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EFFECTS OF DOPANTS AND MICROSTRUCTURE ON THE PROPERTIES OF LEAD ZIRCONATE TITANATE THIN FILMS DEPOSITED BY PULSED LASER DEPOSITION

A Thesis in

Materials Science and Engineering

by

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ABSTRACT

Incorporation of lead zirconate titanate (PZT) thin films into microelectromechanical devices holds great promise because their piezoelectric coefficients are much larger than commonly used materials like ZnO. To date, much of the research on PZT thin films has been on undoped morphotropic phase boundary compositions on flat substrates. Two areas of interest, particularly for microelectromechanical applications, have not been explored in any great detail in the literature. First is the addition of dopants to PZT films to optimize the piezoelectric properties as is typically done in bulk materials. Second is the effect of substrate curvature on the microstructure of the films.

In this work, PZT films grown from both hard (PZT 8) and soft (PZT 5A, 5H, and PLZT) PZT targets have been deposited on platinum coated silicon wafers by pulsed laser deposition under identical conditions, and crystallized by rapid thermal annealing. The electrical properties were studied to determine the effect of dopants present in the film. Dielectric constants of 1000-1500 were achieved in both types of films, with loss values varying from 0.01 for donor doped films to 0.03 for acceptor doped films. Remanent polarizations are typically 30 μ C/cm² for both types of films with no systematic difference in coercive fields. When subjected to ~140 MPa of biaxial tension and compression, only small (~2–7%) reversible changes were observed, indicating a lack of substantial non-180° domain reorientation in the films.

A microstructural study for various deposition conditions was made to determine what type of microstructure corresponded to films with good electrical properties. Through the use of a highly reactive oxygen ambient (10% O₃ in O₂) dense films on flat substrates could be fabricated by room temperature deposition. The effects of various ambient pressures, temperatures, and target to substrate distance are reported. PZT films were also deposited on both platinum and SiO₂ fibers of varying diameter to study the effects of substrate curvature on film microstructure. It was found that dense microstructures could be produced on fibers as small as 0.05 mm in diameter. Cross-sectional images of films on 125µm fibers show columns which broaden significantly with film thickness, leading to dense microstructures which should conserve good mechanical coupling between grains. Piezoelectric fiber coatings of this type can be used in fiber optic modulators.

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BACKGROUND

1.1 Introduction

The properties of a material prepared in thin film form are often different from those of the same material in bulk form. This is not surprising when the various constraints of thin film structures are taken into consideration. Films are, by definition, thin, and they are also in intimate contact with another material, either a substrate or another film. Since the substrate generally has a different thermal expansion coefficient from the film, there are often large residual stresses in films which have been processed at high temperature. Similarly, the bombardment during the growth process itself can lead to residual stresses in films. Thin film microstructures are also often very different from those found in bulk materials.

Lead zirconate titanate (PZT) is a material that has been widely studied for its interesting ferroelectric and piezoelectric properties. In the bulk, PZT has very strong ferroelectric properties and some of the highest known piezoelectric coefficients. It is presently one of the most widely used materials for bulk piezoelectric applications, and significant interest has been shown in it for thin film applications such as non-volatile random access memory (NVRAM), microelectromechanical (MEMS) devices, sensors, and actuators.

To date, much of the research on PZT thin films has been on undoped compositions on flat substrates. For MEMS devices, the piezoelectric coefficients, electromechanical coupling coefficients, and achievable strain level of the material are crucial. In the bulk, dopants are used to influence the magnitude and character of the piezoelectric response from PZT so that it can be tailored for particular applications. Due to the significant amount of research that has been completed on bulk PZT, mechanisms behind dopant property modification in bulk materials are well understood. It is not well known, however, what effects the constraints of a thin film geometry will have on these mechanisms. Factors such as grain size, residual stress, defect density and dopant distribution are expected to be important.

Another factor that has not been well explored is the unique substrate geometries required for many MEMS devices. In particular, several designs such as mini-pipettes and fiber-optic modulators, like the one shown in Figure 1.1, require piezoelectric films to operate on curved surfaces.



Figure 1.1 Fiber modulator device design (from Fox, 1996)

It is not clear what effect a curved substrate such as a fiber will have on the behavior of a PZT film. As the films often have a columnar microstructure, a density gradient in the films might exist between the film/substrate interface and the film surface. If the grains are not in close contact throughout the entire film thickness, the lateral mechnical coupling in the film could be degraded.

The focus of this thesis is to investigate the effects of hard and soft dopants and substrate curvature on the properties of PZT thin films.

1.2 Ferroelectricity

1.2.1 Definition of Ferroelectricity

The proposed IEEE definition for a ferroelectric material is as follows: "In the limit of an ideally oriented single crystal, a ferroelectric phase is one in which the spontaneous polarization can be permanently reoriented between stable states by the application of an electric field" (IEEE to be published). Materials that are capable of this behavior must possess a non-centrosymmetric crystal structure. Of the 32 crystal classes, 21 do not possess a center of symmetry. All of these except one are piezoelectric. Piezoelectricity occurs when an applied stress leads to the development of charge on the sample faces (Jona and Shirane, 1962). Of the twenty classes that exhibit piezoelectricity, ten have a unique polar axis. A unique polar axis is observed as a spontaneous dipole along one direction in the crystal. If the spontaneous dipole is reorientable to another stable state (causing a change in the overall remanent polarization), the material is ferroelectric.

The ten classes with unique polar axes are all pyroelectric crystals. The name comes from the change in polarization value with change in temperature that these materials exhibit. All ferroelectric materials are pyroelectric, but only pyroelectric materials that exhibit reorientable dipoles are ferroelectric.

1.2.2 Properties of Ferroelectric Materials

Table 1.1 shows a list of some ferroelectric materials (denoted by *) and nonferroelectric materials and their room temperature dielectric constants. In comparison to the dielectric constants of many organic and inorganic solids (which are typically < 5 and < 20 respectively (Jaffe et al., 1971)), the dielectric constants of most ferroelectric materials are relatively high. The dielectric constant of a material is the ratio of charge stored in the material relative to the charge that would be stored in vacuum under the same conditions (voltage, electrode separation, etc.). Ferroelectrics have high dielectric constants due to the ease of storing charge in the dipoles present in the material.

Table 1.1 Room Temperature Dielectric Constants of Some Ferroelectric and Non- ferroelectric Polcrystalline Materials	
BaTiO3* PbZro 4eTio coOa*	~2000 (Jaffe et al., 1971)
TiO ₂	85-170 (Kingery, 1976)
Al ₂ O ₃	8-10 (Kingery, 1976)
Fused sinca glass	3.78 (Kingery, 1976)

Most ferroelectric materials have a temperature referred to as the Curie temperature, T_c , at which they lose their ferroelectric properties. This is accompanied by a shift in the crystal structure to one of higher symmetry. In BaTiO₃, for example, at room temperature the structure is tetragonal, but on heating to 130°C, the structure shifts to a cubic symmetry. Since cubic crystal structures possess a center of symmetry, they cannot be ferroelectric. Accordingly, BaTiO₃ is paraelectric above 130°C. Paraelectric materials lack a spontaneous dipole and exhibit non hysteretic polarization vs. electric field behavior.

