discussed. The last section summarizes the study of PZT films by TEM.

3.1 BACKGROUND

Transmission electron microscopy (TEM) is a powerful analytical technique which can provide imaging and diffraction as well as chemical compositional information with nm² resolution. TEM has been widely used in the studies of interfacial segregation, defect analysis, and phase transitions, to name just a few [39]. The earliest TEM study of PZT bulk ceramic by Goo, Mishra and Thomas in 1981 suggested that twin formation occurs when PZT ceramic undergoes a cubic to tetragonal transformation below the Curie temperature and each of the twin plates
becomes a ferroelectric domain [40]. The study also found that these deformation twins aligned along <110> directions on {110} planes. Lucuta and Teodorescu investigated the domain structure in PZT ceramics at the Morphotropic Phase Boundary (MPB) and found that the tetragonal phase can have 900 and 1800 domains [41]. In the MPB region, the 900 domains were predominant. The widths of the domains were about 0.1 – 0.5 μm.

Demczyk has characterized the domain structures of lanthanum modified lead titanate and has shown that the equilibrium domain width (approximately 50 nm) is independent of grain size when the grain size is above a critical value, and is dependent only on the c/a ratio of the ferroelectric phase [42]. Below a critical grain size of 0.3 μm, 900 domain formation is suppressed, and single domain grains predominate.

Dass et al. used convergent beam electron diffraction (CBED) to study the formation of phases at the MPB and concluded that both the tetragonal T phase (4mm) and rhombohedral R phase (3m) are present at the MPB [43]. Microanalysis has shown that the chemical compositions of the T phase and the R phase were very similar (within 2 mole percents which is within the experimental error of Energy Dispersive X-ray Analysis (EDX)). A similar study by Yamamoto et al. had observed that the T and R phases did not coexist in the same grain but existed in each independent grain [44]. They suggested that during the paraelectric to ferroelectric phase transition, each grain had transformed to either the T phase or R phase by the distortion and twist of the [100] and [111] directions, respectively.

Randall, Barber and Whatmore in a comprehensive study of PZT domain configurations [45] found that: (1) the main twinning planes are of the {110} type, and the domain widths were around 0.5 μm, (2) Selected Area Diffraction (SAD)
revealed small splittings in the high order diffraction spots, and the splitting was in a direction of [011], perpendicular to the domain wall, (3) the domains were much less frequently found on {100} planes than on {110} planes with the ratio of {100} domains/{110} domains being approximately 13%, (4) domain pinning by grain boundaries, dislocations and by other domains was observed, which inhibits the domain mobility and gives rise to dielectric loss and a reduction of the spontaneous polarization.

The TEM studies described in the above paragraph cover most of the important developments of the domain structure of the PZT bulk ceramic; however, to the best of my knowledge, the domain structures of PZT thin films has never been explored. In this work, the domain structure of the PZT thin films was investigated and comparison is made between the domain structure of thin films and the bulk ceramics.

The other important aspect of PZT films which has not yet been studied by TEM is the pyrochlore to perovskite transformation. The lack of research on the pyrochlore phase is due to the fact that PZT bulk ceramics are predominantly prepared by mixed-oxide sintering and the metastable pyrochlore phase is not observed in this process. On the contrary, most of the PZT film preparations produce films that are initially amorphous, and post-deposition annealing is generally required to form the desired perovskite phase [46]. The pyrochlore phase is a metastable phase found during the post-deposition annealing. A description of this metastable phase and its transformation to perovskite phase can be found in Section 3.4.
3.2 DOMAIN STRUCTURES OF PZT THIN FILMS

When a PZT material is cooled below its Curie temperature, a displacive transformation occurs and it transforms from a cubic structure to a tetragonal or rhombohedral structure. The distortional strain caused by the transformation is relieved by displacement twinning; each twin is believed to correspond to a single ferroelectric domain. The polarization vectors in each domain align in the same direction. When the polarization axis of one domain is arranged perpendicular to that of the adjacent domain in order to minimize the depolarization energy. These are called 90° domains. Since the ferroelectric properties of PZT films are dependent on the arrangement of these domains, it is of interest to study their orientations and configurations. The domain structure of PZT bulk ceramics has been extensively studied by TEM [45,47,48]. For the PZT ceramic materials, the 90° domains are deformation twins lying on the \{110\} planes with displacements along the \(<110>\) directions and the 180° domains are twins lying on the \{100\} planes and oriented in a zig-zag fashion about the \(<110>\) directions.

3.2.1 Experimental Procedures

PZT films with thicknesses around 400 nm were deposited by RF sputtering on Pt–coated single crystal Si wafers; deposition temperatures were lower than 200° C. As–deposited films were amorphous. Post–deposition annealing was performed at 750° C for 1 hour in a quartz tube furnace in a controlled oxygen atmosphere in order to obtain the desired ferroelectric phase. The compositions of these films, which were later analyzed by electron microprobe, were found to be stoichiometric
with a Zr/Ti ratio of 55/45.

TEM specimens were prepared by mechanically polishing the sample from the back side down to a thickness of 40 μm. Further thinning was done by cold stage Ar ion milling from the back side (5–6 kV, 0.5 mA and 10–15° milling) until perforation. All the TEM imagings and EDX was undertaken on a Philips 420, operating at 100 and 120 kV.

3.2.2 TEM of Domain Structures

Most of the bulk PZT ceramics were fabricated by mixing and sintering the proper amounts of PbO, TiO₂ and ZrO₂ powders. The formation temperature of the sintered PZT samples was around 800°C [49]. In general, PbTiO₃ formed as an intermediate phase prior to the complete formation of the single PZT perovskite phase. As for the sputtered PZT thin films, the formation temperature can be as low as 575°C [46] and an intermediate pyrochlore phase is commonly found at annealing temperatures between 450°C to 575°C. Figure 3.1(a) is a TEM micrograph of the PZT film which had been annealed at 500°C for 1 hour which shows the pyrochlore phase; the pyrochlore grain size is very small and is around 25 nm. The lattice parameter of the pyrochlore phase is around 10.47 Å as determined from the selected area ring diffraction pattern. When the PZT film was annealed at 700°C for 1.5 hour, a very well defined grain structure had formed as shown in Figure 3.1(b). The average grain size of the perovskite phase was about 1.7 μm but a wide variation of grain sizes were found to occur. A prominent feature of Figure 3.1(b) is strings of second phases lying along all the grain boundaries. The concentration profiles of Pb, Zr and Ti were determined across the grain boundaries
Figure 3.1  Transmission electron micrographs of PZT films (a) pyrochlore phase, 500°C/1 hr. (b) perovskite phase, 700°C/1.5 hr
and the results will be discussed in the later section.

In the following discussion, all the PZT films were annealed at 750°C for 1 hour in an oxygen atmosphere. Figure 3.2 is a bright field/dark field pair where the dark field was obtained from the (110) diffraction spot. It is common to observe the domain structures by tilting the TEM sample to any one of the <110> zone axes. The dark field micrograph only shows one variant of domain structure even though there are two domain packets shown in the bright field micrograph. It was common in this experiment to find several orientations of domain structures present in the same grain. The domain width was measured to be around 20 nm and the domain wall thickness was estimated from the dark field micrographs to be about 1.5 nm.

Figure 3.3(a) and 3.3(b) is another BF/DF pair which also shows the domain structure lying on the {110} habit planes. The direction of the domain structure can be determined by setting up a 2-beam condition; it was found that the domains predominantly orient along the <110> directions. Figure 3.3(c) is obtained by intentionally tilting the sample off the [110] zone-axis in order to emphasize the fact that domains can only be seen when the sample is oriented close to one of the <110> zone axis. The area labeled A in Figure 3.3(a) is a thinner area which is probably due to nonuniform ion milling. Contrary to the observation from the electron diffraction indicating that the thinner area (area A) had already been transformed to perovskite, no domain structure was observed. This may be explained that as the thickness of the film approaches the domain wall thickness, the depolarization energy can no longer be decreased by domain formation [3] and transformation can occur without stress relief by twinning.
Figure 3.2  (a) Bright field (b) dark field micrograph and (c) SAD of the domain structure which the dark field shows the orientation of one variant of twinning
Figure 3.3  
(a) Bright field (b) dark field micrograph (c) bright field similar to (a) but intentionally tilt off the [110] zone axis and (d) SAD showing the [110] zone axis.
3.3 MICROANALYSIS OF THE GRAIN BOUNDARY PHASES

The compositions and morphologies of the grain boundaries and the grain boundary phases can greatly affect the ferroelectric properties of the PZT materials. Second phases or micropores at the grain boundaries are commonly formed in the PZT thin films after high temperature annealing. One of the possible explanations is that PbO migrated to the grain boundaries, was lost to the atmosphere and then left behind a string of micropores at the grain boundaries. If the formation of micropores is related to the phenomenon of lead diffusion to the grain boundaries, the study of grain boundary composition may shed some light on the mechanism of micropore formation. In this study, energy dispersive X-ray analysis (EDX) was incorporated with a nanoprobe in the STEM mode to investigate the compositional changes across the grain boundary region.

Previous TEM studies of PZT and PLZT ceramics often found microcrystalline lead oxide either in grain junctions or inside the grains especially when excess PbO is added to aid sintering [47,50]. For the sputtered PZT films, micropores were found in the grain interior and also at the grain boundaries and suggested that the micropores are related to the excess PbO present in the sputter target [51]. In this study, micropores were found in the grain interior and also along the grain boundaries. A more detailed study of these micropores disclosed that they are not actually voids but areas that are much thinner than the rest of the film. Since micropores can act as domain pinning sites and a high density of micropores may set the upper limit on the domain size. The amount of these micropores can be greatly decreased by annealing the film at a lower annealing temperature and was confirmed by TEM in this study. Thus, the formation of these micropores is a temperature
dependent phenomenon.

A quantitative chemical analysis of a grain boundary requires a technique which can detect compositional change in the nanometer range since the width of the grain boundary is in the order of one nm. In this study, the EDX analyses were done in the STEM mode in which the electron beam can be converged by the objective prefield to form a nanoprobe with an effective probe size of 2 nm. The spacing between each EDX measurement is around 80 nm. Due to the small thickness of the TEM sample, beam broadening is considered almost negligible; each measurement can be considered independent of the previous one because of the adequate spatial separations between each measurement. The Pb M peak, the Zr L peak and the Ti K peak were used to determine the chemical composition of the grain boundary. Although there is a minor overlap in energy between the Pb M peak and the Zr L peak, it should not significantly affect the outcome. The result is shown in Figure 3.4 where the lead concentration shows little difference across the grain boundary and is close to the stoichiometric concentration (50%). The Zr and Ti concentration profiles each shows similar behavior also. Microdiffraction on these micropores failed to find any extra diffraction information.

In an oxidation study of tetragonal PbO [52], 0.5 µm PbO particles were heated in air at 351°C for 15 hours to form stable Pb3O4 phases. At lower annealing temperature, PbOx was found (where x ranges from 1.5 to 1.33) [52]. In this study, the PbO–TiO2–ZrO2 amorphous phase was annealed at 750°C for 1 hour in a pure oxygen atmosphere; it is possible during annealing that some of the PbO may oxidize to form PbOx. The as-sputtered PbO phase has a much smaller particle size when compared to the 0.5 µm PbO particle size used in the literature and hence the kinetics of PbO oxidation should consequently be much faster. PbO is stable at
Figure 3.4  (a) STEM micrograph showing the grain boundary and the thin area along the grain boundary and (b) lead concentration as a function of the distance from the grain boundary
O/Pb ratio smaller than 1.02 and both PbO and Pb$_{3}$O$_{4}$ coexist with a O/Pb ratio between 1.02 to 1.33 [53]. The decomposition temperature of PbO$_{2}$ and Pb$_{3}$O$_{4}$ is 290°C and 500°C, respectively. The melting temperature of PbO is 886°C [53].

One possible grain boundary micropore formation is postulated as follows:

1. During high temperature annealing, PbO preferentially diffuses to the grain boundaries.
2. PbO is oxidized in an oxygen atmosphere to form PbO$_{x}$. PbO$_{x}$ is very likely in the form of Pb$_{3}$O$_{4}$ which decomposes at around 500°C.
3. PbO$_{x}$ decomposes or is preferentially ion etched by ion milling and leaves behind strings of thin areas (micropores) along the grain boundaries.

Based on this model, it is plausible that if all the lead-rich second phase decomposes or is etched away during annealing, the EDX analysis on the samples after annealing may not be able to detect the higher lead concentration at the grain boundaries.
3.4 TEM STUDY OF THE PYROCHLORc TO PEROVSKITE PHASE TRANSFORMATION

There is a considerable interest in the ferroelectric thin films, particularly in the lead zirconate titanate (PZT) system for their potential applications in high density DRAM capacitors and nonvolatile memories. Thin film processing techniques such as the sol–gel process, sputtering and electron beam evaporation are commonly used to produce the PZT films. Most of the time, the as–deposited film has an amorphous structure and post–deposition annealing is needed to transform the film from the amorphous structure to the desired ferroelectric perovskite phase. During annealing, an intermediate pyrochlore phase is formed first and eventually transforms to perovskite phase at a higher annealing temperature. Even though the presence of this intermediate pyrochlore phase is commonly observed [12,54], few efforts have been made to study this pyrochlore–perovskite transformation. Observation of the microstructural changes occurring throughout the transformation by transmission electron microscopy (TEM) are reported in this study. A new technique, which simplifies the TEM sample preparation, was used.

In this study, the PZT films were fabricated from 0.025 M metallo–organic solution of lead acetate, zirconium n–propoxide and titanium isopropoxide dissolved in acetic acid; this solution was then hydrolyzed to form the precursor. This precursor preparation is similar in detail to that suggested by Yi et al. [30]. The precursor was then spin–cast on the single crystal sapphire substrates and the TEM grids. The resulting films were air dried for 5 minutes and then annealed at different annealing temperatures for 15 minutes in air.
Figure 3.5  XRD of PZT films on sapphire and annealed at (a) 450°C (b) 550°C (c) 600°C (d) 650°C for 15 min. in air
Conventional TEM sample preparation for ceramic materials generally requires mechanical polishing, dimpling and ion milling. This process is tedious, time consuming, and is prone to introduce defects and/or artifacts. A novel TEM sample preparation, which is particularly suitable for sol–gel process, was used in this experiment. Using this process, the sol was spin–cast at 3000 rpm for 30 seconds directly onto the 400 mesh nickel TEM grids. The surface tension holds the liquid film in place; the film was air dried and then annealed. This process is expeditious; no mechanical or ion beam polishing is necessary. Almost all of the TEM samples made were successful; this would be very unlikely if the samples had been prepared conventionally. One of the few drawbacks of this preparation process is that since the film is fabricated without the support of a substrate, the behavior of this free–standing film may be different from that of the same film deposited on a substrate.

3.4.1 TEM Study of The Metastable Pyrochlore Phase

The PZT perovskite phase has the chemical formula ABO₃ and has either a tetragonal or rhombohedral structure depending on the Zr/Ti ratio. Lead atoms occupy the A sites which are located at the cube corners, Zr or Ti atoms occupy the B sites which are located at the body centers and oxygen atoms can be found in the face center positions. The pyrochlore phase has a cubic structure and the chemical formula A₂B₂O₇₋ₓ (x would be close to 1 in the case of PZT). The structure of a general pyrochlore structure can be regarded as an oxygen–deficient fluorite structure which has a face–centered cubic lattice. A detailed description of the general pyrochlore structure can be found in Reference 55.
In this study, x-ray diffraction was used to monitor the phase changes after annealing. All annealings were performed in a quartz tube furnace at a predetermined temperature for 15 minutes in air. When the as-deposited film on sapphire was annealed at 450°C, no definitive peak was observed and the film remained amorphous as shown in Figure 3.5. As the annealing temperature was increased to 550°C, two very broad pyrochlore peaks were found at 2θ of 29.5° and 34°. At 600°C, both perovskite and pyrochlore phases were present. Formation of a single perovskite phase was observed at or above 650°C. Even though the occurrence of pyrochlore is commonly recognized during the annealing of PZT films under many conditions [54], there is little consensus about either the exact peak position or (hkl) identification of the peaks of the pyrochlore structure because the JCPDS diffraction file of the PZT pyrochlore phase has not yet been established. Okada [12] observed few broad pyrochlore peaks located at d-spacings of 2.95 Å, 2.69 Å and 1.84 Å using Cu Kα radiation. In this study, a computer program, which had been developed by Weidemann [56], was used to calculate the theoretical peak positions and intensities of the PZT perovskite and pyrochlore phases. Relevant input data included the crystal system, the lattice parameters, the x-ray wavelength, the atomic position of each element, their scattering factors and dispersion correction factors. This program also has a provision for fractional atomic site occupation which occurs for different Zr/Ti ratios in both the perovskite and the pyrochlore structure. The scattering factors and dispersion corrections of each element can be obtained from the International Tables for X-ray Crystallography [56]. To calculate the x-ray diffraction data of the perovskite phase, only 6 atomic positions have to be specified, whereas for the pyrochlore phase, 104 atomic positions are needed because of the more complex crystal
structure.