Several different types of ferroelectric behavior are exhibited by many different materials. These can be classified by the nature of the ferroelectric to non-ferroelectric transition, the number of allowable spontaneous polarization directions, the existence of a center of symmetry in the non-polar phase, or by crystal chemical classification of the bonding (Jona and Shirane, 1962).

The materials of interest for this study are those of oxides with a center of symmetry in the non-polar phase, a first order ferroelectric to paraelectric phase transition, and multiple allowable spontaneous polarization directions (i.e. the cubic prototype phase of the perovskite crystal structure develops 6 allowed polarization directions on shifting to a tetragonal symmetry). The dielectric constant of these ferroelectrics changes significantly with temperature, rising to anomalously high values as the Curie point is approached, and dropping off sharply after the Curie point is exceeded. A plot of dielectric constant vs. temperature is shown in Figure 1.2 for a barium titanate single crystal along the a and c axes of the tetragonal phase. The reason for the lower dielectric constant in the direction of the polarization is that the ferroelectric displacement keeps the Ti atom tightly bound in the c direction, but it is relatively free to vibrate in the perpendicular (a) direction (Jaffe et al., 1971).



Figure 1.2 Dielectric constant vs. temperature for single crystal BaTiO₃ in the tetragonal a and c crystallographic directions (from Jaffe et al., 1971)

The rate at which the dielectric constant falls off above the Curie-Weiss temperature can be described in most ferroelectrics by the Curie-Weiss law shown in equation 1.1.

$$k = C/(T-T_0)$$
 (1.1)

Where k is the dielectric constant, C is the Curie constant, T is the temperature, and T_0 is the Curie-Weiss Temperature. If the ferroelectric to paraelectric transition is a second order phase transition, the transition temperature, T_c , and the Curie-Weiss temperature, T_o , will coincide, as in Figure 1.3a. If the transition is first order, then T_o will be lower than T_c .



Figure 1.3 Plot of 1/dielectric constant vs. temperature for a first order (a) and a second order (b) transition

1.2.3 Polarization-Electric Field Hysteresis

In general, a ferroelectric is characterized by a reorientable spontaneous polarization (Jaffe et al., 1971; Jona and Shirane, 1962; Megaw, 1949). A typical polarization-electric field hysteresis loop is shown in Figure 1.4. On application of an electric field to an unpoled ferroelectric material, the previously randomly aligned dipoles are pulled in the direction of the field. At some level of electric field, the spontaneous ferroelectric dipoles are aligned as well as possible with the applied field. Extrapolation of the polarization along the slope of the hysteresis curve back to the polarization axis gives the saturation polarization, P_s, as shown in Figure 1.4. When the electric field is subsequently removed, a portion of the dipoles relax to another crystallographic direction, generally to relieve stress generated during alignment, but many stay aligned. This leads to a net remanent polarization in the direction of the applied field, represented on Figure 1.4 as P_r . To return the material to a non-polarized state, an electric field must be applied which opposes the remanent polarization. The field required to achieve zero net polarization is the coercive field, shown as E_c in Figure 1.4.



Figure 1.4 A typical hysteresis loop exhibited by a ferroelectric material (from Kingery et al., 1976) where P=polarization and E=electric field

1.2.4 Domains

In a ferroelectric single crystal, it is possible to align all of the spontaneous dipoles in the same direction. However, in a polycrystalline bulk ceramic, grains (and their respective crystallographic directions) are randomly oriented with respect to each other. It becomes impossible to apply a field in one direction and align all dipoles in that direction due to the strong anisotropy which ties the dipole to specific crystallographic directions. Most ferroelectric materials have a domain structure. Domains are local regions in which the polarization vectors are pointing in the same direction. Since the free energy of a polydomain state is lower than that of a single domain state, domains will form even in single crystals (Smolenskii et al., 1984).

Domain structures occur spontaneously when cooling from the paraelectric to ferroelectric state as the material passes through the Curie point. Taking into consideration the fact that polarization vectors must align with one of the crystallographically-determined polar axes, domains will have particular allowable orientations with respect to each other. These orientations are determined by the crystallographic planes which undergo the same amount of strain, as described by the Fousek-Janovec criteria (Fousek and Janovec, 1969).

For example, in a tetragonal perovskite crystal there are two types of domain walls, 180° domain walls and 90° domain walls. 180° domain walls correspond to neighboring domains where the polar axes are antiparallel as in Figure 1.5. These two domains can share any plane parallel to the c axis of the material due to the fact that both unit cells are elongated in the *c* direction (Smolenskii et al., 1984). 90° domain walls on the other hand must share the (101) plane due to the requirement for matching strain at the domain wall (Smolenskii et al., 1984).



Figure 1.5 180° and 90° domain walls in a tetragonal crystal. Arrows denote the direction of the spontaneous polarization

1.3 Lead Zirconate Titanate

1.3.1 Crystal Structure

Lead zirconate titanate is a ferroelectric material which, in its paraelectric state, exhibits a cubic perovskite ABO₃ prototype crystal structure with point group Pm3m as shown in Figure 1.6. The A cation (Pb) sits on the corners of the unit cell in 12 coordination with oxygen. The B cations (Zr or Ti) sit in the center of the unit cell in 6 coordination with oxygen.

Perovskite-structured ferroelectrics in general can display three types of ferroelectric crystal structure distortions. These are displacive transitions where one or more sublattices shift relative to the prototype cubic structure. However, they can usually be approximated as a shift in the B cation from its center position. The possible directions for this displacement are shown in Figure 1.7. A shift in the [001] direction results in a tetragonal structure, [011] in orthorhombic, and [111] in rhombohedral, where all directions refer to the cubic prototype cell.

PZT is a solid solution of PbZrO₃ and PbTiO₃. PZT exhibits several different ferroelectric forms, one tetragonal and two rhombohedral. Figure 1.8 shows the phase diagram of the PbZrO₃-PbTiO₃ system (Jaffe et al., 1971). It can be seen that on the Tirich side, the structure is tetragonal, and on the Zr-rich side the structure takes on two different rhombohedral forms.



Figure 1.6 The perovskite crystal structure



Figure 1.7 Directions of displacement for the B cation in the transition to lower symmetry from the cubic perovskite



FT=ferroelectric tetragonal, PC=paraelectric cubic, FR=ferroelectric rhombohedral (HT)=high temperature, (LT)=low temperature, AO=antiferroelectric orthorhombic, AT=antiferroelectric tetragonal

Figure 1.8 Phase diagram of the PbTiO3-PbZrO3 system (from Jaffe et al., 1971)

1.3.2 Properties and the Morphotropic Phase Boundary

PbTiO₃ is ferroelectric and has a Curie temperature of 490°C. PbZrO₃ is antiferroelectric and has a Curie temperature of 230°C. At the boundary between the rhombohedral and tetragonal phases (PbTi_{0.48}Zr_{0.52}O₃) the Curie temperature is ~360°C. This composition is important due to its position on the morphotropic phase boundary.

A morphotropic phase boundary is a nearly temperature independent boundary between two phases where, to a certain extent, the two phases coexist. Thermodynamic analysis for the conditions under which this can occur is presented in some detail in Smolenskii (1984). In PZT, the Ti-rich tetragonal side has six directions along which the polarization may align. The Zr-rich rhombohedral side has eight. The polar axes correspond to the crystallographically equivalent axes of the initial paraelectric to ferroelectric displacement.

On the boundary itself there is a low free energy difference between the two phases, and in essence all fourteen directions can be taken advantage of for reorientation of the dipole. This leads to a maximum of the piezoelectric moduli, electromechanical coupling coefficients, dielectric constant, and elastic compliance; and a minima in the mechanical quality factor and coercive field. The compositional dependence of some of these properties are illustrated in Figure 1.9. Due to the enhanced properties, much attention has been paid to this composition and it will be the focus of investigation for this thesis.



Figure 1.9 Plots of a) dielectric constant and planar coupling and b) piezoelectric d coefficients vs. composition (from Jaffe et al., 1971)

1.4 Intrinsic vs. Extrinsic Contributions to Dielectric Properties

In ferroelectric materials, there are two types of contributions to the dielectric properties, intrinsic and extrinsic. Intrinsic contributions are those that would be present in a single domain single crystal. These can be calculated on the basis of phenomenological theory. Extrinsic contributions are associated primarily with domain wall motion or defect dipole motion.

Figure 1.10 shows a plot of the expected properties calculated from the phenomenological theory for a PZT ceramic as well as those measured on two compositions of PZT (soft and hard). A decrease in the properties of soft and hard PZT is observed with decreasing temperature. It is also observed that the properties converge with the expected contribution from intrinsic responses in the material around 4K. The 'freezing out' of properties at low temperatures indicates the elimination of thermally activated extrinsic contributions. Notice that in hard PZT, ~20% of the contributions to dielectric properties at room temperature are extrinsic. In the soft composition of PZT, more than half of the measured properties are from extrinsic contributions. This data makes it clear that domain wall mobility is much more prominent in soft PZT, than in hard PZT. It is also clear that without extrinsic contributions, the dielectric properties of PZT are significantly decreased. A similar behavior is observed in the piezoelectric properties (Zhang et al., 1983).



Figure 1.10 Properties of hard and soft PZT compared with the expected contribution calculated from phenomenological theory (adapted from Zhang et al., 1983)

1.5 Doped Lead Zirconate Titanate

1.5.1 Ability of PZT to Accommodate Dopants

The perovskite structure and its distorted derivatives are some of the most stable crystal structures (Goodenough and Longo, 1978). Because of their stability the structures easily accept cation dopants of different sizes and charges on both A and B sites. Dopant size is stable within the limits of the Goldschmidt criterion (Goldschmidt, 1927/28) which is given in equation 1.2. For PZT, r_A and r_B represent the ionic radii of Pb and Zr or Ti, respectively, and r_O represents the radius of O.

$$t = \frac{(r_A + r_o)}{\sqrt{2}(r_B + r_o)}$$
(1.2)

The structure is stable for 0.75 < t < 1.00 as long as the cations are stable in 6 or 12fold coordination. This puts the lower limits of cationic radii accepted in the structure at $r_A > 0.9$ Å and $r_B > 0.51$ Å (Goodenough and Longo, 1978).

Due to the stability of the structure, substitutions as outlined above are accepted up to relatively high concentrations. Because of the ability to accept such a variety of different cations, doping PZT and many other perovskite-structured materials to modify their properties is widespread. Some of the common uses and effects of dopants in the PZT system will be discussed in the next section.

1.5.2 Common Doping Schemes in PZT

PZT is usually modified with three types of dopants. First, there are isovalent substitutions which can modify the Curie temperature, thereby changing the room temperature dielectric and piezoelectric properties of the material. Second, there are donor substitutions which create Pb²⁺ vacancies and result in 'soft' PZT. Third there are acceptor substitutions which create O²⁻ vacancies and result in 'hard' PZT.

1.5.2.1 Isovalent Substitutions

Ca²⁺, Sr²⁺, and Ba²⁺ are the most common isovalent substitutions in PZT. Sr²⁺, Ba²⁺, and Ca²⁺ will lower the Curie point when substituted for Pb²⁺ (Jaffe et al., 1971). This raises the room temperature dielectric constant but has little effect on the coupling factor or elastic modulus. The result is an increased d₃₃ coefficient (Jaffe et al., 1971). Sr²⁺ also shifts the location of the morphotropic phase boundary slightly towards the zirconium side (Jaffe et. al., 1971). Sn⁴⁺ on the Zr/Ti site will decrease the tetragonal c/a ratio as well as the Curie temperature (Xu, 1991).

1.5.2.2 Substitutions Causing A site Vacancies

Substitutions of atoms with a higher positive valence than Pb²⁺ and Zr⁴⁺ or Ti⁴⁺ will cause 'soft' properties in PZT bulk ceramics. Commonly used elements are Nb⁵⁺ and La³⁺ which will occupy the Zr/Ti site or the Pb site respectively. Other reported dopants are Ta⁵⁺, Nd³⁺, and Y³⁺ (Kulscar, 1959), W⁺⁶, Th⁺⁶ (Kulscar, 1965), Bi³⁺ and Sb⁵⁺ (Globe Union Inc., 1962). Generally speaking, dopants with large radii will occupy the Pb²⁺ site and those with smaller radii will occupy the Zr/Ti⁴⁺ site. Ionic radii for common soft dopants is shown in Table 1.2.

Table 1.2 Ionic Radii of Common Soft Dopants (Xu, 1991)			
Pb site dopants:	ionic radius (Å)	Zr/Ti site dopants:	ionic radius (Å)
La 3+	1.22	Nb5+	0.69
Nd 3+	1.15	Ta ⁵⁺	0.68
Sb3+	0.90	Sb5+	0.63
Bi ³⁺	1.14	W6+	0.65
Th ⁴⁺	1.10	M770333	100000000

Additions of these materials will cause vacancies, primarily in the Pb²⁺ sublattice, to preserve charge neutrality. This is facilitated by Pb²⁺ volatilization during high temperature treatments, and an energetic preference for A site vacancies over B site vacancies in the perovskite structure (Goodenough and Longo, 1978). Therefore, dopants possessing a valence of one greater than the atom they replace (i.e. La³⁺ on a Pb²⁺ site or Nb⁵⁺ on the Zr/Ti ⁴⁺ site), will produce one Pb²⁺ vacancy for every two dopant atoms.