The comparison of the peak positions and peak intensities of the perovskite phase and the pyrochlore phase from the theoretical calculation and from the JCPDS diffraction file is tabulated in Table 3.1. The comparison of the PZT perovskite phase shows excellent agreement between the experimental results and the computed results. In this study, the x-ray diffraction of the pyrochlore phase only shows two very broad peaks at d-spacings of 3.02 Å and 2.62 Å. The comparison of the computed results of the pyrochlore phase and the results obtained in this experiment by x-ray diffraction and TEM electron diffraction also show very good agreement. The advantage of the electron diffraction over the x-ray diffraction is that many more peaks can be located and thus positive identification of the pyrochlore phase is possible.

In the x-ray diffraction result from the PZT sample annealed at 550°C, the pyrochlore phase had a very broad (222) peak. The average diameter of the crystal size can be related to the peak broadening [58] and was thus calculated to be around 6 nm. Figure 3.6 is a bright field/dark field pair of micrographs of a homogeneous, fine grain phase where the dark field was taken from a small area of the most intense ring. The crystal size as measured from the dark field micrograph was around 8 nm which agrees very well with the result from the x-ray diffraction. The diffraction ring pattern is indexed according to the d-spacings for the pyrochlore phase listed in Table 3.1. Hence, we can identified this fine grain structure as being pure pyrochlore. Fig. 3.7 shows that two particles are found on a homogeneous background; the background phase is pyrochlore and the particle in the center of Figure 3.7(a) can be identified as perovskite by the spot pattern. The d-spacings measured from the spot pattern match very well with the d-spacings listed in
Figure 3.6  (a) Bright field (b) dark field and (c) SAD of the pyrochlore phase showing very fine grain structure
Figure 3.7 TEM micrographs of the perovskite particles growing on the pyrochlore phase. (a) bright field (b) perovskite diffraction pattern and (c) pyrochlore diffraction pattern
Table 3.1 The comparison of the peak positions and peak intensities of the perovskite phase and the pyrochlore phase.

**PZT Perovskite**

<table>
<thead>
<tr>
<th>hkl*</th>
<th>d&lt;sub&gt;calc&lt;/sub&gt;†</th>
<th>I/I&lt;sub&gt;0&lt;/sub&gt;*</th>
<th>I/I&lt;sub&gt;0 calc&lt;/sub&gt;†</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>4.15</td>
<td>4.15</td>
<td>9</td>
</tr>
<tr>
<td>100</td>
<td>4.04</td>
<td>4.04</td>
<td>12</td>
</tr>
<tr>
<td>101</td>
<td>2.89</td>
<td>2.89</td>
<td>(\sqrt{100})</td>
</tr>
<tr>
<td>110</td>
<td>2.85</td>
<td>2.85</td>
<td>(\sqrt{100})</td>
</tr>
<tr>
<td>111</td>
<td>2.35</td>
<td>2.35</td>
<td>15</td>
</tr>
<tr>
<td>002</td>
<td>2.07</td>
<td>2.07</td>
<td>9</td>
</tr>
<tr>
<td>200</td>
<td>2.02</td>
<td>2.02</td>
<td>16</td>
</tr>
<tr>
<td>102</td>
<td>1.84</td>
<td>1.84</td>
<td>5</td>
</tr>
<tr>
<td>201</td>
<td>1.81</td>
<td>1.81</td>
<td>(\sqrt{6})</td>
</tr>
<tr>
<td>210</td>
<td>1.81</td>
<td>1.80</td>
<td>(\sqrt{6})</td>
</tr>
<tr>
<td>112</td>
<td>1.68</td>
<td>1.68</td>
<td>12</td>
</tr>
<tr>
<td>211</td>
<td>1.66</td>
<td>1.66</td>
<td>25</td>
</tr>
</tbody>
</table>

* JCPDS card No. 33-784
† calculated from the 'powder' computer program
\(\phi\) Zr/Ti = 52/48

**PZT Pyrochlore**

<table>
<thead>
<tr>
<th>hkl</th>
<th>d&lt;sub&gt;calc&lt;/sub&gt;†</th>
<th>I/I&lt;sub&gt;0 calc&lt;/sub&gt;†</th>
<th>d&lt;sub&gt;x-ray&lt;/sub&gt;</th>
<th>d&lt;sub&gt;tem&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>6.04</td>
<td>31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>311</td>
<td>3.16</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>222</td>
<td>3.02</td>
<td>100</td>
<td>3.02</td>
<td>3.03</td>
</tr>
<tr>
<td>400</td>
<td>2.62</td>
<td>31</td>
<td>2.62</td>
<td>2.63</td>
</tr>
<tr>
<td>331</td>
<td>2.40</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>511</td>
<td>2.02</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>440</td>
<td>1.85</td>
<td>52</td>
<td>1.84</td>
<td>1.85</td>
</tr>
<tr>
<td>531</td>
<td>1.77</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>622</td>
<td>1.58</td>
<td>44</td>
<td>1.58</td>
<td></td>
</tr>
<tr>
<td>444</td>
<td>1.51</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>1.31</td>
<td>8</td>
<td></td>
<td>1.31</td>
</tr>
</tbody>
</table>

** any peak with I/I<sub>0</sub> < 5% is not tabulated
t† calculated from the 'powder' computer program
x-ray observed by x-ray diffraction in this study
tem observed by TEM electron diffraction in this study
Figure 3.8  The microstructural development of the PZT film as a function of annealing temperature
Table 3.1.

All of the perovskite phase regions formed during the 650°C and 700°C annealings had bending contours across the whole particle, while at 750°C annealing, the bending contours disappear. The pyrochlore-perovskite transformation involves a volume change (5.7 volume %) and this volume change will induce strain in the perovskite phase. For a very thin, free standing film, as in this case, the strain can be relieved by bending the perovskite particles and that explains why all the perovskite particles found at temperatures from 600°C to 650°C have bending contours. At higher annealing temperatures, the stress is thermally relieved and also all the pyrochlore phase transforms to the perovskite phase; thus the lattice mismatch between the two phases disappears as we can see in Figure 3.8(g). When we examined the electron diffraction result from area A, in addition to the single spot pattern from the perovskite, we also observed the presence of a faint pyrochlore ring (arrowed in Figure 3.7(b)). Since the selected area aperture covered the area which was completely within the perovskite particle, the only reason for the existence of the pyrochlore ring was that the perovskite particle was actually sitting on top of a much thinner pyrochlore film, in other words, the perovskite phase grew on top of the pyrochlore film.

Figure 3.8 is a set of TEM micrographs showing the development of the perovskite phase as a function of annealing temperatures. All the diffraction patterns were obtained from an area with diameter about 5 μm. For annealing temperatures at or below 550°C, the microstructure had a mottled structure and the corresponding electron diffraction pattern shows a single diffuse ring which indicates an almost amorphous structure. More careful observation of the diffuse ring reveals that the d-spacing of the diffuse ring is corresponded to the d-spacing of the most
intense (222) ring of the pyrochlore phase. Based on this information, we can assume that the pyrochlore phase has already been nucleated and is forming very minute clusters at temperatures as low as 450°C.

At 650°C annealing, well defined pyrochlore grains are formed and the corresponding sharp diffraction ring pattern signifies very fine grain structures. The uniform intensity from these diffraction rings means there is no preferred orientation from the fine pyrochlore grains. In addition to the formation of the fine grain pyrochlore phase, very small amounts of perovskite grains are found in well separated locations (see Figure 3.8(e)).

At higher annealing temperatures, more perovskite grains are formed, each identifiable by its characteristic diffraction spot pattern. Figure 3.8(f) is an example of a spot pattern of a perovskite grain with a [110] type orientation.

At 750°C annealing, all of the pyrochlore phase has been transformed to perovskite as shown in Figure 3.8(g). Therefore, the onset transformation temperature of the perovskite phase is around 650°C and complete transformation of perovskite phase occurs at temperatures at or above 750°C. It is interesting to note that the transformation temperature of perovskite as measured by x-ray diffraction is about 100°C lower than the temperature measured by TEM.

This discrepancy of transformation temperature can be related to the way in which the thin film is fabricated. Even though the heat treatments are the same for the samples characterizing by either XRD or TEM. X-ray samples were deposited on sapphire substrate while the TEM samples are free standing films. From theoretical calculations, the density of the perovskite phase is 8.05 gm/cm³ and that of the pyrochlore phase is 7.55 gm/cm³. Thus, a decrease in volume is expected to accompany the pyrochlore–perovskite transformation. For the free standing films,
especially for the very thin samples, the strain energy required to form the perovskite phase is diminished due to the strain relaxation in the direction normal to the film. Hence, the transformation temperature observed is always lower than the transformation temperature determined by XRD. Nevertheless, the TEM study of the PZT films has demonstrated the pertinent evolution of the pyrochlore to perovskite transformation.

3.5 SUMMARY

(1) The ferroelectric domains of the sputtered PZT films have been studied by TEM and EDX. $90^\circ$ domains that oriented along $<110>$ direction and have $\{110\}$ habit planes were found.

(2) The high temperature annealed films contain many micropores especially on the grain boundaries. EDX analysis across the grain boundaries does not show any significant increase in lead concentration at the grain boundaries.

(3) A new TEM sample preparation method was suggested and used in this study. The spin casting method is expeditious and easy to obtain good quality thin foils.

(4) The pyrochlore phase is shown to have very fine grain structure and the perovskite phase is observed to grow on the pyrochlore phase at temperature around $650^\circ$C. The discrepancy of the transformation temperature is discussed and can be attributed to the size effect of the thin films.
Chapter 4 Formation kinetics of PZT thin films

In the first section of this chapter, the phase transformation of PZT bulk ceramic and thin film materials are reviewed. The formation kinetics of the PZT films are investigated in the second section. Finally, based on the understanding of the formation kinetics of the PZT films, two different processes, namely, the high pressure transformation and the seeding process, which are both designed to lower the transformation temperature of the PZT films, are described in the last section.

4.1 INTRODUCTION

In most of the PZT film depositions, post-deposition annealing is needed to produce the desired perovskite phase [47,59]. Amorphous PZT phase is reported to transform to a metastable pyrochlore phase at temperatures as low as 350°C and finally forming perovskite phase at temperatures higher than 500°C [60]. The understanding of the transformation kinetics of the pyrochlore to perovskite phase transition is crucial to the development of better ferroelectric materials. The information gathered from the kinetic study can be used in modifying the process to produce the PZT films with desirable microstructure and properties. One of the goals of studying the kinetics is to prepare PZT films with perovskite structure at a
lower transformation temperature. The transformation kinetics and the low temperature processings are discussed in the following sections.

4.2 FORMATION KINETICS OF PZT FILMS

Reaction mechanisms of PZT bulk materials, prepared by the mixed-oxide sintering, have been extensively investigated [61–63]. In the PbO–ZrO$_2$–TiO$_2$ system, the PbTiO$_3$ always forms first at temperatures ranging from 450ºC to 600ºC. Single PZT phase was observed at temperature around 785ºC but no PbZrO$_3$ was observed [63]. It was believed that ZrO$_2$ reacted directly with PbTiO$_3$ to form PZT bulk ceramics. However, it is anticipated that the results of the kinetic studies for these PZT bulk materials are vastly different from and may not even be relevant to those for the PZT thin films. In considering the mixed-oxide sintering, the average particle size for the three oxides is in the order of 1 μm, whereas for the sputtered films and the sol gel films, the average diffusion distance is in the 1 nm to 10 nm range. The short diffusion distance also explains why the transformation for PZT films is generally 150ºC to 200ºC lower than that of the PZT ceramics.

Recently, new studies on the preparation of titanate fine powders by co-precipitation and other chemical methods have emerged and should provide some insights on the formation kinetics of PZT thin films. Hertl studied the kinetics of barium titanate formation (average particle size about 40 nm) by x-ray diffraction (XRD) [64] and found that the rate-determining step is the topochemical reaction of Ba with TiO$_2$ at the interface. The effective activation energy is 105 kJ/mol. Shaikh and Vest investigated the kinetics of PbTiO$_3$ formation [65]. These
titanates were prepared from metallo-organic decomposition (MOD) TiO₂ and PbO fine powders with average particle sizes of 6 nm and 220 nm, respectively. For the PbTiO₃ formation, the kinetic parameter \( n \) from the Avrami's equation is determined to be 1.5, which corresponds to a diffusion-controlled reaction. The Avrami's equation can be represented by a general equation of \( \zeta = 1 - \exp(-k t^n) \), where \( \zeta \) is the volume fraction, \( t \) is annealing time and \( n \) is the Avrami's parameter. The activation energy for the PbTiO₃ formation is from 60–87 kJ/mol depending on the precursor used. They proposed a model in which the TiO₂ particles completely cover the shell of the PbTiO₃ already formed around the PbO particles. The reaction rate is controlled by the diffusion length, which is assumed to be the PbTiO₃ shell thickness. Yoshikawa and Tsuzuki did research on the crystallization of Pb₀.₉₂La₀.₀₈(Zr₀.₆₅Ti₀.₃₅)₀.₉₈O₃ (PLZT 8/65/35) [66]. The Avrami's parameter is determined to be around 1.0, which implies that random nucleation is the rate-determining step. The effective activation energy for the PLZT powder is 297 kJ/mol. The activation energy for isothermal grain growth is 60 kJ/mol.

In the case of PZT thin film, to the best of my knowledge, there is only one kinetic study reported by Chen and Mackenzie [67]. Chen studied the formation kinetics of the perovskite phase of sol gel derived PZT films. These films were prepared by a precursor which was comprised of Pb 2-ethylhexanoate, Zr n-propoxide, Ti isopropoxide, and isopropanol. The films were dip-coated to a thickness of 2 μm on fused silica substrates. The formation rate of perovskite phase is determined by measuring the x-ray intensities of the (111) perovskite peak and the (400) pyrochlore peak. Chen had noticed that the pyrochlore and the perovskite both have constant crystal size and qualitatively concluded that the crystallization process is nucleation dominated. The activation energy for perovskite formation is
found to be 26 kJ/mol.

In Chen's paper, however, there is no explanation about why he did not use the major pyrochlore and perovskite x-ray peaks, which are the (110) and the (222) peaks, respectively. When the intensity ratios of the minor peak and the major peak \(I/I_0\) are compared, the intensity ratio of the \((111)/1_{110}\) and of the \((1400)/1_{222}\) are about 12.9% and 30.7%, respectively. We speculate that Chen did not use the major peak because the (222) pyrochlore peak and the (110) perovskite peak are located very close to each other (2θ of 29.5° and 30.9°), and the overlapping of the two peaks make the measurements of the individual phases difficult. Even with a film thickness of 2 µm, the diffracting volumes from the minor peaks of the PZT films would be very small when compared to those volumes of the PZT fine powders. Hence, there is anticipated difficulty in using XRD to measure the phase constitution of PZT thin films in practice.

In our work, a different approach was used to measured the nucleation rate and the growth rate of the perovskite phase. This approach involves direct observation of the nucleation and growth of the perovskite phase by scanning electron microscopy (SEM) and some of the data obtained were also spot—checked by XRD. One of the advantages of this approach is that the nucleation rate, growth rate, and volume fraction of the transformed perovskite phase can be measured separately. In contrast, most of the x-ray diffraction techniques can only be used to determine the volume fraction of the transformed phases. Using XRD, the growth rate has to be inferred by the peak broadening [58]. Generally, the Sherrer's equation is commonly used to calculate the particle size. It can be expressed as follows:

\[
B = \frac{0.9 \lambda}{t \cos \theta}
\] (4.1)
where $B =$ broadening of diffraction line at FWHM, $\lambda =$ wavelength of the x-ray source, $\theta =$ diffracting angle, and $t =$ diameter of the particle.

However, the upper limit of particle size that can be measured by this peak broadening technique is about 100 nm. This is because the peak broadening can be caused by the incident beam divergence, size of the sample, width of the x-ray source, and the nonuniform strain in the sample [58]. Under most conditions, crystal size of 100 nm only represents the early stage of the crystal growth. Therefore, the peak broadening method is quite limited in general kinetic studies.

In short, a brief survey of kinetic studies of various titanate powders and the PZT film is given. X-ray diffraction was used in all of the previous mentioned kinetic studies and the application of x-ray diffraction has been briefly discussed. A relatively uncommon approach was proposed in this work to study the formation kinetics of the PZT thin films. Its results will be compared to the XRD results. This direct observation approach is described in the following section.

4.2.1 Kinetic Study of PZT Thin Films

Proper post-deposition annealing is crucial to the ferroelectric and optical properties of PZT thin films. Post deposition annealing is often needed to produce the desirable perovskite structure, but a high annealing temperature can directly influence the electronic properties of the electronic circuit components beneath the PZT films during annealing. Also, extensive blistering occurs at the substrate–film interface at high annealing temperatures. The objective of this study is to understand the reaction kinetics of the formation of the PZT perovskite phase in the thin film form. Isothermal annealings were performed at temperatures close to the
transformation temperature and the resulting phases and microstructures were studied by XRD and SEM.

4.2.2 Experimental Procedures

PZT films with thicknesses around 350 nm were sputter–deposited on Pt coated single crystal Si wafers at a relatively low temperature ($\lesssim 200^\circ$C). The post–deposition annealing procedures were performed in a quartz tube furnace in a controlled oxygen atmosphere. The compositions of the films were determined by electron microprobe and found to be stoichiometric with a Zr/Ti ratio of 55/45. Based on the previous x–ray study on perovskite formation [46], the pyrochlore to perovskite transformation temperature was determined to be around 550$^\circ$C. Thus the kinetics of the perovskite formation were studied isothermally between 525$^\circ$C and 575$^\circ$C for various annealing times. SEM was used to monitor the reaction parameters such as the size of the phases, the number of nucleation sites, and the volume fraction of the transformed phase.

4.2.3 Kinetics Studies

When the amorphous PZT films were heated in the temperature range of 525$^\circ$C–575$^\circ$C, pyrochlore and perovskite phases were sequentially formed as determined by x–ray analysis. This transformation is polymorphic since there is no noticeable change in chemical composition observed. Figure 4.1(a) shows the circular–shaped perovskite phases (area (a)) growing on the pyrochlore layer (area (b)); energy dispersive x–ray analysis (EDX) of areas (a) and (b) reveals there is very little
Figure 4.1 SEM micrographs of PZT film annealed at 550°C for 10 min., (a) secondary electron imaging, (b) backscattered electron imaging. Arrows on both micrographs show the outline of the same feature.
difference in chemical composition between the pyrochlore phase and the perovskite phase. Figure 4.1(b) is a backscattered electron micrograph portraying the same area of Figure 4.1(a). Since the magnitude of the electrons backscattered from the surface is directly related to the atomic weights of the phases presented on the surface, the lack of contrast in Figure 4.1(b) also suggests that the compositions of the 2 phases are very similar. The appearance of the pyrochlore phase (area b) is almost featureless, and corresponds to a microcrystalline structure. From the x-ray peak broadening calculation, the grain size of the pyrochlore phase is about 5 nm. In addition to the grain size broadening, strain induced broadening can also be operating since the pyrochlore phase is highly nonstoichiometric and apparently has a high oxygen defect concentration. Transmission electron microscopy (TEM) confirmed the fine grain nature of the pyrochlore phase; the grain size measured by TEM was around 6 nm.

Figure 4.2 shows the linear dimension of the growing phase \( r_{\text{max}} \), plotted as a function of time, \( t \), at 3 different temperatures. The data were collected for annealing conditions at which the phases are well separated from each other to avoid soft impingement, see Figure 4.3. In the case of soft impingement, the amount of material that can be transported to the growing particles will gradually become depleted resulting in a decreased growth rate as time increases. However, the linear behavior of the plots (Figure 4.2) implies a relatively constant growth rate which can be calculated from the slope. The growth rates are 0.23, 0.63 and 0.95 \( \mu \text{m min}^{-1} \) measured at 525°C, 550°C and 575°C, respectively. The linear dimension of growth as a function of reaction time is often expressed by an equation of the following form:
\[ r_{\text{max}} = k t^n \] (4.2)

By taking the natural log of the above equation and plotting \( \ln r_{\text{max}} \) versus \( \ln t \),

\[ \ln r_{\text{max}} = \ln k + n \ln t \] (4.3)

the slope \( n \) can be calculated. In this study, the \( n \) values obtained were 1.05, 1.31, and 0.99 for the 525°C, 550°C, and 575°C, respectively. For \( n \) values equal to 1.0, interface controlled growth is implied and since there is no compositional change in polymorphic transition, the structural change is accomplished at the phase interface. Thus, the growth of the perovskite phase is believed to be interface-controlled.

From Figure 4.2, we can also measure the incubation time; this is the time taken for an embryo to grow to the critical nucleus size. Although it is very difficult to determine the specific time at which the nuclei become stable, incubation times can be estimated by back extrapolating to the intercept of the time axis. The incubation times for this experiment were found to be: 2.3 minutes at 525°C, 0.87 minutes at 550°C, and 3.5 seconds at 575°C. The actual annealing time is the difference between the apparent annealing time and the incubation time.

The number of nucleation sites per unit area for each heat treatment can be measured directly from the electron micrographs as shown in Figure 4.3. Since any nucleus smaller than 0.5 \( \mu \)m is very difficult to resolve in the micrograph, these measurements represent the lower bound of the actual values. Figure 4.4 shows random volume nucleation, possibly due to the very fine grains of the pyrochlore phase. The nucleation rate in all three cases was found to increase at the early stage.
Figure 4.2 The linear dimension of the growing phase as a function of annealing time at different temperatures

-73-
of the reaction, reaches a maximum and decreases afterward; the decrease in nucleation rate can be explained by the soft impingement where even the grains are not physically impinging. In this case, the solute concentration is depleted by the proximity of the neighboring grains. Site saturation is not reached at this later stage of reaction.

A model is suggested to account for the nucleation and growth of the perovskite phase in the thin film form. At annealing times shortly after the incubation period, nuclei will grow isotropically in three dimensions until the thickness of the particles is equal to the thickness of the film and in this case, the thickness is around 350nm. Further grain growth involves mass transport from the lateral directions parallel to the plane of the substrate and the growth rate in the direction perpendicular to substrate plane becomes very small and leads to a two dimensional growth. The final grain shape should resemble a flat disc if the lateral growth is isotropic.

Based on this model, the kinetics of transformations where nucleation and growth occurs simultaneously can be expressed in a way that closely follow that of Burke and Turnbull [68].

\[ X_t = 1 - \exp \left( - \int V_P \, dN_c \right) \]  \hspace{1cm} (4.4)

where \( X_t \) is the volume fraction transformed to perovskite, \( V_P \) is the volume of the particle, and \( N_c \) is the number of nuclei per unit volume.

In the general case, \( V_P = g G_x G_y G_z (t-\tau)^3 \) where \( G_i \) is the growth rate in the \( i \) direction, \( g \) is the shape factor and a linear dimension of the particle at time \( t \) where \( t > \tau \) will be given by \( G(t-\tau) \). In the present study, the particle shape is assumed to be cylindrical thin plate with radius \( G(t-\tau) \) and thickness \( \delta \). Therefore the volume
of the particle is \( V_p = \pi G^2 (t-\tau)^2 \delta \) and the nucleation frequency \( I = \frac{dN_c}{dt} = \frac{dN}{\delta dt} \) where \( N \) is the number of nuclei per unit area as measured from the electron micrographs and \( \delta \) is the film thickness.

\[
X_t = 1 - \exp \left[ - \int_0^t \pi G^2 (t-\tau)^2 \delta \frac{N}{\delta} d\tau \right]
\]

\[
X_t = 1 - \exp(-\frac{\pi}{3} G^2 N t^3)
\]

Equation (4.6) is valid only if the growth rate and the nucleation rate is time independent. In the present study, the growth rate is relatively constant under the experimental conditions investigated even though they did show decreasing trend at the later stage of growth, however, the nucleation rate is definitely time dependent. An approximation can be made by using an average nucleation rate in equation (4.6). The average nucleation rate is calculated by the slope of Figure 4.4. The calculated and measured volume fraction is compared in Table 4.2 using the average nucleation rate approximation and shows good agreement at the early stage of growth but deviates greatly at the later stage of growth. Recall that the nucleation rate reaches a maximum and decreases rapidly at the later stage of growth for all three annealings. Since the average nucleation rate is larger than the actual nucleation rate at this stage, the computed volume fractions will be much larger than the measured values.

In order to verify the model, the nucleation and growth process can be assumed to have the general form

\[
X_t = 1 - \exp (-kt^n)
\]
Table 4.1. Comparison of volume fractions obtained from experiments and from theoretical calculation

<table>
<thead>
<tr>
<th></th>
<th>525°C</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t(min)</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha_{\text{calc}} )</td>
<td></td>
<td>0.7</td>
<td>15.0</td>
<td>51.9</td>
<td>98.4</td>
<td>100</td>
</tr>
<tr>
<td>( \alpha_{\text{obs}} )</td>
<td></td>
<td>1.0</td>
<td>6.8</td>
<td>13.5</td>
<td>16.5</td>
<td>29</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>550°C</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t(min)</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha_{\text{calc}} )</td>
<td></td>
<td>0.8</td>
<td>5.4</td>
<td>16.2</td>
<td>54.1</td>
<td>87.6</td>
</tr>
<tr>
<td>( \alpha_{\text{obs}} )</td>
<td></td>
<td>2.2</td>
<td>5.0</td>
<td>13.3</td>
<td>22.4</td>
<td>44.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>575°C</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t(min)</td>
<td>1.5</td>
<td>2.5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha_{\text{calc}} )</td>
<td></td>
<td>2.9</td>
<td>13.3</td>
<td>69.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha_{\text{obs}} )</td>
<td></td>
<td>2.5</td>
<td>6.0</td>
<td>23.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.3  SEM micrographs of PZT films annealed at 525°C for (a) 10 min. (b) 25 min. and (c) 45 min.
Figure 4.4  The nucleation rate as a function of annealing time at different temperatures
where $k$ is the rate constant which depends on the nucleation and growth rate and is very sensitive to temperature, $n$ is the time exponent which is temperature independent but sensitive to the time dependence of the the nucleation rate and the growth rate and geometry of the particle. The time exponent $n$ and the activation energy of the transition can be determined by equation (4.8):

$$
\ln \ln \frac{1}{1-X_t} = \ln k + n \ln t \tag{4.8}
$$

By plotting $\ln \ln (1/1-X_t)$ against $\ln t$ as shown in Figure 4.5, the slope is the time exponent $n$ and the y axis intercepts is $\ln k$. The $n$ values for 525°C, 550°C, and 575°C are 2.1, 2.6, and 2.0, respectively. When $2 \leq n \leq 3$, it indicates a 2 dimensional growth with a decreasing nucleation rate [69] which is in agreement with the other results in this study. For the ideal two-dimensional growth process with constant nucleation and growth rate, the $n$ values is 3.0 as derived in equation (4.6), the decreasing nucleation rate in this experiment may account for the $n$ values smaller than 3.0 and in the present cases, $n = 2.0 - 2.6$.

The reaction rate constants which were measured for 3 different temperatures and the corresponding data are presented on the Arrhenius plot given in Figure 4.6. From the measurements of volume fraction of the perovskite phase, the activation energy of the perovskite formation was found to be 494 kJ/mol. Likewise, from the measurements of nucleation particles and the growth of the perovskite, the activation energy of nucleation and the activation energy of growth of perovskite phase were determined to be 441 kJ/mol and 112 kJ/mol, respectively.
Figure 4.5  Avrami plot of volume fraction (ln ln \{1/1-X\}) as a function of the natural logarithm of annealing times
Figure 4.6  
An Arrhenius plot of reaction constant as a function as a function of the reciprocal of temperature
4.2.4 X-ray Diffraction Analysis

Previous x-ray diffraction results (46) showed that when the as-sputtered films were annealed at 400°C for up to 20 hours, no definitive peak was observed and the film remained amorphous. As the annealing temperature was increased to 450°C, a fairly broad pyrochlore major peak was found after 5 hours of annealing. At 550°C both perovskite and pyrochlore phases were present. Formation of single perovskite phase was observed at or above 600°C. Figure 4.7 shows the emergence of the perovskite phase from the pyrochlore phase when each of the three PZT films was heated to 550°C for 2 minutes, 6 minutes and 15 minutes, respectively. The pyrochlore phase which is identified by the broad (222) peak is shown to form at relatively short annealing time at 550°C. The corresponding volume fractions of perovskite phase measured by SEM are 5%, 22%, and 70%, respectively. In this case, the volume fraction of the perovskite from SEM analysis and the relative intensity of the perovskite from the x-ray analysis are in good agreement.

4.2.5 Summary

The diffraction data of metastable PZT pyrochlore phase is calculated by a computer program and the result is confirmed by x-ray and electron diffraction experiments. In the thin film form, the paraelectric pyrochlore phase transforms into ferroelectric perovskite phase at temperatures around 525°C. Thin cylindrical plates of perovskite phase are grown in 2 dimensions parallel to the plane of the substrate. The growth rate is relatively constant and is believed to be interface controlled. The activation energy of the reaction is 494 kJ/mol.
Figure 4.7  XRD of the PZT films annealed at 550°C for (a) 2 min. (b) 5 min. and (c) 15 min.
4.3 LOW TEMPERATURE PROCESSING

In order to integrate PZT films into the existing semiconductor processes, many process problems have to be solved. One of these problems is the high temperature post-deposition annealing needed to form the desirable perovskite phase. This annealing is required because most of the as-deposited films are amorphous, and they form an intermediate nonferroelectric pyrochlore phase before the formation of the perovskite phase. The transformation temperatures for initial perovskite formation \( T_i^{\text{per}} \) and complete perovskite formation \( T_c^{\text{per}} \) of the PZT films are functions of the compositions and of the type of substrate used for deposition. Typical annealing temperatures for the 53/47 films are from 650°C to 750°C. At these annealing temperatures, interdiffusion among the PZT films, the contact electrodes, and the underlying metallization becomes a genuine concern; furthermore, thermal stresses developed during the high temperature annealing may affect the long term reliability of the device.

The objective of this study is to develop novel processes for thin film deposition which require a lower perovskite transformation temperature. In this study, two different approaches for low temperature perovskite transformation are investigated. They are: (1) high pressure transformation and (2) a two-step seeding process. These processes are described in the following two sections.

4.3.1 High Pressure Transformation

Generally, the pyrochlore to perovskite transformation is polymorphic. In other words, compounds of identical chemical composition can transform from one phase
to another by crystal structure change. The difference of Gibbs free energy between each of the two polymorphs can be expressed as:

\[ \Delta G = \Delta E - T \Delta S + P \Delta V \]  

(4.9)

At the equilibrium transformation temperature, the two polymorphs should have the same Gibbs free energy and thus,

\[ \Delta E - T \Delta S + P \Delta V = 0 \]  

(4.10)

In order to maintain balance in equation (4.10), increases in pressure results in increase in internal energy, decrease in entropy, or both assuming the volume is constant. Pyrochlore structures in general have more open crystal structures when compared to perovskite structures. In the case of PZT materials, the pyrochlore phase has a specific volume about six percent larger than that of the perovskite structure. Consequently, increasing the pressure encourages the pyrochlore phase to transform to the perovskite phase.

Examples of polymorphic transformation under high pressure can be found in many studies [70–71]. Viskov and co–workers reported that many thallium–containing compounds would not transform from the pyrochlore structure to the perovskite structure even when they were annealed at 800°C. But these same compounds would transform to the perovskite phase at 600°C under a pressure of 40–60 kbar [70]. In this work, the transformation temperature – pressure relationship was explored and the results are discussed in section 4.3.3.
4.3.2 Experimental Procedures

In this study, a high pressure synthesis was performed with help from the Fluid Inclusion Laboratory in the Geology Department. PZT samples were first deposited on platinum coated silicon substrates. These PZT films having film thicknesses of 350 nm and dimension of 0.6 cm by 1.5 cm were inserted into platinum capsules, backfilled with pure oxygen and then sealed by electrical resistance welding. Each capsule was placed into a super alloy high pressure container. Each container was then placed in a tube furnace and pressurized by a pressure line to the desired pressure.