The effects of these vacancies on the properties of the PZT are quite pronounced. Table 1.3 shows a list of properties exhibited by soft PZT relative to unmodified PZT (after Jaffe et al., 1971).

Table 1.3 Properties of Soft PZT Relative to Unmodified PZT
increased dielectric constant
high dielectric loss
increased elastic compliance
low mechanical Q
high piezoelectric coupling factor
low coercive field/relatively square hysteresis loop greatly increased electrical resistivity small aging effects
easy nonelastic mechanical deformation yellow color
translucency easy phototropic darkening

One explanation has been given by Gerson (1960). He suggested that the Pb vacancies facilitate the inevitable shape changing processes which occur in the unit cell during switching processes, and that this results in domain wall motion which requires less mechanical or electrical drive than in an unmodified material.

Another consideration is that defect dipoles in soft PZT consist of one dopant atom and one Pb²⁺ vacancy. Unlike hard PZT (as will be addressed in the next section), these defect dipoles are not mobile. Their random alignment is not connected with the domain configuration, and therefore, they are less likely to pin domain walls.

Easier domain wall motion has several effects on the overall properties of the material. The coercive field, being a direct measure of electrical driving force necessary to change dipolar alignment, is decreased. Also, more domain wall motion will occur in a soft material for a given electric field, generating a higher dielectric loss. The reduced aging of the material and its low mechanical quality factor (Q_m) are explained by the idea that domain wall motion will occur preferentially to storing of large amounts of stress in the material (Jaffe et al., 1971).

Other effects occur due to stoichiometry considerations. The increased bulk resistivity occurs because donor dopants counteract the normal p-type conduction that occurs in undoped materials (Moulson and Herbert, 1990). P-type conduction occurs when Pb vacancies (which occur during normal processing of undoped materials) act as centers of negative charge. These sites have an effective valence of -2, and therefore offer an acceptor level with two holes. Also, unintentional impurities in the source powders for PZT are typically of lower valence, acting as acceptor dopants and contributing holes. These holes can easily gain enough thermal energy at room temperature to participate in conduction processes. Therefore, p-type conductivity results. Since donor dopants provide electrons, they combine with the holes to reduce overall conduction in the PZT.

1.5.2.3 Dopants Causing Oxygen Vacancies

Substitutions of atoms with a lower positive valence than Pb²⁺ and Zr⁴⁺ or Ti⁴⁺ cause 'hard' properties in PZT bulk ceramics. Commonly used elements are K¹⁺ and Na¹⁺ on the A sites, and Fe³⁺, Mg²⁺, Al³⁺, Ga³⁺, In³⁺, Cr³⁺, Co³⁺, Mn³⁺, Ni²⁺, and Sc³⁺ on the B sites (Xu, 1991). Radii of some of these dopants are shown in Table 1.4.

Table 1.4 Ionic Radii of Common Hard Dopants (Xu, 1991)			
Pb site dopants:	ionic radius (Å)	Zr/Ti site dopants:	ionic radius (Å)
K1+	1.33	Fe ³⁺	0.67
Na ¹⁺	0.94	Al ³⁺	0.57
		Sc3+	0.83
		In ³⁺	0.92
		Cr ³⁺	0.64

As in soft PZT, additions of the aliovalent ions causes vacancies in the lattice to preserve charge neutrality. Acceptor impurities cause O vacancies. Dopants possessing a valence of one less than the atom they replace (i.e. Na¹⁺ on a Pb²⁺ site or Fe³⁺ on the Zt/Ti⁴⁺ site), will produce one O²⁻ vacancy for every two dopant atoms. For dopants with a valence of two lower than the atom they replace (Mg²⁺ on a Zr/Ti⁴⁺ site), one O²⁻ vacancy is created for every dopant atom.

Like soft PZT, these vacancies have distinct effects on the properties of the material. Table 1.5 lists the properties of hard PZT relative to soft PZT (after Jaffe et al., 1971):

Table 1.5 Properties of Hard PZT Relative to Soft PZT
relatively low dielectric constant low dielectric loss
high coercive field
moderately lowered electrical resistivity relatively dark color
 relative insensitivity to light more difficult depoling and poling

Since the perovskite structure is dependent on the oxygen sublattice for stability, O²⁻ vacancies cannot be accommodated to such a high degree as A site vacancies. Therefore, doping levels in hard PZT are somewhat limited (Goodenough and Longo, 1978). However, allowable limits are high enough for modification of the material's properties.

Oxygen vacancies tend to shrink the unit cell size in PZT (Jaffe et al., 1971). Also, the defect dipoles in hard PZT consist of one dopant atom and an oxygen vacancy. Because the crystal is a network of oxygen atoms with A and B cations in the interstices, oxygen vacancies are fairly mobile. The energy required to exchange place with a neighboring oxygen atom can be achieved at poling temperatures. Thus during poling, the defect dipoles tend to align with respect to the applied field. The resulting internal bias stabilizes

the domain configuration. The result is a material with domain walls which are pinned by the defect dipoles.

Because the domain walls are pinned, an increased amount of electrical or mechanical drive is needed to move them. Therefore, the coercive field is high. Limited motion of domain walls limits the dielectric constant and enhances the mechanical Q. Also, since there is less wall motion under an ac driving field, dielectric loss decreases.

The electrical conductivity is increased in hard PZT. As stated before, typical conduction in unmodified PZT is p-type. The reason for this is the presence of holes due to lead vacancies from PbO volatilization or unintentional acceptor type doping from naturally occurring impurities. In acceptor doped PZT, the presence of lead vacancies is depressed by the formation of oxygen vacancies for charge neutrality. However, the presence of holes in also exacerbated by the increased level of acceptor atoms in the structure, and therefore electrical conductivity increases (Moulson and Herbert, 1990).

1.6 Thin Film Piezoelectrics

1.6.1 Effects of Microstructure

1.6.1.1 Planar Substrates

PZT films have been explored for many applications ranging from capacitor cells for various random access memory (RAM) geometries to microelectromechanical devices to optical devices (Auciello and Ramesh, 1996). In predicting the behavior of these materials it is important to understand how films will behave relative to bulk materials so that accurate device performance estimations can be made.

Thin films usually have microstructures which are different from those of bulk materials. Grain sizes are typically smaller, with different grain shapes and orientations than in bulk materials. In the bulk, grains are surrounded on all sides in a three dimensionally connected array of material. In a thin film, frequently the grains are columnar, so that a single grain spans from the substrate to the surface of the film. This leads to grain-grain contact in two dimensions.

Due to the different types of contact between grains, grain-grain interactions may be different in thin films. In particular, grain-grain interactions can be controlled by microstructural modification to enhance or suppress mechanical coupling in the lateral direction. This is similar to what is done in bulk materials with polymer-ceramic composites. A material which has good coupling in the *c* direction (parallel to poling axis), and poor coupling in the *a* direction (perpendicular to poling axis) would behave much like a 1-3 composite. This high anisotropy arrangement could be produced in a film with a highly porous microstructure where columnar grains were not in close lateral contact. In films with close lateral contact between grains, good coupling in both the *a* and *c* directions would be expected to be maintained, and piezoelectric anisotropy would be lower.

Conversely, it is much easier to obtain microstructures which are oriented in a thin film. Crystallographic orientation promotes better dipolar alignment, and hence stronger ferroelectric and piezoelectric activity when the field is directed along the direction of polarization. This is a direct, relatively easy way to improve the properties of piezoelectric thin films. Piezoelectric coated fibers present some interesting possibilities for microelectromechanical device designs (Fox et al., 1996) and polymer/fiber or polymer/tube composites (Zhang et al., 1992). One of the properties that may be compromised in such a geometry is the coupling between grains. Consider, for example, the columnar microstructure of a PZT film. If columns are grown on a curved substrate such as a fiber, the lateral surface area (parallel to the substrate) of the columns must increase from substrate to film surface for the film to remain dense. If the lateral grain size is constant, there will be a tendency for the grains to grow apart as the film gets thicker. This could lead to a density gradient between the film/fiber interface and the film surface. The result of the gradient could be reduced mechanical coupling between grains, and low d₃₁ values for a film poled through its thickness.

It would be expected that this problem would be highly dependent on the grain size to radius of curvature relationship, i.e. if grain size were very much smaller that radius of curvature, the effect would be less pronounced. On the other hand, if the grain structure was made up of randomly oriented, non-columnar grains, a density gradient throughout the films would be much less likely.

1.6.2 Domain Wall Mobility in Films

As stated above, there are several concerns in incorporating PZT thin films into MEMS devices. In the bulk, PZT is often doped to be either hard or soft, where soft PZT's typically have the highest piezoelectric coefficients. This makes those compositions of particular interest for applications requiring larger piezoelectric displacements. As explained in section 1.5.2.2, soft PZT's have mobile domain walls. Hard PZT's on the

other hand have pinned domain walls. The enhanced properties of soft bulk PZT are typically attributed to motion of the mobile domain walls (Jaffe et al., 1971).

There are a number of factors which can influence domain wall mobility in thin films. If domain wall mobility is decreased in films, a departure from the properties normally associated with bulk hard and soft PZT are likely to be observed. Four factors in particular, grain size (Cao and Randall, 1996), dopant distribution (Klissurska et al., 1995), residual stress (Tuttle et al., 1995), and high defect concentrations present possible obstacles to mobile domain walls in PZT films. The influences of these factors on bulk materials have been studied in some detail, but their relationship to the properties of thin films has not been well explored. It is necessary to better understand the effects of each to determine whether or not soft thin films of PZT can, in fact, be fabricated.

1.6.2.1 Grain Size

In a TEM study of domain size vs. grain size in Nb-doped PZT ceramics, Cao and Randall (1996) observed that in ceramics of less than 1µm grain size, fewer domain variants were present in each grain than in larger-grained samples. Similarly, Kim (1994) observed in a systematic study of properties of PZT vs. grain size that below 1µm a reduction in remanent polarization and increase in coercive field were observed. This, in turn led to a decrease in the piezoelectric coefficients in small grained ceramics. Part of this was attributed to a decrease in domain wall mobility associated with the changes in domain structure with size.

Frequently, thin films are less than 1µm in thickness and have small lateral grain size dimensions (often 0.05-1µm). This is well into the range where size effects are observed in bulk materials. Thus, changes in the equilibrium domain structures in thin films may make it difficult to achieve the high dielectric and piezoelectric properties of soft PZT.

1.6.2.2 Dopant Distribution

The manner of incorporation of the dopants will play a large role in determining their net effect on the properties of the film. If donor dopants were not incorporated into the PZT grains, (for instance, if they had segregated to the grain boundaries) the films would effectively be undoped. In such a situation, the film would behave intrinsically hard despite having a global stoichiometry which corresponds to a soft bulk composition. It has also been shown that in Nb doping of sol-gel films (Klissurska et al., 1995a) the Nb tends to inhibit the transformation from pyrochlore to perovskite, resulting in microstructural anomalies such as surface pyrochlore layers. This second phase appreciably degrades the dielectric and electromechanical properties of the films.

1.6.2.3 Residual Stresses

Another factor which could influence domain wall mobility is residual stresses in the film. In general, local stresses can pin walls. For any applied stress, whether it be electrical or mechanical, the effect of this local stress must be overcome before the domain walls can become mobile. We know that because of thermal expansion coefficient mismatch, PZT films on silicon substrates are under tensile stress after crystallization. It is well documented that stress will change the properties of bulk hard and soft PZT (Zhang et al., 1997, Jaffe et al., 1971, Brown et al., 1961). It has also been found that applied stresses affect soft PZT more than hard PZT. For example, in biaxial compression up to 200 MPa perpendicular to the poling axis, hard PZT was shown to undergo a 50% reduction in capacitance with almost a full recovery to its original properties upon removal of the stress. Soft PZT under the same amount of compressive stress was shown to

undergo a 60% reduction only recovered to ~70% of its original value when the stress was removed (Brown, 1961). These changes were attributed to domain reorientation associated with the ferroelastic nature of non-180° domain walls. Thus, soft PZT, given the higher wall mobility and lack of internal field tending to repole the sample, showed larger changes and more hysteresis on unloading. Consequently, the residual stresses experienced by ferroelectric films might be expected to affect the domain populations and domain wall mobility.

1.6.2.4 Defect Concentrations

In thin films grown by vapor deposition techniques, both microstructural and crystallographic defects are frequently a problem. Voids, dislocations, very small quantities of second phase, boulders (especially in PLD films), or stoichiometric variations can all lead to properties different from those observed in bulk materials. In addition, detection and quantification of these types of defects is often difficult. For example, stoichiometry typically cannot be determined with enough accuracy to know if a film is 1-2% deficient of one particular constituent, or to ascertain if modest stoichiometric variations through the thickness of the film are present. Although techniques for these types of measurements are well established for bulk materials, there is simply not enough material available to allow for accurate results on a thin film. Similarly, while cross-sectional examination of film microstructure can indicate the presence of voids, quantifying and determining the relative effects on the properties of a film is difficult. The density of crystallographic defects like dislocations, interstitials, etc. is also very difficult to determine.

Bombardment, low mobility of deposited species, and volatility of film constituents are some of the sources for these defects. As these sources are inherent to the film growth technique, it is difficult to completely eliminate their effects on the crystallographic and microstructural aspects of the film.

The concentration of defects are important because of the nature of the property comparison being made. The differences in hard and soft bulk PZT arise from a controlled level of dopant-induced point defects. If significant concentrations of other defects, either microstructural or crystallographic, are present, they may have an effect on the properties of the films. Without a complete characterization of the relative defect concentrations and the effect of each defect type, it is difficult to know their overall contribution to the properties of the film. If, however, the effects of processing-induced defects outweighs the effects of the dopant induced defects, it is possible that the processing-induced defects, rather than the dopant-induced defects, will dominate film properties.