4.3.3 High Pressure Perovskite Formation

PZT films of 53/47 composition were annealed at 450°C for 5 hours in the same setup under both normal pressure and at an elevated pressure of 50 bar. A previous study [46] had shown that only the pyrochlore phase was present when samples were annealed at 450°C even up to 20 hours. Temperatures close to 600°C are needed to transform pyrochlore to perovskite phase at atmospheric pressure. For the PZT films annealed at normal atmospheric pressure, only pyrochlore phase was observed. However, as the pressure was increased to 50 bar, only the perovskite phase was observed. This is evident in the X-ray diffraction as shown in Figure 4.8. The perovskite phase formed under high pressure, which has a fine grain structure with a fine grain size of about 0.3μm.

The theoretical predicted condition for the conversion of pyrochlore phase to perovskite phase as specified by Viskov [70] is such that if the ratio of the (Volume
Figure 4.8  XRD of the PZT films annealed at (a) atmospheric pressure and (b) at a pressure of 100 bar
of perovskite/Volume of pyrochlore) raised to the third power is less than 0.40, then, it is possible to convert pyrochlore to perovskite. In the case of 53/47 PZT films, the ratio of specific volume to the third power is about 0.396 which does satisfy the above requirement. In summary, it can be shown that high pressure can be used to lower the transformation temperature of the pyrochlore to perovskite transformation. Although this high pressure process is unlikely to be used in large scale production, this high pressure process confirms the fact that the pyrochlore to perovskite transformation involves a volume decrease.

4.3.4 Seeding Process

Kinetics of nucleation and growth of the PZT perovskite phase has been studied in Section 4.2 by scanning electron microscopy [72]. Analysis of the kinetic data showed that the activation energies of the nucleation and growth of the 53/47 PZT perovskite phase are 441 kJ/mole and 112 kJ/mole, respectively. A separated kinetics study of PZT perovskite transformation by an optical method also indicated that the activation energy of the nucleation is much higher than that of the growth of the perovskite phase [73]. Chen and Mackenzie have also commented qualitatively that the perovskite transformation is nucleation controlled [67]. Therefore, the transformation is believed to be nucleation controlled. Since the nucleation is the rate-limiting step of the transformation, the kinetics of the transformation can be expedited when a large amount of nucleation sites are created on the substrate. The underlying principle of the two-step process is to provide a large number of such favorable nucleation sites by the seeding layer.
According to the phase diagram of PZT [74], the boundary between the ferroelectric and antiferroelectric phase is around 8 mole % of Ti. Any composition of PZT with Ti content higher than 8% is in the ferroelectric region. The commonly used composition is about 53% Zr and 47% Ti (53/47), which is located at the morphotropc phase boundary. Films of this composition possess the very good ferroelectric properties required for fast and reliable memory switching.

Seeding processes have been demonstrated to enhance the kinetics of the crystallization of gel particles [75] and to encourage the formation of epitaxial film [76]. A simple two-step process which utilizes the seeding process to produce ferroelectric films at low transformation temperatures is described. This process can be, in principle, applied to other material systems that undergo a similar polymorphic phase transformation.

4.3.4.1 Experimental Procedures

A. Precursor and film preparation

PZT thin films were fabricated from sol–gel precursors (0.4M) of lead acetate, titanium isopropoxide, and zirconium n–propoxide dissolved in glacial acetic acid and n–propanol. The proper amounts of Zr and Ti alkoxides were premixed in the presence of propanol and acetic acid before the addition of lead acetate. These solutions were hydrolyzed with appropriate amounts of water and were further diluted with propanol and acetic acid to form the final precursors. Seven precursors with different Zr and Ti compositions were prepared and the Zr/Ti ratios are 0/100, 30/70, 40/60, 53/47, 65/35, 75/25, and 100/0. The compositions of the films made
by these precursors were characterized by an electron microprobe. The compositions of each of the films prepared by the sol–gel method were within 1 atomic percent of their target compositions.

Thin films were deposited by spin coating on single crystal sapphire substrates. The thicknesses of the films were controlled by the spin speed and the concentration of the precursor. After spin coating, each film was placed on a hot plate at 150°C for 5 minutes to remove the organic solvents. Film thickness can be built up by repeating the spin coating and the drying. Final annealing was performed in a tube furnace in air.

B. Two-step process

In this study, the first step involved depositing a very thin layer of lead titanate (PT) onto a sapphire substrate. The spin speed used was 9000 rpm for 30 seconds. The film was then heated at 150°C for 5 minutes and annealed at 500°C for 15 minutes in air. The final PT film thickness was about 45 nm. At this stage, the PT film had already transformed into the perovskite structure.

The second step involved depositing the PZT films with the desired composition and thickness onto the PT-coated substrate. In this study, a Zr/Ti composition of 53/47 and a thickness of 300 nm were chosen based on previous experiments which had shown that PZT films having this combination exhibited very good ferroelectric properties. PZT films were obtained by spinning and drying twice with a spin speed of 1500 rpm. Final annealings were performed in a tube furnace at temperatures ranging from 500°C to 750°C. These films were then characterized by x-ray diffraction, scanning electron, and optical microscopy.
4.3.4.2 Low Temperature Transformation by Seeding

In most of the thin film deposition techniques, such as the sol–gel method, metalorganic decomposition (MOD), and sputtering, as–deposited PZT films generally have amorphous structures. Post–deposition annealing is needed to produce the desirable ferroelectric perovskite phase. The amorphous structure first transforms into a metastable pyrochlore phase, and this pyrochlore phase then transforms into the perovskite phase at a higher annealing temperature. The pyrochlore phase has an oxygen–deficient fluorite structure and it is non–ferroelectric. The details of the pyrochlore to perovskite transformation have been studied by transmission electron microscopy [51]. The transformation of the pyrochlore phase to the perovskite phase can be monitored by x–ray diffraction. For the 53/47 PZT films, the perovskite phase has sharp and well–defined major peaks at 2θ of 31.3°, 38°, and 55.5°. The pyrochlore phase has very broad major peaks at 2θ of 29.5°, 34.2°, and 49.2°. Figure 4.9 shows the x–ray diffraction spectra of PZT 53/47 films annealed from 500°C to 650°C for a fixed annealing time of 15 minutes. At 500°C, only the pyrochlore phase is found. At 550°C, both the perovskite phase and the pyrochlore phase are present in the film; and at 600°C, the transformation is completed, and only a single perovskite phase is present. Thus, in this case, the $T_{i}^{\text{per}}$ is about 525°C and the $T_{c}^{\text{per}}$ is 600°C for the 53/47 PZT films.

Similar experiments have been performed on films with compositions ranging from pure lead titanate (PT) to pure lead zirconate (PZ); the results are summarized in Figure 4.10. Figure 4.10 illustrates the presence of the perovskite and pyrochlore phases as a function of annealing temperatures and compositions. The $T_{i}^{\text{per}}$ and $T_{c}^{\text{per}}$ of the Zr–rich phases are much higher than that of the Ti–rich
Figure 4.9  XRD of unseeded 53/47 PZT film annealed at (a) 500°C (b) 550°C (c) 650°C for 15 min. The symbols PE and PY indicate perovskite phase and pyrochlore phase, respectively.
Figure 4.10  
Initial and complete perovskite transformation temperatures as a function of Zr and Ti composition in the PbZrO$_3$–PbTiO$_3$ solid solution
Figure 4.11  Grain size of the perovskite phase as a function of Ti atomic concentration
phases. The $T_c^{\text{per}}$ of the PT film is 500°C, which is 100°C lower than that of the 53/47 PZT film.

In addition to the notable variation of transformation temperatures as a function of composition, the microstructures of the perovskite phases of PZT films are greatly influenced by the composition (Zr/Ti ratio) as shown in Figure 4.11. Figure 4.11 plots the grain size of the perovskite phase of the PZT films as a function of Ti atomic concentration. From pure PT to 30/70 PZT films, the grain size is very small (about 0.3 μm) and the grain size distribution is very small. From 40/60 to 65/35 PZT films, the grain size increases moderately and the grain size distribution has a much larger variation. From 75/25 PZT to PZ films, the grain size is much larger when compared to PZT films at lower Ti atomic concentrations. Also, for the Ti-rich PZT films (from PT to 30/70 films), the grain size is a weak function of the annealing temperature. In other words, once the formation of the perovskite phase is completed at or above $T_c^{\text{per}}$, the increase of grain size due to further annealing is barely discernible. On the contrary, the grain size of the Zr-rich PZT films (from 65/35 to PZ films) rapidly increases as the annealing temperature increases. Figure 4.12 shows the grain structures of PZT films of different compositions. The Ti-rich phases have much smaller grain sizes when compared to those of the Zr-rich phases. The grain size distribution is much more uniform in the Ti-rich phases.

Based on these microstructural observations, we can surmise that the Ti-rich phases should have lower nucleation barriers than the Zr-rich phases. A lower nucleation barrier means that more nuclei can form at a particular annealing temperature. In the case of the Ti-rich phases, site saturation might happen at $T_i^{\text{per}}$ when all the potential nucleation sites are consumed. Consequently, the grain
Figure 4.12 Microstructure of the perovskite phase as a function of compositions
size of the Ti-rich phases is only determined by the spacings between nuclei and this would explain the small deviation of grain size distribution observed. On the other hand, in the case of Zr-rich phases, much fewer nuclei are formed at $T_{i}^{\text{per}}$ and most of the nuclei can grow into much larger grains. Nevertheless, higher temperatures are required to initiate transformation because the transformation is nucleation controlled. If the nucleation sites are randomly distributed and only a small number of nuclei are present, it is very likely that there will be a large variation in grain size; this is what occurred in the Zr-rich samples.

For the two-step process in this study, PT was chosen as the first layer to be deposited. Subsequently, 53/47 PZT films were deposited on top of the PT films and annealed at temperatures ranging from 450°C to 600°C in 25°C intervals at fixed annealing times of 15 minutes. These two-layer films will be called PT-PZT films hereafter.

The results of $T_{c}^{\text{per}}$ as a function of annealing temperature and time are summarized in Figures 4.13 and 4.14. Figure 4.13 denotes that at a fixed annealing time of 15 minutes, the $T_{c}^{\text{per}}$ of the PT-PZT film is 525°C. As the annealing time is increased to 1 hour, the $T_{c}^{\text{per}}$ is further decreased to 500°C, as seen in Figure 4.14. Hence, the transformation temperature of the 53/47 PZT films is decreased by 100°C due to the presence of the seeding layer.

In the PZT thin film system, previous work has shown that nucleation is the rate-limiting step; hence, the lowering of $T_{c}^{\text{per}}$ by the two-step process is most likely related to the lowering of the activation energy for the nucleation of the perovskite. The two energy barriers that oppose nucleation are the strain energy and the surface energy that are incurred during transformation. However, the strain energy should not depend on whether or not the PZT film is formed in the presence
Figure 4.13  XRD of the seeded 53/47 PZT films annealed at (a) 500°C (b) 525°C and (c) 550°C for 15 min.
Figure 4.14  XRD of the seeded 53/47 PZT films annealed at 500°C for (a) 15 min. (b) 30 min. and (c) 1 hr.
of a PT seeding layer. Thus, the major effect of the two-step process is the possible decrease of surface energy, which in turn, increases the nucleation rate.

The lowering of the surface energy can be explained by the lattice matching of the PZT/PT and PZT/sapphire interfaces. Both the PT and the 53/47 PZT phases have a tetragonal "perovskite" structure. The lattice parameters, $a$ and $c$, for the PT and the 53/47 PZT structures are 0.3899, 0.4036 nm and 0.4153, 0.4146 nm, respectively [9]. The sapphire substrate has a rhombohedral structure but is commonly represented by a hexagonal unit cell. The lattice parameters, $a$ and $c$, are 0.4758 and 1.2991 nm [77]. For the PZT/PT interface, the lattice mismatch in the $a$ direction is about 3.4% and less than 0.2% in the $c$ direction. For the PZT/sapphire interface, there are no common matching planes. If the lattice mismatch is small, the interface can be coherent or semicoherent. Either coherent or semicoherent interfaces will have much lower surface energies when compared to incoherent interfaces. It is plausible that a seeding layer, which has a crystal structure similar to that of the deposited film and has a small lattice mismatch, can provide the preferred nucleation sites and thus increases the formation kinetics of the deposited film.

Figure 4.15 shows a comparison of the grain sizes of the 53/47 PZT films with and without the seeding layer after each was annealed at the same temperature of 650°C. The grain size of the 53/47 film without the seeding layer is about 3.0 μm and is an order of magnitude larger than the grain size of the film with the seeding layer. In fact, the grain size of the PT–PZT film is very close to the grain size of the PT seeding film. This observation suggests that the seeding layer provides a large number of nucleation sites for the formation of the perovskite phase. Since the transformation rate is nucleation controlled, the grain size of the PT–PZT film is
Figure 4.15  Microstructure of (a) unseeded PbTiO$_3$ film annealed at 650$^\circ$C (b) unseeded 53/47 film annealed at 650$^\circ$C and (c) seeded 53/47 film annealed at 650$^\circ$C
only limited by the distance that the perovskite phase can grow before the grains impinge on each other. Further grain growth by Oswald ripening is a very slow process due to the effect of thermal grooving, especially in the form of a two-dimensional thin film [78].

In summary, we have established that the grain size of the PZT film with a high Zr/Ti ratio is directly related to the grain size of the seeding layer as shown in Fig. 7. Hence, we can effectively control the grain size of any top layer film by choosing a seeding layer with the desired grain size.

4.3.4.3 Electrical Properties of Seeded PZT Films

Electrical properties of the seeded PZT films were measured by a modified Sawyer–Tower hysteresis measurement setup. Details of the electrical measurements can be found in Section 6.2. The results in terms of saturation polarization ($P_s$), remanent polarization ($P_r$), and coercive field ($E_c$) are summarized in Table 4.2.

For the unseeded PZT films, well-defined hysteresis loops were not observed for samples annealed at temperature lower than 600°C. For the seeded PZT films, switching was observed for samples annealed at 550°C, and at 525°C if the samples are annealed for 1 hour instead of 15 minutes. As discussed in the last section, $T_c^{per}$ can be lowered by 75°C by using a seeding process. But from the standpoint of electrical properties, only an improvement of 50°C was attained. The reason for the discrepancy between the $T_c^{per}$ and the temperature at which hysteresis loop is attained could be due to the sensitivities of these two measurement methods (the XRD and the electrical tester). Electrical properties are a strong function of the

-102-
microstructure in the PZT films. Any small amount of nonswitching pyrochlore phase would greatly degrade the ferroelectric properties. On the other hand, the limit of detection of XRD for a second phase in a matrix phase is about 2 atomic percent, so it is possible that a small amount of pyrochlore may be present at $T_c^{\text{per}}$.

From these electrical measurements, we also observe that the $P_s$, $P_r$, and $E_c$ of the seeded PZT films are higher than the unseeded films. The hysteresis loop of the seeded samples appears much wider or 'fatter' than those from the unseeded samples. This could be attributed to that fact that it is more difficult to switch a PbTiO$_2$ film than a comparable 53/47 film. The much higher $E_c$ values reflect this difficulty of switching the multilayer seeded samples.

<table>
<thead>
<tr>
<th>Process</th>
<th>Temp (°C)$^*$</th>
<th>$P_s$ (μC/cm$^2$)</th>
<th>$P_r$ (μC/cm$^2$)</th>
<th>$E_c$ (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>unseeded 53/47</td>
<td>600</td>
<td>45</td>
<td>38</td>
<td>30</td>
</tr>
<tr>
<td>seeded 53/47</td>
<td>550</td>
<td>32</td>
<td>8</td>
<td>35</td>
</tr>
<tr>
<td>seeded 53/47</td>
<td>575</td>
<td>75</td>
<td>60</td>
<td>49</td>
</tr>
<tr>
<td>seeded 53/47</td>
<td>600</td>
<td>73</td>
<td>60</td>
<td>53</td>
</tr>
</tbody>
</table>

$^*$ annealing temperature

4.3.4.4 Summary

We have demonstrated a two-step seeding process which can lower the pyrochlore to perovskite transformation temperature of the 53/47 PZT films by 100°C. Electrical properties were also obtained for those seeded samples which is annealed 50–75°C lower than $T_c^{\text{per}}$ of the unseeded PZT films. The nucleation rate of the film can be controlled by the introduction of the seeding layer. The results from x-ray diffraction and microstructural studies supports this supposition.
Chapter 5 Stress in Lead Zirconate Titanate Thin Films

This chapter is divided into four sections. In the first section, the origins of thin film stress and the techniques of measuring thin film stresses are described. Assumptions and limitations of the governing equation of thin film stress will be discussed in Section 5.2. Stress measurements to evaluate physical properties such as thermal expansion coefficients, and elastic constants of the PZT films are discussed in Section 5.3. More importantly, stress–temperature measurements can be used to study the phase transformation of PZT films of various compositions.

5.1 INTRODUCTION

Mechanical stress is frequently present during and after thin film depositions. Film cracking occurs when the induced tensile stress exceeds the tensile strength of the film. Delamination and buckling of films occur when excessive compressive stress is present. In addition to these mechanical failures, metallization hillock, stress–induced void formation and stress–related electrical degradation are some of the stress–related reliability problems commonly found during thin film processing. Stress measurements are commonly used in the semiconductor industry to monitor variability in the thin film deposition.

For the PZT system, film stresses can alter the switching properties, the Curie
temperature as well as the phase formation. The study of stress during the post-deposition annealing provides much-needed information regarding the transformation stress of the pyrochlore to perovskite transformation. There are reasons to believe that these transformation stress is the one of the major driving forces for the perovskite formation. However, to the best of my knowledge, there is no published data on the thin film stress of PZT films. The objective of this study is to investigate the stress formation of the PZT films and from these results, to obtain a better understanding of the relationship between the stress and phase transformation of the PZT films. More detailed study of these transformation stress can be found in Section 5.3.

5.1.1 Origins of Stress in Thin Films

The origin of stresses in thin films has been reviewed extensively by Campbell [79] and Hoffman [80]. The intent of this section is to give a brief overview of the origins of the thin film stress. In general, the stresses in thin films can occur during deposition process and/or post-deposition annealing and the total film stress can be expressed as:

\[ \sigma_t = \sigma_{th} + \sigma_e + \sigma_i \]  

where \( \sigma_t = \) total stress, \( \sigma_{th} = \) thermal stress, \( \sigma_e = \) extrinsic stress and \( \sigma_i = \) intrinsic stress.

Thermal stress is primarily caused by the difference of the thermal expansion between the film and the substrate during temperature changes. The thermal stress
can be expressed by:

\[ \sigma_{th} = \frac{E_f}{(1-\nu_f)} (\alpha_f - \alpha_s) (\Delta T) \]  \hspace{1cm} (5.2)

where \( \alpha_s \) is the thermal expansion coefficient of the substrate, \( E_f, \nu_f \) and \( \alpha_f \) are the Young's modulus, Poisson's ratio and thermal expansion coefficient of the film, respectively, and \( \Delta T \) is the temperature difference.

Extrinsic stress is caused by the volume changes that mostly associated with phase transformation and other film–ambient interactions. The extrinsic stress can be expressed by:

\[ \sigma_e = \frac{E_f}{(1-\nu_f)} \left[ \frac{\Delta V}{V} \right] \]  \hspace{1cm} (5.3)

where \( \Delta V/V \) is the fractional volume change in the film.

Intrinsic stress or growth stress accounts for all the displacement constraints encountered during thin film growth processes except for those caused by the thermal stress and the extrinsic stress. Some of the examples are: (1) coalescing of island of materials during the initial stage of film formation [81], (2) atomic peening during sputtering [82], (3) lattice mismatch between film and substrate, and (4) impurities or gas incorporation in the film.

In the case of PZT films, the intrinsic stress is mainly caused by the drying of the solvents to form the amorphous film. The extrinsic stresses can be related to one of the following processes depends on the temperature and the thermal history of the films. These anticipated processes are the evaporation of the organics from the oxide network, the pyrochlore to perovskite transformation and the cubic to
tetragonal/orthorhombic transformation at the Curie point.

5.1.2 Methods of Stress Measurement

Stresses in thin films can be measured by x-ray diffraction [83], substrate curvature [84], cantilevered bending beam [85], optical interferometry [86], and laser scanning [87]. Among these different stress measuring techniques, the calculations of thin film stress are primarily based on two principles. The stress can be calculated either by measuring the curvature of the substrate before and after the processing or the x-ray peak shifts due to the lattice distortion. Recently, x-ray diffraction (especially in the glancing angle mode) and laser scanning are the two methods most commonly used to study thin film stress. Both techniques are non-contact and generally non-destructive, and can produce accurate and consistent results. The x-ray diffraction method requires more expertise about the crystallographic knowledge of materials and it is relatively slow when compared to the laser scanning method. However, the sample geometry requirement for the laser scanning is much more stringent and it would not work well with very small samples or asymmetric samples, for instance, a rectangular plate. Because of this sample geometry restriction, x-ray diffraction is much more useful in samples of small geometry such as the IC interconnect and laser scanning is more useful in the study of the whole wafer (up to 200mm). In this study, all the thin film stress measurements were done by the laser scanning since this method is more relevant to our study. The stress calculation of the laser scanning method is based on the curvature method. The curvature method, its assumption and its limitation will be discussed in the following section.
5.2 CURVATURE METHOD, ASSUMPTIONS AND LIMITATIONS

The biaxial stress presented in the film can be partially relaxed by bending the substrate elastically, and measurement of these substrate bending by measuring its curvature is a common method of determining the stress in the film. This method was originally derived by Stoney [88]. The Stoney's equation for the disc geometry can be expressed as:

\[ \sigma = [E/(1-\nu)]_s \frac{t_s^2}{8 t_f} \left( \frac{1}{R} \right) \]  \hspace{1cm} (5.4)

where \( \sigma \) is the average stress, \( t_s \) and \( t_f \) are the substrate and film thicknesses, \([E/(1-\nu)]_s\) is the elastic constant of the substrate and \( R \) is the radius of curvature of the substrate.

The complete derivation of equation (5.4) can be found in [88] and was reviewed by [87]. The Stoney's equation is very easy to use since \( t_s, t_f \) and the elastic constant of the substrate is easily determined and the only variable that needs to be measured is the radius of curvature before and after the thin film processing. One advantage of the curvature method is that it is film-independent. In other words, the physical properties of the film, which are sometimes very difficult to determine, is not needed in the stress calculation. On the other hand, this equation is valid only if the following assumptions are satisfied:

1. The bending of the substrate reaches equilibrium when the substrate is strained by the film.
2. The film–substrate bond is strong enough to suppress slippage (decohesion).
3. The substrate is linear—elastic, homogeneous, and uniformly thick. The substrate is not plastically deformed.

4. The bending displacement is small when compared with the thickness of the substrate.

5. The stress is uniform throughout the film thickness.

6. No stress relief or change in elastic constants take place as the film is built up.

7. The thickness of the film is much smaller than the thickness of the substrate.

Some of the assumptions list above may not be totally justified in practical applications. For instance, the stress in the film is not expected to be completely uniform under many circumstances, and the stress we normally measured is the average stress of the whole film; also, stress relief is known to happen in many cases, which complicated the stress measurements. Some of the limitations that greatly influence the validity of the stress measurement are assumptions 3, 4, and 7. The difficulties of the Stoney's equation are the omissions of the effect of substrate—film thickness ratio and the effect of the ratio of the elastic constants. A classic paper by Brenner and Senderoff [89] discussed the effect of thickness ratio and elastic constant ratio on unconstrained plate which is similar to most film growth situations. They proposed the stress correction M by which the simple Stoney average stress $\sigma$ should be multiplied to obtain the corrected average stress $\sigma_{cor}$.

$$\sigma_{cor} = \sigma (1 + M)$$

(5.5)

The two term approximation correction factor Brenner suggested is
\[ M = (1 + \eta/\beta) \]  \hspace{1cm} (5.6)

where \( \beta \) is the substrate to film thickness ratio \((t_s/t_f)\) and \( \eta \) is the ratio of the elastic constants \( E_f/1-\nu_f \) and \( E_s/1-\nu_s \). \( E \) is the Young's modulus and \( \nu \) is the Poisson's ratio. The subscripts \( f \) and \( s \) refer to film and substrate, respectively.

A more complete correction factor was proposed by Klockholm [90] which takes into the account of the higher order variations. The Klockholm factor is:

\[ M = 1 + \frac{\beta^3(\eta+1)}{(\beta^3+\eta)(\beta+\eta)} + \frac{3\eta \beta (\beta+1)}{2} \]  \hspace{1cm} (5.7)

Figures 1 (a), (b), and (c) show the comparisons between the Klockholm correction and the two-term approximation correction, for \( \beta > 1000 \), there is not much difference between the two corrections and in fact \( M \) is so close to 1 that the simple Stoney's equation is valid. For \( \beta < 10 \), the effect of elastic constant becomes important and for \( \eta = 10 \), can result in error of \( 20 - 100\% \) if no correction is taken. In most cases, the range of \( \eta \) should be within 0.1 to 10. Nevertheless, the elastic constants of some films are difficult to determine; and also, for amorphous films, the elastic constants can be differed by as much as 40 \% when compared to the bulk materials. As for crystalline films, the difference of elastic constants between the films and bulk materials generally less than 10\%, and for first approximation, at least for crystalline films, the elastic constant of the bulk material can be used for stress calculation.

For the problem of plastic deformation of the substrate, generally, most of bulk single crystals will begin to undergo a plastic deformation when the shear stress is of the order of \( 10^{-4} - 10^{-5} \) times the shear modulus of the material. When the film
Figure 5.1  
(a) Correlation factor (M) as a function of thickness ratio at $E_f/E_s$ of 0.1
Figure 5.1 (b) Correlation factor (M) as a function of thickness ratio at $E_f/E_s$ of 1
Figure 5.1 (c) Correlation factor (M) as a function of thickness ratio at $E_f/E_s$ of 10
thickness is very thin, compared to the substrate thickness, the plastic flow by
dislocation movement is negligible. But if the $\beta$ is $> 10^4$, we have to consider
whether the plastic flow may take place in the substrate.

In summary, when the film thickness is much smaller than the substrate, the
Stoney's equation is valid especially when the $\eta$ is small. A two-term
approximation, equation (5.5), is good for most of the cases except in the extreme
case, where the film thickness is not much thinner than that of the substrate. As a
rule of thumb:

For

(i) $\beta > 1000$ and any $\eta$ or

(ii) $\beta > 10$ and $\eta < 0.2$

$M$ is sufficiently close to 1 that no correction is needed.

5.3 STRESS IN PZT THIN FILMS

Mechanical stress in thin films often leads to film cracking or buckling. In the
case of PZT films, film cracking often occurs when silicon substrates are used. The
cracking is caused by the large thermal stress generated during thermal processing
of the PZT films and the Si substrates. The coefficient of linear thermal expansion
($\alpha_{th}$) of Si is about $2.5-3.5 \times 10^{-6}/^\circ C$ [91] while $\alpha_{th}$ for PZT films varies from $7-10$
$\times 10^{-6}/^\circ C$ depending on composition [92]. Better choices of substrate materials such
as platinum and sapphire greatly improves the thermal cracking problem. The $\alpha_{th}$
for Pt and sapphire is $9.0$ and $7.7 \times 10^{-6}/^\circ C$, respectively [91,93]. The $\alpha_{th}$ of these
two substrates are well matched with those of the PZT films.
In addition to the cracking problems, thin film stresses are reported to cause
degradations in electrical properties, and changes in transformation temperature. In
this work, the thin film stress is studied as a function of annealing temperature.
Intrinsic growth stresses ($\sigma_I$), extrinsic transformation stresses ($\sigma_e$) and
transformation temperatures can be obtained from these stress–temperature plots.
PZT films with three different compositions were investigated and their stress
response to the changing temperature was documented for each in Section 5.3.2.

5.3.1 Experimental Procedures

Stress measurements were conducted on the Flexus F2400 thin film stress
tester, which is capable of running in–situ stress measurements at temperatures up
to $900^\circ$C. This stress tester uses a laser and a position–sensitive detector to
measure the displacement of the laser reflection from the wafer surface. Theses
displacements are converted to radii of curvature and thin film stresses are
calculated by the Stoney's equation. The sensitivity of this tester is limited to a
radius of curvature of 4000 m, which corresponds to about 1.3 MPa for a 0.3 $\mu$m
film on a 525 $\mu$m thick substrate. In this experiment, $\beta$ was determined to be 1750,
and $\eta$ varied from 0.6–0.9. Hence, no correction factor is needed and the thin film
approximation is valid. Detailed operations of this stress tester can be found in
Appendix B.

PZT films with three compositions (0/100, 53/47 and 75/25) were deposited on
100 mm diameter Pt coated Si wafers by the sol–gel process described in Appendix
A. Film thicknesses were around 0.3 $\mu$m. 100 mm diameter single crystal Si wafers
and 50 mm diameter sapphire wafers were also used. The film configuration of the
Figure 5.2  Schematic diagrams of anticipated stress–temperature (S–T) plot
Pt wafers is as follows: Pt (400 nm)/Ti (30 nm)/SiO$_2$ (200 nm)/{100} Si substrate.

For each sample, two identical heating–cooling cycles were run sequentially. The samples were heated from room temperature to 750$^\circ$C and cooled down to room temperature twice. These temperature cycles will be designated as 1st run and 2nd run. The rationale for measuring with two heating–cooling cycles will be apparent when the results are discussed in Section 5.3.2. The heating rate was 5$^\circ$C/min, cooling rate was 2.5$^\circ$C/min, and the atmosphere was air.

5.3.2 The Study of Transformation Stresses of PZT Films

Any transformation or chemical reaction involving a constrained volume change will also lead to a change in stress. During thermal processing, PZT films will undergo a volume change for at least 4 different reasons. Figure 5.2 (a) and (b) are schematic diagrams, which indicate the locations (region 1–5) where anticipated changes in stress may occur. With reference to Figure 5.2, these regions of interest are:

In the 1st run:

1. Growth stress due to the evaporation of volatile solvents (at room temperature).
2. Evaporation of the organic ligands (200–350$^\circ$C).
3. Pyrochlore to perovskite phase transformation (450$^\circ$C–750$^\circ$C).
4. Cubic to non–cubic (tetragonal or rhombohedral) transformation (at Curie temperature).

In the 2nd run:

5. Non–cubic to cubic or cubic to non–cubic transformation (at Curie temperature).
The anticipated signs of film stresses (tensile or compressive) of all the transformations mentioned above should be tensile except the non-cubic to cubic transformation during cooling. The magnitude of the stress depends partly on the magnitude of the volume change. Nevertheless, a high compressive thermal stress is expected during heating and an equally high tensile thermal stress is expected during cooling. These high thermal stresses are caused by the large difference of the $\alpha_{th}$ between the PZT films and the Si substrates. The thermal stress might dominate the shape of the stress-temperature profiles.

The choice of substrates for in-situ heating stress measurements is not trivial because PZT films generally are reactive with many types of metals and non-metals at high temperatures. The substrate should be inert to PZT materials at temperatures up to 750°C in ambient condition. Pt-coated substrate is the natural choice because it is also used in the electrical property measurements. The problems with Pt-coated substrate, however, are mainly in term of cost, availability and the added complexity of the multi-layer configuration. Since Pt-coated Si wafers are not commonly available from the vendor and the whole wafer is needed for each test run, availability is always a problem.

Other alternative substrates have been sought but with very limited success. Bare Si wafers and Pd-coated Si wafers were used in the heating experiments but both of them reacted with PZT films at high temperature. Single crystal sapphire wafers were also used. Sapphire is very inert with most chemicals; indeed, reaction with the PZT film at high temperatures was not observed.

However, the problem in using sapphire wafers was the low signal-to-noise ratio obtained with the Flexus tester. Since this ratio depends on the optical reflectivity of the sample. The polished surface of a sapphire wafer has a very low
Figure 5.3  (a) 1st run S–T plot of Pt substrate without film deposition
PLT Pt on Si 750C 2nd run

Figure 5.3 (b) 2nd run S–T plot of Pt substrate
optical reflectivity when compared with that of Si or a typical metal. For example, reflectivities in terms of detector voltage for the Pt, Si and sapphire wafers are 5.5 V, 2.5 V and 0.5 V, respectively. The lowest detection limit for the Flexus tester is 0.35 V. Therefore, the stress measurements using sapphire wafer are very noisy and any small variation in stress becomes masked by the noise. Ideally, a substrate with a single layer configuration, highly reflective surface, inert to the deposited film at high temperature, and having $\alpha_{th}$ close to that of the deposited film is best suited for stress measurement using the Flexus tester. In short, since such an ideal substrate has not been found, Pt-coated wafer is still one of the better alternatives.