1.7 PZT Thin Films

Most research in the area of PZT thin films has been done on undoped compositions near the morphotropic phase boundary. As these films are incorporated into devices, their properties should be optimized. Since very few commercial bulk PZT compositions are undoped, it is unrealistic to think that PZT thin films will not also be doped. Also, when considering the possible applications of PZT thin films, especially in the area of microelectromechanical devices, the piezoelectric properties of bulk doped PZT's would be the most useful (namely, high piezoelectric coupling coefficients). The effects of dopants in PZT films have not been studied in great detail, and therefore it is a topic which should be addressed.
1.7.1 Undoped PZT

1.7.1.1 PZT Films on Flat Substrates

Many researchers have explored PZT thin films. They have been produced by a wide variety of methods including sol-gel (Tuttle et al., 1996; Warren et al., 1995; Kwok and Desu, 1992), physical vapor deposition, (Huffman et al., 1990), organometallic chemical vapor deposition (De Keijser et al., 1994), D.C. magnetron sputtering (Sreenivas et al., 1988), ion beam sputtering (Auciello et al., 1994), and pulsed laser deposition (Ramesh et al., 1995; Krupanidhi et al., 1992).

PZT films have been examined for ferroelectric nonvolatile memories, optical waveguide devices, and microelectromechanical systems. The essential properties are different for different applications. For instance, in memory applications, permittivity and its thickness dependence, absolute polarizability (remanent polarization), time and frequency dependence of polarizability, leakage current, and fatigue resistance are important (Kingon et al., 1996). In microelectromechanical applications, the d₃₃ and d₃₁ coefficients and Young's modulus become more important (Polla and Francis, 1996). Table 1.6 shows a listing of typical measured ferroelectric properties for PZT films from the perspective of importance to microelectromechanical systems (Polla and Francis, 1996, Shepard et al., 1997).

Relative dielectric constant	800-1200
tan d at 1kHz	0.02-0.04
Remanent polarization	25-35µC/cm ²
Coercive field	40-150 KV/cm
Resistivity	10 ¹¹ Ωcm
Dielectric Breakdown Strength	0.6-0.8 MV/cm
Piezoelectric d ₃₃ coefficient	70-200 pC/N
Young's Modulus	91 GPa

1.7.1.2 PZT Films on Fibers

A few researchers have looked at PZT coatings on fibers (Fox, 1995, Lisbôa et al., 1995, Yi et al., 1989). Yi et al. (1989) coated 250µm diameter alumel wires with PZT by painting on successive sol-gel coatings. They measured piezoelectric displacements for these structures of 0.2µm for 620 Hz/24V applied to a 55mm long, 10µm thick coating. Lisbôa et al. (1995) worked with 180µm diameter, 5.8 cm long aluminum coated optical fibers and were able to apply coatings of small PZT particles dispersed in solution resulting in thick films of ~120µm. These films were used to modulate the optical signal carried in the fibers over the frequency range from 200kHz to 25MHz. As these films were all produced by thick film techniques, columnar microstructures were not observed. Also, each researcher worked with a single fiber thickness, and therefore a change of properties or microstructure with fiber curvature were not addressed.

Fox (1995) has shown the feasibility of putting thin PZT films on fibers by producing hollow PZT tubes. PZT coatings were produced by multimagnetron reactive sputtering onto 23µm polyester fibers which were subsequently burnt out, leaving microtubes. The microstructures of the microtubes were not observed to be columnar in nature. This could be related to the absence of a surface for nucleation of the PZT. Columnar microstructures in films which are post deposition crystallized often result from nucleation at a substrate surface. In these tubes, the polyester fiber was burnt away before reaching the crystallization temperature of PZT. The inner diameter of the tubes was found to decrease by 17%, which may have aided in the observed density. No electrical properties were reported for the tubes.

Fox et al. (1996) have reported extensively on ZnO coatings on optical fibers. Property degradation with radius of curvature for the ZnO films was not reported. In this work it was reported that ZnO fiber coatings could be produced more easily than PZT for the same

deposition technique. In addition, ZnO films could be made thicker than PZT films. Small grain separations have been observed at the surface of thicker ZnO films (Fox, 1996).

1.7.2 Doped PZT films

The most common dopant reported for modified PZT in the literature is Nb. This has been accomplished with sol-gel (Barlingay and Dey, 1996, Klissurska et al., 1995a and 1995b, Dimos et al., 1994), D. C. magnetron sputtering (Weaver et al., 1991, Griswold, et al., 1991.), and pulsed laser deposition (Dhote et al., 1996, Björmander et al., 1995, Ramesh et al., 1994a and 1994b). Work on Fe³⁺ doped sol-gel PZT has also been reported by Barlingay and Dey (1996).

Although Nb doping has been found to increase the electrical resistivity of PZT films, as of yet, no researchers have demonstrated an enhancement of dielectric properties by donor doping. Instead, it has been demonstrated that Nb doping can seriously degrade the quality of sol-gel films. This is mainly due to the stabilization of the pyrochlore phase by Nb doping, resulting in surface or intragranular Pb deficient material. The amount of surface or intragranular pyrochlore phases increased with further Nb additions (Barlingay and Dey, 1996, Klissurska et al., 1995a and 1995b). No significant concentration of Nb in the intragranular phase was observed by TEM (Klissurska, 1995) leading to the conclusion that the Nb itself was incorporated into the films. Unfortunately, the macroscopic effects of second phases on the film microstructures led to an inability to detect the actual effects of the dopants on the properties of the films. Note that the stoichiometry of the precursors was based on the assumption that Nb additions caused Pb vacancies.

Barlingay and Dey (1996) have suggested that possibly, unlike bulk materials, Nb doping results in B site vacancies rather than A site vacancies in PZT films. One of the reasons for this is the increased activity of Pb by its addition in excess of the stoichiometric requirements during batching. In films that they prepared assuming B site vacancy compensation, second phases were not observed. However, the resulting properties for these films showed lower remanent polarization values and similar coercive field values to Fe doped films prepared in the same fashion.

In work by Dimos et al. (1994) Nb and La doped films were produced. The films were single phase by x-ray, but TEM studies were not completed. La doped films demonstrated a reduction in coercive field, but this was accompanied by a reduction in remanent polarization relative to undoped films produced in the same manner. This was attributed to the lowering of the ferroelectric to paraelectric transition temperature. Both types of dopants resulted in a significant increase in room temperature and high temperature resistivity with increased dopant concentration.

Similar results were found in vapor deposited films. Higher electrical resistivities have been shown for donor doped PZT compositions (Björmander et al., 1995, Weaver et al., 1991, Griswold et al., 1991). However, in general, the remanent polarizations and dielectric constants of doped films tend to be lower than those of undoped films. The lack of microstructural analyses on these films does leave open the possibility that a second phase may be causing these degraded properties.