Stress measurements were first conducted on a Pt-coated Si substrate without any deposited PZT film to establish the baseline of stress as a function of temperature. These results are shown in Figure 5.3(a) and (b); the square and the inverted triangle symbols represent data obtained during heating and cooling, respectively. In the first heating–cooling cycle (1st run, Figure 5.3(a)), the stress was compressive as expected since the $\alpha_{th}$ of Pt is much larger than that of Si. But at around 270°C, a break of linearity was observed indicating there may be a transformation or reaction associated with a constrained volume decrease. This transformation continued from 270°C to 550°C. At temperatures above 550°C, another reaction may have taken place. The reaction product might come from the reaction between Si and the adjacent metal layer (Ti) since similar behavior was observed when Pd-coated Si wafer was heated to 600°C. In the cooling cycle, no obvious deviation from linearity was observed and this represented a reversible thermal stress behavior. In the 2nd run, when the stress–temperature profiles superimpose on the cooling profile of the 1st run, there is an exact match between them. This is strong evidence that after the heating cycle of the 1st run all
Figure 5.4  (a) 1st run S–T plot of PbTiO$_3$ film
Figure 5.4  (b) 2nd run S–T plot of PbTiO$_3$ film
Figure 5.5 (a) 1st run S–T plot of 53/47 PZT film
PLT-53 53/47 Pt-sub. 2nd run

Figure 5.5  (b) 2nd run S-T plot of 53/47 PZT film
Figure 5.6  (a) 1st run S–T plot of 75/25 PZT film
Figure 5.6 (b) 2nd run S–T plot of 75/25 PZT film
transformations were completed and only reversible thermal stress was observed. The difference in \( (d\sigma/dT) \) at around 570°C was probably due to an intrinsic change in thermal expansion coefficient.

Figure 5.4–5.6 show the stress–temperature profile of PZT films with Zr/Ti ratios of 0/100, 53/47, and 75/25, respectively. The transformation stresses and Curie temperatures were determined from Figure 5.4–5.6 and summarized in Table 5.1. The discussion of each region of thin film stress will occur in the sequence in which they are specified in Figure 5.2.

In region (1), the growth stress for each of the films having 3 different compositions are all very high and each growth stress is tensile. The origin of this growth stress was from drying the film twice from room temperature to 150°C very rapidly on a hot plate. The objective of the drying was to remove all the volatile solvents, alcohols, acetic acid and water from the PZT films. Based on the TGA result from Figure 2.4, 93 weight percents of the removable organics was removed from the film and this drying created a large volume shrinkage. Hence, a high tensile stress is expected in the growth stress of the sol–gel derived PZT films.

In region 2, we would expect a smaller increase in tensile stress due to the continuous removal of solvents and organic ligands. However, this small increase in tensile stresses was not observed for films of each of the 3 different compositions. This may be due to the much smaller shrinkage (7 wt.%) over a span of 300°C. Since the heating rate for this stress experiment was about 10°C/min., it is possible that the film stress due to removal of organic ligands was evenly distributed over a time span of 30 minutes and thus became less apparent.

In region 3, pyrochlore to perovskite transformations were expected to occur at temperatures from 500°C to 650°C depending on the particular compositions.
Unfortunately, another transformation was also taken place between the substrate and the adjacent layer in about the same temperature range. Thus, the total stress measured is the sum of the two stresses originating from each of the two transformations. Quantitative analysis of each individual transformation stress is difficult.

Based on the doctoral research of Gardner [94], the average or uniform biaxial stress within each layer of the multilayer films is independent of the adjacent layers and dependent only on the substrate. He emphasizes that vertical deformation will not induce stresses in other films because they are not vertically constrained. Thus, stresses can only be induced in adjacent layers as a result of contraction or expansion from the curvature of the substrate. Based on this hypothesis, the film stress caused by the pyrochlore to perovskite transformation can be estimated by taking the difference between the total stresses from measurements with and without the PZT film. The results can be found in Table 5.1. The transformation stress in the pure PbTiO$_3$ film were the highest while the one in the 53/47 was the lowest. These results are anticipated because pure PbTiO$_3$ has the largest unit cell distortion in the pyrochlore to perovskite transformation.

In Region 4, we would expect to observe the cubic to non–cubic transformation at the Curie temperature. This transformation was indicated by the discontinuity in the stress–temperature profile. Likewise, in Region 5, a change of in the film stress in the positive direction (tension) was observed during heating while compression occurred during cooling. The stress–temperature profile during heating and cooling was found to be completely reversible. When the samples underwent cubic to noncubic transformations, the elastic constants and the $\alpha_{th}$ of these samples also underwent a change. Consequently, these changes of elastic constant
Table 5.1 Mechanical Stress and Curie Temperature as a Function of Composition

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma_1$ (MPa)</th>
<th>$\Delta \sigma_1$ (MPa)</th>
<th>$T_c^{\text{exp}}$ ($^\circ$C)</th>
<th>$T_c^{\text{ref}}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTiO$_3$</td>
<td>741 (T)</td>
<td>283 (T)</td>
<td>515</td>
<td>490</td>
</tr>
<tr>
<td>53/47</td>
<td>1102 (T)</td>
<td>54 (T)</td>
<td>449</td>
<td>411</td>
</tr>
<tr>
<td>75/25</td>
<td>1206 (T)</td>
<td>74 (T)</td>
<td>369</td>
<td>335</td>
</tr>
</tbody>
</table>

$\sigma_1$ = intrinsic growth stress, (T) = tensile stress
$\Delta \sigma_1$ = total stress difference
$T_c^{\text{exp}}$ = Curie temperature measured in this experiment
$T_c^{\text{ref}}$ = Curie temperature given in the literature
and $\alpha_{th}$ resulted in the discontinuity found in the stress–temperature profiles at the Curie temperature.

In addition to the change of elastic constant and $\alpha_{th}$ at the Curie temperature, the associated volume change also induces extrinsic stress in the films. Among the three compositions studied, PbTiO$_3$ has the largest decrease in unit cell volume, from 62.8 Å$^3$ at 25°C to 62.0 Å$^3$ at 490°C. The 53/47 PZT has the lowest unit cell volume change at the Curie temperature [95]. Therefore, there is an apparent stress increase in the PbTiO$_3$ film during heating cycle at the Curie temperature while in there is only a discontinuity but no abrupt stress increase presented in the 53/47 film at the Curie temperature.

The Curie temperature can be determined by the resulting discontinuities in the '2nd run' stress–temperature profiles. The measured Curie temperatures were listed in Table 5.1 and was found to be 25°C to 38°C higher than those reported in the literature. This can be explained by the large intrinsic tensile stress present in the film. The non–cubic to cubic transition at the Curie temperature involves a volume decrease, the intrinsic tensile stress would counteract this volume decrease and therefore increase the Curie temperature.

In summary, stress–temperature measurements provide valuable information about the different types of transformations and reactions that occur during the heating and cooling of ferroelectric films. Among the different processing steps, drying the PZT films on the hot plate was found to create very high tensile stress in the films. Further modification of the sol–gel process is needed to alleviate the growth stress in the PZT films.
Chapter 6. Electrical Properties of PZT Films

The electrical properties, that are relevant to the applications of PZT thin films in the area of electronic memories, are introduced in the first section. In the second section, an experimental setup to measure the characteristic hysteretic properties of these ferroelectric films is described. The effect of composition and annealing temperature, and the effect of the thickness are investigated and results are presented in Section 6.3–6.5, respectively.

6.1 INTRODUCTION

Ferroelectric materials have a wide range of applications because of their characteristic crystal symmetries. In addition to their ferroelectric properties, ferroelectric materials also possess dielectric, pyroelectric, piezoelectric, and electro–optic properties due to their noncentrosymmetric crystal structure. Applications include capacitors, infrared detectors, thermistors, acoustic transducers, waveguide devices, optical memories and nonvolatile memories [96,97]. In our work, the intended application of the PZT films is the nonvolatile memories; therefore, only those electrical properties relevant to the ferroelectric memory will be discussed in the later sections.
The attempts of applying ferroelectric materials for the electronic memories in the 1950s and 1960s were unsuccessful because of two major obstacles [98,99]. The first problem concerned the effective isolation between each memory cell. Earlier circuit design of ferroelectric memories involved a simple row and column architecture. The probability of unintentionally switching the adjacent memory cell in such an arrangement is 1 in $10^3$ to 1 in $10^6$. This error rate is unacceptably large for commercial applications. The other problem was the high operating voltage required to switch the ferroelectric domain. Single crystal or polycrystalline ceramic ferroelectrics were used at that time and high voltages on the order of 100 volts were needed for switching because their thicknesses were in the mm range.

Recently, these obstacles have been overcome by advances in semiconductor technology. In the past few years, good quality ferroelectric films (thicknesses ranging from 0.2 to 0.5 μm) were fabricated by various methods; some of these deposition methods have been discussed in Chapter 2. Since the switching voltage is directly proportional to the film thickness, thin film capacitors require much lower switching voltages when compared to ceramic capacitors. The isolation problem is solved by separating the memory cells by pass-gate transistors. All modern DRAMs and SRAMs use such a transistorized designs.

The hysteretic responses of ferroelectric materials have been briefly discussed in Section 1.1 and 1.2. Saturation polarization ($P_s$), remanent polarization ($P_r$), and coercive field ($E_c$) are three of most important parameters that are commonly used to characterize the hysteretic responses of ferroelectric materials. The polarization values represent the amount of stored electric charge present in the saturation state and the remanent state. The coercive field is the electric field required to completely switch the ferroelectric domains from one polarization state to the
opposite polarization state. In addition to these ferroelectric properties, the shape, the squareness and the symmetry of the hysteresis loop are important to the understanding of the switching behavior of the ferroelectric films. Also, dielectric constant, dielectric loss, and leakage current are relevant properties that are needed to evaluate the merits of these thin films. In general, for memory applications, the coercive voltage should be symmetrical and smaller than 2.5 V since the standard operating voltage for electronic memories is 5.0 V. It is also desirable to maximize the switching polarization \((P_s + P_r)\) and minimize the nonswitching polarization, \((P_s - P_r)\), because the difference of these polarizations is needed to detect the stored information.

The projected requirements for the key parameters of 64 and 256-Mbit MOS DRAMs is suggested by Tasch and Parker [2]. The projected storage charge density for the 64 and 256-Mbit are 0.5–10 \(\mu\)C/cm\(^2\) and 2.5–47 \(\mu\)C/cm\(^2\), respectively. This large range of charge densities reflects the uncertainties about the exact parameters such as die size, required storage charge, and storage area used in the actual high density DRAM production. Nonetheless, the total charge capacity of these memory cells generally should be as large as possible to avoid the occurrence of soft errors.

Requirements for electrical properties that is relevant to ferroelectric memories are also specified as follows [100]:

1. Polarization charge > 1–20 \(\mu\)C/cm\(^2\).
2. Coercive voltage < 2.5 V and stable.
3. Breakdown voltage > 7 V.
4. Full polarization switched in < 260 ns.
Once the basic requirements for ferroelectric memories are defined, the ferroelectric films with the desirable electrical properties can be fabricated by tailoring the film composition, film thickness and thermal processing conditions.

The objectives of this study on the electrical properties are: (1) to determine and evaluate the electrical properties of the sol–gel PZT films of different compositions and different thermal processing conditions, (2) to recommend compositions and processing parameters which are suitable for ferroelectric memory applications.

In order to develop a commercially viable ferroelectric memory technology, the electrical degradation issues have to be addressed. Electrical fatigue, aging, and time dependent dielectric breakdown (TDBD) are some of the crucial reliability issues of the degradation of the ferroelectric films. Progress in the understanding of the fatigue mechanism and the modeling of the hysteresis loop has been made by Yoo and Desu [100–105]. Appropriate electrode materials which significantly improves the fatigue properties of PZT films have been identified by Kwok et al. [106]. A patent disclosure of these special class of oxide electrodes has been filed [107]. Nevertheless, a comprehensive study of the degradation mechanisms of the ferroelectric films is a substantial project and is beyond the scope of this dissertation.
6.2 ELECTRICAL PROPERTY MEASUREMENTS

In this section, the sample preparation, hysteresis, C-V characteristics, and dielectric measurements are described.

6.2.1 Sample Preparation for Electrical Measurements

For most of the electrical property measurements in this study, a parallel-plate capacitor configuration was used. The PZT films were deposited on Pt/Ti/SiO₂/Si substrates by the sol-gel process as described in Chapter 2. A 400 nm thick sputtered platinum (Pt) layer on a silicon substrate was used as a bottom electrode since Pt is an effective barrier layer against the reaction between Si and the PZT film. PZT films were deposited using the procedures as described in Appendix A. The film thicknesses, in most cases, were around 0.35 μm. Electron beam evaporation was used for the deposition of palladium (Pd) top electrode. Palladium top electrodes (200–300 nm thick, 0.015 cm in diameter, and 2x10⁻⁴ cm² in area) were pattern-deposited onto the PZT films using a shadow mask. The cross-section of the test capacitor can be found in Figure 6.1. No annealing is needed after the Pd top electrode deposition. The access to the Pt bottom electrode is by scratching the PZT film by a sharp diamond pencil or locating a shorted capacitor. A good ohmic contact to the bottom electrode is crucial to obtaining accurate electrical property measurements.
Sample Configuration for Electrical Measurements

Figure 6.1 Cross-section of the test capacitor
Figure 6.2  Schematic diagram of Sawyer–Tower circuit

Cf = Ferroelectric Capacitor
Cs = Sense Capacitor
Figure 6.3  A typical hysteresis loop of the PZT film
6.2.2 Hysteresis Measurement

The ferroelectric properties of the PZT films were determined by hysteresis loop measurement using a modified Sawyer–Tower circuit [98]. The schematic Sawyer–Tower circuit is shown in Figure 6.2 and a typical hysteresis loop is shown in Figure 6.3. In this study, a commercial available ferroelectric test system (Radiant Technology RT66A) is used for ferroelectric property. The RT66A test system can measure hysteresis data, C/V data, leakage current and fatigue properties and the test system is fully automated and controlled by a personal computer. The block diagram of the RT66A tester is shown in Figure 6.4. The basic operations of the RT66A tester is described in Appendix B.

In this work, all of the hysteresis measurements were run under the virtual ground mode [108]. The virtual ground mode measures the charge stored in the ferroelectric sample by integrating the current required to maintain one terminal of the sample at zero volts. The applied voltage \(V_{\text{app}}\) used was 5 V unless specified otherwise.

The leakage current can also be measured by the RT66A tester. A selected voltage, \(V_{\text{app}}\) is applied to the sample for 2 seconds to eliminate the slow switching effect; the current through the sample is then measured. For this tester, the maximum applied voltage is 20 V. In this study, voltage steps of 1, 2, 3, 4, 5, 7.5, 10, 12.5, 15, 17.5 V were used.

Dielectric constants and dielectric loss \((\tan \delta)\) were measured by a Hewlett-Packard 4192A LF impedance analyzer. In most of the experiments, an oscillation level of 1 V and no bias was used. The frequency used was in the range of 100 Hz to 10 MHz.
Figure 6.4  Block diagram of the RT66A tester
Figure 6.5  Polarization as a function of applied voltage
Figure 6.6 Coercive field as a function of applied voltage
6.3 THE EFFECT OF COMPOSITION AND THERMAL PROCESSING CONDITIONS

In this section, the effects of applied voltage, excess Pb concentration, composition (Zr/Ti ratio), and annealing conditions on the electrical properties are investigated.

6.3.1 The Effect of Applied Voltage

In this experiment, the polarizations and coercive field of a 53/47 PZT film were measured as a function of applied voltage. This sample was annealed at 650° C for 15 minutes in air. The results of this experiment are shown in Figure 6.5 and 6.6. Both \( P_s \) and \( P_r \) increase as the applied voltage increases but the rate of increase was slower at higher applied voltage. Both \( P_s \) and \( P_r \) began to level off at applied voltages greater than 8 V. This slower increase in \( P_s \) and \( P_r \) at higher applied voltages indicates that as the applied field increases, it becomes more difficult to switch those domains which are aligned less favorably with the applied field. For the same reason, the coercive field becomes higher at higher applied voltages because a much higher field is required to switch a small amount of unfavorably aligned domains.

6.3.2 The Effect of Excess Lead Concentration

For most of the PZT film processing involving high temperature deposition or annealing, it is likely that lead loss would occur because lead and lead oxide are
volatile even at relatively low temperatures. It is not uncommon to add up to 20% excess Pb content in the sputter target to compensate for the lead loss during sputtering. For the sol–gel processing, it is also customary to add more lead during precursor preparation. However, it is unclear how much extra lead content is needed to compensate the lead loss during processing. Four samples with exactly the same processing conditions but with excess lead concentrations varying from −10% to +20% were used to evaluate the proper lead concentration for the particular sol–gel process used. The relationship between the polarization and the coercive field as a function of percent of excess lead can be found in Figure 6.7 and 6.8. $P_s$ and $P_r$ both increase as the percent of excess Pb increases and level off at 10% excess Pb. The coercive field of the sample with 10% deficiency in Pb concentration is about twice as large as that of the rest of the samples. The variability of the coercive field of the 10% Pb–deficient sample is much larger than that of the other three samples which may indicate a much less uniform composition distribution. The chemical composition of the PZT film with 10% extra Pb was investigated by electron microprobe analysis (EPMA) and was found to have about 3–4% excess Pb remaining. This indicates that during the processing, about 6–7 atomic percent of Pb was lost.

In short, 10% excess Pb is beneficial in maintaining the stoichiometry of the PZT films during thermal processing and thus 10% excess Pb was used in the precursor preparation.
Figure 6.7  Polarization as a function of excess lead concentration
Figure 6.8  Coercive field as a function of excess lead concentration
6.3.3 The Effect of Composition

The PZT oxide system is basically a solid solution of PbTiO₃ (PT) and PbZrO₃ (PZ). According to the binary phase diagram of PT and PZ, PZT phases with Zr/Ti ratios from around 92/8 all the way up to 0/100 are ferroelectric phases. In principle, PZT films with Zr/Ti ratio in this range can be used in ferroelectric devices. But in practice, the ferroelectric properties (Pᵣ, Pₛ and Eᵣ) are a strong function of the composition and it is desirable to determine the optimum composition for memory applications.

Ferroelectric data on 53/47 hot-pressed bulk ceramics are: Pᵣ, 35 μC/cm² and Eᵣ, 10 kV/cm. For a single crystal PbTiO₃, Pᵣ is 75 μC/cm² and Eᵣ is 6.7 kV/cm [109]. The electrical properties of PZT films prepared by sputtering, CVD, and the sol-gel process have been reported by many researchers; some of these results are tabulated in Table 6.1. The majority of the data were reported on 50/50 PZT and PbTiO₃ films. Although the variation of electrical properties is quite large, few common observations can be made from Table 6.1. (1) Coercive fields of films are always larger than those of the bulk ceramics. (2) Eᵣ of PbTiO₃ films are generally larger than Eᵣ of 50/50 PZT films. (3) The remanent polarization is close to that obtained from the bulk ceramics.

Most of the sputtered films listed in Table 6.1 had thicknesses equal to or larger than 2 μm. Consequently, the applied voltages used in the hysteresis measurements were usually larger than 10 V. The polarization values of these sputtered films using 5 V applied voltage could be much smaller.

In this work, PZT films with Zr/Ti ratios ranging from 65/35 to 0/100 were prepared and heat treated at 800°C and 650°C for 15 minutes in air. Figure 6.9 and
6.10 illustrate the polarization as a function of composition with films annealed at 600°C and 650°C, respectively. Both Figure 6.9 and 6.10 show a similar trend. Under the same annealing condition, the 53/47 samples possessed the largest P_s and P_r among the other samples. Ti-rich samples and Zr-rich samples had lower P_s and P_r when compared to the 53/47 sample. The variation in E_c as a function of composition is given in Figure 6.11 and 6.12. Minimum E_c are found in 53/47 samples and the maximum E_c are found in PbTiO_3 samples.

The remanent polarizations of the 53/47 PZT films and the PbTiO_3 films are comparable to those published for the corresponding bulk ceramics. Maximum polarization at the morphotropic phase boundary (MPB) composition (53/47) can be explained by the large number of polarization directions at the MPB. At MPB, TEM studies have shown that both the tetragonal phase and the rhombohedral phase coexist at compositions close to the MPB composition. There are eight polarization directions in the rhombohedral phase and six in the tetragonal phase. For the samples with compositions close to the MPB, all fourteen polarization directions can be operated for domain switching. Consequently, P_r is largest and E_c is smallest at the MPB composition.

The E_c of all the samples we tested were always larger than the E_c of the bulk ceramic reported in the literature. This can be explained by the constraints of domain switching arising from (1) the fine grain size and (2) the stress present in the PZT films [8,10,11]. Smaller grain size generally results in larger E_c because the domain size depends on the grain size and the grain boundaries often impede the domain movement.

For the 65/35 film annealed at 600°C, both P_s and P_r are very small because at that temperature pyrochlore has just started to transform to perovskite. At 650°C,
Figure 6.9 Variation of polarization with composition, 600°C annealing temperature
Figure 6.10  Variation of polarization with composition, 650°C annealing temperature
### Table 6.1 Comparisons of electrical properties of PZT films

<table>
<thead>
<tr>
<th>Process</th>
<th>Zr/Ti</th>
<th>$P_r (\mu C/cm^2)$</th>
<th>$E_c (kV/cm)$</th>
<th>$\epsilon^*$</th>
<th>t($\mu m$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputter</td>
<td>0/100</td>
<td>8</td>
<td>70</td>
<td>300</td>
<td>3</td>
<td>Okuyama [6]</td>
</tr>
<tr>
<td>Sputter</td>
<td>0/100</td>
<td>14</td>
<td>151</td>
<td>290</td>
<td>2.4</td>
<td>Matsui [7]</td>
</tr>
<tr>
<td>Sputter</td>
<td>0/100</td>
<td>35</td>
<td>160</td>
<td>97</td>
<td>2</td>
<td>Iijima [8]</td>
</tr>
<tr>
<td>Sputter</td>
<td>45/55</td>
<td>40</td>
<td>150</td>
<td>400</td>
<td>1–4</td>
<td>Takayama [9]</td>
</tr>
<tr>
<td>Sputter</td>
<td>52/48</td>
<td>9</td>
<td>18</td>
<td>750</td>
<td>2</td>
<td>Castellano [10]</td>
</tr>
<tr>
<td>Sputter</td>
<td>50/50</td>
<td>21</td>
<td>18</td>
<td>950</td>
<td>2</td>
<td>Krupanidhi [11]</td>
</tr>
<tr>
<td>Sputter</td>
<td>52/48</td>
<td>20</td>
<td>23</td>
<td>750</td>
<td>9</td>
<td>Okada [12]</td>
</tr>
<tr>
<td>Sputter</td>
<td>52/48</td>
<td>30</td>
<td>25</td>
<td>700</td>
<td>1</td>
<td>Sreenivas [13]</td>
</tr>
<tr>
<td>Sputter</td>
<td>90/10</td>
<td>35</td>
<td>35</td>
<td>350</td>
<td>12</td>
<td>Adachi [14]</td>
</tr>
<tr>
<td>CVD</td>
<td>0/100</td>
<td>0.16</td>
<td>15</td>
<td>100</td>
<td>8.3</td>
<td>Nakagawa [15]</td>
</tr>
<tr>
<td>CVD</td>
<td>0/100</td>
<td>—</td>
<td>—</td>
<td>240</td>
<td>0.6</td>
<td>Dormans [16]</td>
</tr>
<tr>
<td>CVD</td>
<td>23/77</td>
<td>60</td>
<td>170</td>
<td>400</td>
<td>0.22</td>
<td>Dormans [16]</td>
</tr>
<tr>
<td>CVD</td>
<td>57/43</td>
<td>50</td>
<td>75</td>
<td>870</td>
<td>0.35</td>
<td>Dormans [16]</td>
</tr>
<tr>
<td>Sol–gel</td>
<td>45/55</td>
<td>20</td>
<td>100</td>
<td>1000</td>
<td>0.45</td>
<td>Dey [17]</td>
</tr>
<tr>
<td>Sol–gel</td>
<td>52/48</td>
<td>18</td>
<td>35</td>
<td>1250</td>
<td>1</td>
<td>Dey [17]</td>
</tr>
<tr>
<td>Sol–gel</td>
<td>50/50</td>
<td>13</td>
<td>143</td>
<td>577</td>
<td>0.35</td>
<td>Carrano [18]</td>
</tr>
<tr>
<td>Sol–gel</td>
<td>50/50</td>
<td>31 ($P_s$)</td>
<td>45</td>
<td>300</td>
<td>2</td>
<td>Fukushima [19]</td>
</tr>
</tbody>
</table>

* $\epsilon$ – dielectric constant
Figure 6.11  Variation of Coercive field with composition, 600°C annealing temperature
Figure 6.12  Variation of coercive field with composition, 600°C annealing temperature
the $P_s$ and $P_r$ of the 65/35 film improve significantly. Figure 6.13 illustrates the
hysteresis loops of two samples; one has the perovskite structure (loop (A)) while
the other has the pyrochlore structure (loop (B)). The hysteresis loop (B) from the
pyrochlore phase has an almost linear behavior that is similar to a linear dielectric.
The C–V plot, Figure 6.14, obtained from the hysteresis loop (A) shows two very
similar traces with almost the same maximum capacitance when subjected to $+V_{app}$
or $-V_{app}$. There is a slight shift of the two C–V traces toward the $+V_{app}$. This
can be explained by the small asymmetry of the top and bottom electrode
configuration. Nonetheless, the C–V plot shown in Figure 6.14 indicates a good
quality ferroelectric sample.

Permittivity of the PZT films has also been studied; the variation of dielectric
constant as a function of frequency is shown in Figure 6.15. The dielectric constants
of the 40/60 samples and 53/47 samples are about 50% higher than those
of the 65/35 and 75/25 samples. The dielectric constant of all the samples we
studied was frequency dependent and decreased with an increase in frequency. The	
$\tan \delta$ of the samples tested had an average value of 0.08. The dielectric constants of
these PZT films are comparable or higher than most of the reported values.

Leakage currents of the PZT samples tested, with the exception of PbTiO$_3$,
were relatively low and in the range of nA. The leakage currents of these samples
behaved linearly at low voltage, and began increasing more sharply at applied
voltages larger than 10 V. This variation of leakage current as a function of applied
voltage is depicted in Figure 6.16. The pre–breakdown voltage for most of the
samples was around 20 V. The actual breakdown voltage may be higher since
accumulative damage might occur when the same sample is subjected to repeatedly
increasing voltage pulses.
Figure 6.13  Comparison of two hysteresis loops, well-defined loop from the perovskite phase, near-linear loop from the pyrochlore phase.
Figure 6.14  Capacitance–voltage (C–V) plot of a good PZT capacitor.
Figure 6.15  Variation of dielectric constant with frequency
Figure 6.16  Leakage current of PZT films of different compositions
6.3.4 The Effect of Annealing Temperature

Post-deposition annealing of sol–gel PZT films is always needed to form desirable ferroelectric structure. The annealing temperature is a function of film composition and should be larger than the pyrochlore–perovskite transformation temperature. The transformation temperature can be as low as 450°C for PbTiO$_3$ films and as high as 650°C for PbZrO$_3$ films.

Ideally, the annealing temperature should be as close to the transformation temperature as possible since one of our main objectives is to lower the processing temperature. High annealing temperatures lead to excessive lead loss so the upper limit of annealing temperature in this study was limited to 750°C [46]. On the other hand, any small amount of nonferroelectric pyrochlore phase remaining after annealing would undoubtedly degrade the electrical properties.

In this experiment, PZT films with Zr/Ti ratios ranging from 0/100 (PbTiO$_3$) to 75/25 were fabricated by the sol–gel process. The film thicknesses for all the samples were about 0.35 μm.

In this experiment, PZT films with compositions ranging from pure PbTiO$_3$ to 75/25 were annealed at different annealing temperatures. The $P_s$ and $P_r$ of films of each composition were plotted as a function of annealing temperature and presented in Figure 6.17–6.22. Generally speaking, $P_s$ and $P_r$ are very small when the PZT film is annealed at temperatures close to the pyrochlore to perovskite transformation temperature ($T_c^\text{per}$). In this work, $T_c^\text{per}$ are determined by XRD. This is because even at $T_c^\text{per}$, the PZT film might not be completely transformed to perovskite and any small amount of pyrochlore remaining may reduce the polarization values. At 50°C higher than the $T_c^\text{per}$, the hysteresis loops of most of
the films are well developed and further increase in annealing temperature improve
the polarizations only slightly.

In summary, annealing temperatures should be about 50°C higher than the
$T_c^{\text{per}}$ to ensure the complete transformation to the perovskite phase. Further
increases in annealing temperature only provide marginal improvement in
polarization switching.
Figure 6.17  Polarization of PbTiO₃ as a function of annealing temperature
Figure 6.18  Polarization of 30/70 PZT film as a function of annealing temperature
Polarization as a function of annealing temperature

Figure 6.19  Polarization of 40/60 PZT film as a function of annealing temperature
Figure 6.20  Polarization of 53/47 PZT film as a function of annealing temperature
Figure 6.21  Polarization of 65/35 PZT film as a function of annealing temperature
Figure 6.22  Polarization of 75/25 PZT film as a function of annealing temperature
6.4 THE EFFECT OF FILM THICKNESS

Film thickness has a profound influence on the electrical properties of ferroelectric films. Since the applied voltage needed for complete domain switching is directly proportional to the film thickness, the film thickness of ferroelectric memory devices is dictated by the standard voltage used in the DRAM applications. Presently, 5 V is commonly used in the DRAM circuitry but the voltage requirement is expected to decrease to 3.3 V and finally down to 2.5 V in the next 2–3 generations of DRAM circuit design. This trend of lowering voltage the requirements stems from the attempt to minimize the heat generation arising from very high density circuit design.

The advantages of small film thickness are the low voltage required for polarization switching and fast switching time (10 nanosecond range) since both the switching voltage and switching time are directly proportional to the film thickness [3]. However, reducing the film thickness might lead to problems with pinholes and generally increased the coercive field. For very thin films, dielectric breakdown becomes a major concern. This problem becomes critical when the film thickness of the SiO₂ dielectric film is in the nm range. For 1 Mbit DRAM devices, the SiO₂ film thickness is so thin (6 nm) that process control is very difficult. Electron tunneling becomes a valid concern. One of the advantages of replacing SiO₂ film with ferroelectric film is large processing window for film thickness. The optimum film thickness of ferroelectrics used in FRAM remains unclear and this section attempts to answer this issue.

In this study, the electrical properties of PZT films of different thickness are determined. PZT films with thicknesses ranging from 45 nm to 700 nm were
Figure 6.23  Polarization as a function of film thickness
Coercive field as a function of film thickness

53/47
650°C
$V_{app} = 5\text{ V}$

Figure 6.24  Coercive field as a function of film thickness
obtained by varying the spin speed and the number of coatings. The composition of these films was 53/47 and all were annealed at 650°C for 15 minutes in air. Figure 6.23 and 6.24 show the relationship between polarization and coercive field as a function of film thickness. Both $P_s$ and $P_r$ remain relatively unchanged as the film thickness decreases. The coercive field increases linearly with the film thickness down to 170 nm and increases rapidly for thinner film.
There are no data available from the 45 nm thick sample because all of the capacitors tested were shorted during the measurement. Very small shiny specks from the 45 nm thick sample were observed under the optical microscope (magnification — 60X) which indicates dielectric breakdown may occur. From the discussion of the last section, the pre—breakdown voltages for PZT films with composition ranging from 30/70 to 75/25 (0.35 μm thickness) are around 20 V. The pre—breakdown field was calculated to be about 571 kV/cm. For the 45 nm and 88 nm thick samples under a switching voltage of 5 V, the switching fields are 1111 and 568 kV/cm. Therefore, it is not surprising that the 45 nm film would breakdown at a switching voltage of 5 V.

Taylor has investigated the effects of thickness on the electrical properties of the PZT 50/50 bulk ceramics [110] and reported that $E_c$ is relatively constant when the thickness (t) is larger than 2 μm and $E_c$ increases very sharply when t becomes less than 50 μm. However, $P_s$ and $P_r$ are independent of t. This can be explained by the fact that: (1) the thin sample has a thin surface layer with properties different from those of the bulk and (2) the internal field is by the space charge.

Another study of the thickness effect of the sputtered PLZT films has shown that the $P_r$ decreases and the coercive field increases with decreasing film thickness [15]. The range of film thickness used in this study varied from 0.5 μm to 4.5 μm and these films were subjected to an applied field of 137 kV/cm. Krupanidhi investigated the dielectric constant of the sputtered PZT films as a function of film thickness. The dielectric constant was independent of film thickness when the thickness becomes larger than 1 μm [11].

The thickness effect on the coercive field can be considered in the following manner. If the ferroelectric switching involves simultaneous reorientation of every
domains in the sample, the coercive field should be thickness-independent but the magnitude of the coercive field would be extremely large. In real ferroelectric samples, the coercive field is much smaller because the switching of domains occurs by a nucleation and growth process. Initially, only those domains aligned favorable to the applied field will switch first, usually nucleates at the surface or at one of the inhomogeneities. When these nuclei reach a critical size, they grow very rapidly normal to the film surface along the direction of the applied field. After the growing domains reach the opposite film surface, then they spread laterally until the whole crystalline film is completely switched. Because the coercive field depends on the switching kinetics of the domains, therefore, there is reason to believe the coercive field is a function of the film thickness.