The only favorable change in properties was reported by Griswold et al. (1991). They demonstrated an increase in fatigue resistance with Nb doping. However, the details of fatiguing conditions were not reported.

Lee and Ramesh (1996), Dhote et al. (1996) and Ramesh et al. (1994a and 1994b) have done work on pulsed laser deposition of La and Nb doped PZT films on bilayered electrodes of LSCO and platinum. They report films with remanent polarizations of ~25-30 μ C/cm². The films they grew were highly [100] oriented, and the properties were not directly compared with undoped films. The properties are not, with the exception of conduction characteristics, superior to undoped properties reported for similar growth techniques.

Characteristic of the works cited above are two things. First, few studies involve direct comparisons of donor and acceptor doped films. Second, all of the studies above involved only one dopant species per film. A lack of direct comparison of films grown under the same conditions as a function of doping makes interpretation of the available data difficult. Consequently, one of the goals of this thesis is to examine the impact of doping on film properties. Since commercial compositions were used, bulk properties for various compositions are known. This provides a solid basis from which to compare the properties of the films. In addition, it is hoped that by using targets doped with multiple cations that the differences between "hard" and "soft" films will be clear. PLD was chosen as the deposition technique due to the ease of deposition of multi-component oxide materials with complex doping schemes.

1.8 Pulsed Laser Deposition

1.8.1 General Description

Pulsed laser deposition (PLD) is a conceptually simple film deposition technique. A high energy laser is shown on a target of the desired film stoichiometry, which causes a nonequilibrium ablation of the material. A substrate is placed in the vicinity of the plume of the ablated material, allowing it to deposit there. A typical PLD setup is shown in Figure 1.11.



Figure 1.11 A typical PLD setup

Pulsed laser deposition has many advantages as a thin film technique. It is a simple technique that does not involve complicated geometries or, with the exception of a laser, equipment. This often translates into a somewhat smaller startup cost than many other growth techniques. Also, through the use of a target with the same composition as the film (or sometimes compensated with an excess of any volatile components), stoichiometry, especially for complex oxides, is much easier to control than in many other techniques. A wide variety of materials can be grown in the same chamber by switching to new targets of the desired composition.

1.8.2 Laser-Target Interaction

Plume formation can be broken down into four steps as described by Haglund (1996). First, single and multiple phonon processes allow for the absorption of laser energy into the target material. Second, energy is transferred into the target through radiative and nonradiative relaxation processes. Third, particles are ejected from the surface of the solid, and fourth, a dense plume of neutral and ionized species forms and expands into the surrounding gas. Haglund proposes that steps 1-3 are controlled by elementary excitation and relaxation processes in the target which are dependent on material properties. He proposes that by accurately defining the cohesive energy of the solid and the electronphonon coupling strength, the ablation threshold can be determined for specific materials. This makes it highly dependent on the nature of the bonding in the material to be ablated. He also proposes that the expansion of ejected particles into the ambient gas atmosphere during deposition is largely controlled by gas dynamics.

Other researchers have proposed different mechanisms for plume formation including subsurface heating and phase explosion models (Kelly and Miotello, 1996) and thermal/hydrodynamic vaporization models (Leboef et al., 1996, Chen et al., 1996). These models depend on material parameters such as absorption coefficient and solid to liquid/liquid to vapor transition energies.

Leboef et al.(1996) propose that during plasma formation, ionization of plume species arises from non-equilibrium processes and absorption of laser light by the plume. They suggest that absorption occurs through photoionization of an excited state atom, and electron-neutral and electron-ion inverse bremmstrahlung. It is also reported that this interaction is much more significant at higher laser energies. The definition of "high" is somewhat dependent on the ionization and excitation energy of the material involved, but does fall within the range of useful PLD energy densities.

The plasma expansion has been treated by Leboef et al. (1996) and Geohegan and Puretzky (1995 and 1996). The expansion of the plasma is modeled as a 'snowplow' where the outer plume species are compressed during expansion by the surrounding gas, so that at high pressures, shock waves of material travel outwards from the target to the substrate. In this process are included reactive and kinetic collisions which result in new chemical species (typically a metal-oxygen collision for oxide deposition), and kinetic energy transfer between species. Also, it is reported that a "fast component" of the plume can exist which propagates with little or no collisional interaction with the ambient gas, resulting in high kinetic energies (up to 250 eV for Y⁺). This portion is often not detected by standard optical imaging of plume species owing to its reduced luminescence from limited interaction with ambient gas and plume species (Geohegan and Puretzky, 1995). The presence of the fast component is highly dependent on ambient pressure and distance from the target, as high energy particle density decreases exponentially with propagation distance through the ambient gas (Geohegan and Puretzky, 1995) Conversely, at vacuum pressures, the plume expands relatively freely, resulting in a more evenly distributed expansion.

Although there is not a consensus on the correct model of laser-target interactions, several studies of plume chemical species and energies have been completed which complement the modeling. A general trend is found that as laser fluence increases, the velocity and energy of plume species, as well as the total ion flux increases (Dam et al., 1996, Mertin et al., 1996, Metev et al., 1996). The same trends are found with decreasing ambient gas pressure (Hendron et al., 1996, Geohegan and Puretzky, 1995, Geohegan, 1992).

1.8.3 Compositional Fidelity

PLD is known for ease of transfer of complex stoichiometries from target to film. However, different sticking coefficients, preferential scattering in the plume, resputtering, or evaporation of volatiles components of the film can disrupt the compositional fidelity often associated with PLD. Typically, any volatile elements in the target must be compensated for if growth is carried out at high temperatures. The required amount of compensation is material, deposition pressure, and deposition temperature dependent, but for PZT is reported to be anywhere from 5-75% excess. For room temperature deposition, this has not typically been the case (Kruphanidhi et al., 1992, Chiang et al., 1992). In oxide deposition, ambient oxygen is important to reduce volatility. For example, PbO is less volatile than Pb, therefore keeping plume species oxidized tends to reduce volatility effects.

Aside from volatility, resputtering and scattering angle can affect film stoichiometry. Ma et al. (1996) and Hau et al. (1994) have reported incidences of Pb resputtering by energetic Ti and Zr atoms during PLD of PZT. Low temperature, moderate bombardment deposition practices can minimize these effects. Geohegan (1995) has also suggested the possibility of species-dependent scattering in the plume, which encompasses the idea of particles of different mass having different expansion trajectories. Either of these mechanisms could cause spatial variations in film stoichiometry.

1.8.4 Boulders

One of the biggest problems in pulsed laser deposition is boulders (Chrisey and Hubler, 1995). While most of the deposited species are small, highly energetic atomic clusters, other ejecta are large particles, referred to as boulders, which either break off of the target without evaporating or are pieces of ejected molten material.