Kay and Dunn has proposed a power law relationship between the coercive field ($E_c$) and the film thickness ($t$) \cite{111}. It can be expressed as:

$$E_c = A t^n \quad (6.1)$$

The exponent $n$ for triglycine sulfate is $-0.66$ as determined by Kay and Dunn. Fatuzzo et al. has predicted that the $n$ for BaTiO$_3$ ceramics is about $-1$ \cite{112}. Recently, Modak and Dey found that the $n$ for sol-gel 52/48 PZT films is $-0.76$ \cite{113}. In this work, Figure 6.24 is replotted as log ($E_c$) versus log ($t$) and the slope $n$ is found to be $-0.86$ as shown in Figure 6.25.

The coercive field of the 88 nm-thick sample is much larger than expected from the power law relationship. This could be attributed to (1) the crystallinity is more ordered in very thin films, nucleation of switching domains is more difficult, (2) thin film stress is reported to rise exponentially with decreasing film thickness, and this
Coercive field as a function of film thickness

$E_c \propto t^{-0.86}$

53/47
650°C
$V_{opp} = 5 \, V$

Figure 6.25 Log–log plot of coercive field as function of film thickness
stress may affect the nucleation and growth of those switching domains [114].

In summary, PZT with film thickness smaller than 90 nm results in a very high coercive field. Therefore, for memory applications, film thickness equal to or greater than 170 nm should be used. In this work, film thickness of 350 nm is commonly used and at this thickness, the possibility of dielectric breakdown at an applied voltage of 5 V can be greatly reduced.
Chapter 7. Conclusions and Recommendations

The main objectives of this research were to develop a viable fabrication process for PZT thin films, to investigate the formation kinetics of the ferroelectric perovskite phase, to devise procedures for low temperature perovskite formation, and to understand the relationships between processing, microstructure, film stress, and electrical properties of these PZT thin films.

From the results and discussions given in previous chapters, the following were concluded:

1. A modified sol–gel process was developed by the judicious choices of precursors, solvents, the chelating agent, the proper order of mixing, and the thermal processing parameters such as molar concentration, spin speed, drying temperature, annealing temperature, annealing environment, and heating rate. Precursor solutions with long shelf–life have been prepared. PZT films with good electrical properties have been successfully fabricated. In all, the modified sol–gel process is a simple, consistent, expeditious method to prepare good quality PZT films.

2. Ferroelectric domain structures of PZT thin films have been studied by TEM and results show that domain structures generally orient along the \(<110>\) directions lying on the \{110\} planes. Most of the domains observed were 90°
domains. The average domain width was about 20 nm and the domain wall thickness was about 1.5 nm.

3. The pyrochlore phase of the PZT film was identified by its characteristic electron diffraction pattern; pyrochlore has a very fine grain structure with a grain size on the order of 8 nm. This TEM study of the pyrochlore phase is believed to be one of the first reported.

4. The Pyrochlore to perovskite phase transformation has been investigated by TEM. Groups of 3–4 perovskite particles were found to grow from the fine grain pyrochlore phase. The formation temperature of the perovskite phase was higher than expected and can be explained by the size effect.

5. Based on the kinetics study, the growth of the perovskite phase was determined to be interface controlled. The formation of the perovskite phase is nucleation controlled. The activation energy of the nucleation and growth of the perovskite phase is 441 kJ/mol and 112 kJ/mol, respectively. The activation energy for the overall formation is 494 kJ/mol.

6. A seeding process, which a seeding layer was chosen to encourage the nucleation of the perovskite phase, was invented to expedite the perovskite nucleation. Consequently, the transformation temperature was lowered by nearly 100°C. The seeded PZT samples also had good electrical properties.
7. Thin film stresses of PZT films have been studied as a function of temperature. Stress-temperature profiles obtained from the heating-cooling cycles provided valuable information about the transformation stress as the temperature changed. Among the thin film processing steps, the drying of PZT films created the highest film stress in the samples.

8. PZT films with Zr/Ti ratio of 53/47 have the highest remanent polarization and the lowest coercive field. The optimum annealing temperatures are about 500°C higher than the completion temperature of the perovskite formation of the same composition. PZT films with thicknesses greater than or equal to 170 nm have electrical properties similar to those of thicker films.

Possible future works related to the current research include the following:

1. Extension of the kinetic study to include the entire PbTiO₃-PbZrO₃ solid solution.

2. Study the pyrochlore to perovskite formation by in-situ hot-stage TEM experiments with emphasis on the growth kinetics and orientation relationship of the perovskite phase.

3. Incorporate A-site and B-site dopants such as La, Nb, Fe ions in the PZT film preparation and study the effect of dopants on the electrical properties, especially on the long-term reliability problems.
4. Extension of the electrical measurements to include electrical degradations such as fatigue, aging, TDB and dielectric breakdown.
Appendix A

Sol–gel processing of PZT films: experimental procedures

This appendix is divided into two sections, first section deals with preparing PZT precursor. The procedures for preparing a 50 mL, 0.4 M solution is listed. The second section provides information about preparing thin film from the precursor.

A1. Precursor preparation

1. Add appropriate amount of Zr n–propoxide into a clean 50 mL beaker. The amounts of Zr, Ti alkoxides and Pb acetate required to make PZT of desired compositions are tabulated in Table A.1. All the additions of chemicals are done in a analytical balance in ambient condition.

2. Add Ti isopropoxide into the Zr n–propoxide solution and mix the two alkoxides in ultrasonic cleaner for 5 min.

3. Add 5 mL of acetic acid to the Zr–Ti solution.

4. Add 10 mL of n–propanol to the above solution.

5. Add 8.345 g. of Pb acetate (10% excess) to the above solution.

6. Heat the Pb–Zr–Ti solution in a silicon oil bath to 95°C, stir the solution with the wooden end of a cotton–swab stick to dissolve the Pb acetate.

7. Be very careful not to let the temperature go over 95°C, you should see bubbles coming out of the solution, those are the dehydrated water evaporates from the solution. Add 0.5 to 1 mL of acetic acid to the solution if the solution becomes viscous. This whole process should take about 5–7 min.
8. Remove the solution from the oil bath, clean the outside of the beaker and cover the beaker with a plastic film and let the solution cool down to close to room temperature.

9. Add 1.188 g distilled water into the solution and mix them in the ultrasonic cleaner for 2 min.

10. Add 10 mL of acetic acid to the solution.

11. Add appropriate amount (about 15 mL) of n-propanol to make 50 mL of final precursor solution.

12. Store the precursor solution in capped test tubes and keep them in a dry and cool place.

13. The solution should be used as soon as possible.

A2. Film preparation

1. Place a clean substrate on the platform of the spin coater.

2. Heat up the hot plate to 150°C.

3. Turn on the mechanical pump.

4. Set the time (autostop) to 30 sec. and spin speed to 1500 rpm.

5. Cover the whole substrate with precursor solution, this will minimize the streaking.

6. Start the spin coater by the foot peddle.

7. Transfer the substrate to the hot plate and dry for 5 min.

8. Remove the substrate from the hot plate and wait until it is cool down to room temperature before another spin coating if required.

9. Repeat the spin-dry cycle two times to obtain a film thickness of 350 nm.
10. Anneal the film in a tube furnace in air, place the sample into the heating zone within a couple of seconds since most of times, a fast heating rate is beneficial.

Table A.1  Quantity of chemicals required to make 50 mL of 0.4M PZT solution

<table>
<thead>
<tr>
<th>Zr/Ti ratio</th>
<th>Pb(Ac)$_2$</th>
<th>Zr(P$_r^3$)</th>
<th>Ti(P$_r^1$) (in grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>8.345</td>
<td>0.0</td>
<td>5.685</td>
</tr>
<tr>
<td>30/70</td>
<td>8.345</td>
<td>2.808</td>
<td>3.980</td>
</tr>
<tr>
<td>40/60</td>
<td>8.345</td>
<td>3.744</td>
<td>3.411</td>
</tr>
<tr>
<td>53/47</td>
<td>8.345</td>
<td>4.961</td>
<td>2.672</td>
</tr>
<tr>
<td>65/35</td>
<td>8.345</td>
<td>6.084</td>
<td>1.990</td>
</tr>
<tr>
<td>75/25</td>
<td>8.345</td>
<td>7.020</td>
<td>1.421</td>
</tr>
<tr>
<td>100/0</td>
<td>8.345</td>
<td>9.360</td>
<td>0.0</td>
</tr>
</tbody>
</table>

---

-182-
Appendix B

Experimental Procedures for Film Stress Measurements

The elastic constant, thickness and diameter of the substrate are pertinent parameters needed for stress measurements. These parameters for some of the common substrates are listed in Table B.1.

Three different types of stress measurements can be performed by the Flexus tester. They are: (1) single stress, (2) stress–time and (3) stress–temperature measurements. But all 3 types of stress measurements require first measuring the curvature of the substrate without the film on it.

The step–by–step procedures are described as follows:

1. Turn on the main power switch. Turn on the laser by turning the key to the vertical position. Turn on the fan, the controller and the water switch if any heating is used.
2. Place the 2", 3" or 4" sample holder (template) onto the Al pedestal depending on the diameter of the sample.
3. The Flexus tester is computer–driven. Before testing, the screen should show the main menu after booting up.
4. Hit 'F5' to change the configuration of the test parameters. They are (1) the diameter of the substrate (50, 75, and 100 mm), (2) the elastic constant of the substrate in $10^{11}$ Pa, (3) the substrate thickness (in $\mu$m). Use 'ESC' to go back to main menu.
5. Place the sample in the sample holder. For the 2" wafer, the flat should be facing and touching the inside edge and the left-hand-side edge of the square 2" holder. For the 3" and 4" sample, the major flat of the sample should be facing the user. The same orientation has to be used when the sample is placed onto the high temperature holder; the reason for this will be discussed later.

6. Hit 'A' for measurement of the initial curvature of the substrate. It is always necessary to do the first measurement A. If the film is deposited without the first measurement, the stress of the film cannot be measured.

7. Input the filename, ID number.

8. The first measurement should take about 10 seconds. If the tester is not working at this stage (i.e. the laser is not moving, and no moving sound is heard), one of the following may be the reason: (1) the shutter is not open, (2) the reflectivity of the sample is lower than the detection level (0.35V) (check the intensity by going to 'calibration', and then 'intensity check'), (3) the laser is not on the sample, you can bring it to the center by hitting F4, or the laser can move onto the sample by using 'F1' — to the right and 'F2' — to move to the left, (4) incorrect data may have been input, check to make sure there is no white space in the data entry space, where it is not allowed.

9. Remove the sample, and deposit film onto the substrate.

10. Place the sample in the holder, and Hit 'B' for stress measurement.

11. Input the filename, ID no. and film thickness in angstroms. Hit 'enter' to measure. The first screen shows the actual curvature and the second screen shows the light intensity plot. The stress value is also given. Note down the stress value at this point if stress—temperature measurement is needed.
12. For stress-temperature measurement, make sure the fan, controller and the cooling water are all on. Put on the glove to prevent contamination of the quartz chamber and the sample holder. Remove the pedestal, the quartz cap and the stainless steel heat shield, then remove the quartz sample holder from the quartz chamber.

13. Place the sample onto the quartz sample holder. Place the whole setup back into the heater chamber, replace the heat shield, the quartz cap and then the pedestal. If a controlled atmosphere is desired, turn on the gas slowly and make sure the quartz cap is still tight and that small bubbles are coming out from the exhaust end when the tubing is placed under water.

14. Hit 'D' to start the stress-temperature measurement, input the filename, ID no., film thickness and the initial stress value obtained from measurement 'B'.

15. Next, the computer will ask for a temperature profile.

16. An example of the temperature profile is shown below:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Duration</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>2.5</td>
<td>29</td>
</tr>
<tr>
<td>750</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>25</td>
<td>5</td>
<td>29</td>
</tr>
<tr>
<td>25</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

This profile means that the sample will ramp up to a final temperature of 750°C in 2.5 hours, so the heating rate is about 5°C/min. Within that 2.5 hour, 29 measurements are made meaning each measurement is about 25°C apart.

The second line tells the system to hold the temperature at 750°C for 1 hour, and make 12 measurements in that one hour, i.e. measure every 5 minutes. The third line requests the controller to ramp the temperature down to 25°C in 5 hours. The corresponding cooling rate is roughly 10°C/min. The fourth line is sometime
necessary because of the fact that the cooling rate is much slower at lower temperatures. After 5 hours of cooling, the temperature may still be around 85°C. Therefore, another 3 hours may be needed to bring the sample down to room temperature.

17. The stress–temperature profile will be shown on the screen and also saved in the c:\dat\ directory.

Table B.1 Parameters of common substrates used in stress measurements

<table>
<thead>
<tr>
<th>Material</th>
<th>diameter (mm)</th>
<th>thickness (μm)</th>
<th>(E/(1-\nu)(10^{11}\text{ Pa}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (100)</td>
<td>50</td>
<td>382</td>
<td>1.805</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>442</td>
<td>1.805</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>525</td>
<td>1.805</td>
</tr>
<tr>
<td>Si (111)</td>
<td>100</td>
<td>525</td>
<td>2.290</td>
</tr>
<tr>
<td>sapphire</td>
<td>50</td>
<td>332</td>
<td>5.296</td>
</tr>
</tbody>
</table>

The elastic constants of other materials such as Al, quartz, Al\(_2\)O\(_3\), GaAs, Ge, Soda glass and Borosilicate glass are listed in the Flexus software. To access these data, Hit (F) Editor, then (6) Data Processing, then (5) Elastic & expansion coefficient data base and scroll through the data base by the PgUp or the PgDn key.
Appendix C

Basic Operation of The Hysteresis Measurements

The basic operation of the hysteresis measurement can be described as follows:
1. The maximum applied voltage and number of points are selected by the user.
2. Then the number of points is divided by 4. This is the number of points for each voltage segment (4 segments: $V_{\text{max}}$, 0 V, $-V_{\text{max}}$, 0 V).
3. The $V_{\text{max}}$ is divided by the number of points in a segment to generate the voltage steps and an array of drive voltages is generated and stored in the software.
4. The integrated capacitor and the sample are shorted and then opened.
5. The computer program will step through the hysteresis array, pick up the appropriate voltage values and send these voltages to the driver section. After waiting a specified period for the sample to fully charge from the voltage step, the output of the integrator is measured.
6. When the acquisition is completed, the integrator and the sample are left shorted. The data is processed by the software program for analysis and plotting.
Bibliography

4. L. Parker and A. Tasch, "Ferroelectric materials for 64 Mb and 256 Mb DRAMs," IEEE Circuit and Devices, January 1990, pp. 17


17. S. Dey and R. Zuleeg, "Integrated sol–gel PZT thin–films on Pt, Si, and


43. M. Dass, U. Dahmen, G. Thomas, T. Yamamoto and K. Okazaki, " Electron microscopy characterization of lead zirconate titanate ceramics at the


50. E. Goo, M.S. Thesis, University of California at Berkeley (LBL #10651), (1976)


71. L. Sevast'yanova, E. Zubova, K. Burdina and Y. Venevtsev, "New perovskite Pb(Ga\textsubscript{0.67} W\textsubscript{0.33})O\textsubscript{3} and Pb\textsubscript{2}CrTaO\textsubscript{6}, synthesized at high pressure," Izv. Akad. Nauk SSSR, Neor. Mat. 10(7) (1974) 1359–1360.


90. E. Klockholm, "X-ray diffraction and stress in thin films symposium". I.B.M. research center, Yorktown height, N.Y. (March 1969)


96. S. Swartz, S. Bright, J. Busch and T. Shrou, "Sol–gel processing of


VITA

Chi Kong Kwok was born and raised in Hong Kong. He received his B.Sc degree (distinction) in Mechanical Engineering from University of Hawaii at Manoa. He was one of the three top students in his graduating class of the College of Engineering and was selected as one of the marshals in the graduation ceremony. He received his M.Sc degree from University of California at Berkeley under the supervision of Dr. Gareth Thomas. His research in U.C. Berkeley involved transmission electron microscopy and tribology studies. He also worked in Lawrence Berkeley National Laboratory.

In 1986, he joined the Department of Materials Engineering Science at Virginia Polytechnic Institute and State University. Under the supervision of Dr. Seshu Desu, he started his doctoral research in the area of ferroelectric thin films in March, 1989. He had 11 published articles and another 4 articles had been submitted for publication. He had also filed 3 patent disclosures in the area of ferroelectric films.

He is a member of MRS, ACerS and Phi Kappa Phi honor society.