As stated above, ablated material is ejected perpendicular to the surface of the target. When the substrate is facing the target (on-axis ablation), the ejected boulders fly from the target and often strike the substrate because of its large surface area facing the target. As boulders are usually larger than the thickness of the film, incorporation of these boulders into the film causes seriously degraded properties for large area measurements.

Boulder populations can be minimized through the use of high density targets, high energy/short pulse width lasers, and frequent target resurfacing/limiting number of pulses per target location (Doughty et al., 1995, Chrisey and Hubler, 1995). Very dense targets are more likely to ablate evenly than targets with pores or inclusions. Short, energetic pulses help provide ablation without excessive heat transfer to the inner part of the target as described above. Frequent resurfacing of the target helps to prevent degradation of the surface which can encourage the formation of boulders.

However, even if all of the above-mentioned factors are optimized, boulders are difficult to completely eliminate. Their presence can usually be made sparse enough on the sample surface that property measurements can be made, but their presence frequently limits the amount of uniform, high quality area on a sample. Several methods have been developed to minimize them, including off-axis ablation, mechanical velocity filters, target rastoring methods, changing angle of incidence of the laser, and crossed flux PLD. However, these techniques tend to either be more complicated or as detrimental to film quality as the boulders themselves. Therefore, the ultimate decision is typically to use the deposition conditions which provide the best film quality in spite of boulders.

1.9 Scope of the Thesis

With the above mentioned questions in mind, the focus of this thesis is twofold. The first objective is to determine microstructure-property relations in PZT films. This will be done by examining the impact of various deposition parameters on the microstructure of films on flat and curved substrates. A determination of whether dense films can be deposited on curved substrates will be made. Second, the properties of films deposited from hard and soft PZT targets under identical conditions will be compared to determine whether or not soft properties can be achieved. The four factors of residual stress, dopant distribution, defect density, and grain size effects will be explored in an attempt to determine their effects on the properties of the films.

EXPERIMENTAL PROCEDURE

2.1 Growth

2.1.1 Equipment

2.1.1.1 Pulsed Laser Deposition System

The PLD system used in this work was centered around a 18"diameter/ 14" high cylindrical stainless steel vacuum chamber as illustrated in Figure 2.1. There is a diffusion pump (Varian type 0188) connected in series with a roughing pump (Alcatel 3033CP) which can produce a 10⁻⁸ torr base pressure in the system. Pressure is measured inside the chamber by a Baratron[®] capacitance manometer for pressures from atmosphere to 10⁻⁴ Torr or by an ion gage for pressures of 10⁻⁴ Torr and below.

The laser for the system is a Lambda Physik EMG150. A KrF gas mixture was used to produce a laser wavelength of 248 nm. The maximum energy output for this laser is ~800mJ. To enhance beam uniformity, only the center ~50% of the beam was used. For film growth, the typical output utilized was between 150 and 350 mJ.

The beam is focused through a plano-convex lens with a focal length of 50 cm, and enters the chamber through a quartz window. Due to absorption and reflection losses, 60% of the beam energy from the laser reaches the target (90-210 mJ). Divergence of the beam dictates that the smallest focusable spot in this system is 4mm². It follows that the maximum attainable energy density (for typical usage energies) is 5.25 J/cm².



Figure 2.1 The PLD system

The 1" diameter target is located in the center of the chamber at the end of a 9" stainless steel rod which is connected to a variable speed motor outside the chamber through a rotary feedthrough. The target center is 9" above the bottom of the chamber, and can rotate anywhere from 0-10 rpm. This geometry leaves an appreciable amount of free space for different configurations of substrate heaters and equipment.

This system is also capable of several different atmospheres. It is equipped with two MDC mass flow controllers which are used for oxygen and argon, and two which can be changed for other special atmospheres. It is also equipped with a PCI (model G-1) ozone generator which can produce up to 10% O₃ in O₂. The flow rate of the O₃/O₂ mixture is controlled by a needle valve. To set the ambient gas pressure, the flow rate of the gases is fixed, and the gate valve separating the chamber from the diffusion pump is partially closed to reduce the pumping speed.

A block heater was used to heat flat substrates. It consists of a block of 304 stainless steel with embedded Inconel® coated Kanthal® heating elements. It is capable of temperatures up to 750°C. The substrates were attached to the heater with silver paint for uniform thermal contact. The growth temperatures reported are the block temperatures measured with an embedded type K thermocouple. Because the heater is freestanding within the chamber, the target to substrate distance can be changed easily, and the heater can be used for on or off-axis deposition (substrate parallel or perpendicular to the target).

2.1.1.2 The Fiber Rotator

A fiber rotator was built for this system which can hold fibers 50 µm and larger in order to deposit fiber coatings. It is illustrated in Figure 2.2. An optical rail was attached to the top of the chamber. A carrier for the rail, illustrated in Figure 2.3, supports two bearings which hold a cylindrical rod with a fiber chuck mounted on the end so that fibers can be grasped and held in the vicinity of the plume. The carrier can be moved easily on the rail so that the target to fiber distance can be changed. The holder can also be moved from side to side on the carrier so that the fiber is not confined to the center region of the plume. The fiber chuck is rotated by a chain driven gear connected through a ferrofluidic feedthrough to a motor outside the chamber.

A radiant heater which can attain temperatures up to 750°C was built to accompany the rotator. It is illustrated in Figure 2.4. It is a double walled stainless steel cylinder which contains vertically wound Inconel[®] coated Kanthal[®] heating elements in a 1.25" diameter circle. There is an opening in the front to allow the plume species to enter the furnace and an opening in the removable lid to allow the bottom of the rotator to extend inside the heater. The temperature is measured inside the heater by a type K thermocouple which is permanently affixed inside the heater (to prevent movement of the bead from the center of the cylinder).



Figure 2.2 The fiber rotator a) top view and b) side view



Figure 2.3 The fiber holder schematic



Figure 2.4 The fiber heater

2.1.2.1 Flat Films

Lead zirconate titanate (PZT) films were grown on flat Pt coated Si wafers (Nova Electronics). Typical deposition conditions for the production of films with good electrical and structural characteristics are shown in Table 2.1. Commercial composition targets of hard (Piezokinetics 8) and soft (Piezokinetics 5A, Channel PZT 5700, and PLZT) PZT were ablated in various pressures of 10% O₃ in O₂. Target to substrate distance was varied along with pressure to find optimal deposition conditions. A laser energy density of 2-3 J/cm² was used. Amorphous films were deposited at either room temperature or 380°C during deposition to produce amorphous films, or at 650°C to produce crystalline films. If heated during deposition, the films were cooled to room temperature in 140 torr of O₂. Amorphous films were crystallized in a rapid thermal processor (RTP) at 650°C for 60s (AG Associates 210T-03). The heating rate in this machine is a minimum of 44°C/sec.

The Pb composition of some of the targets was modified by burying the doped PZT target in 80%/20% PbZrO₃/PbO powder and holding at 1000°C for 3 hours. EDS measurements show ~8% more Pb in the targets that underwent this heat treatment than in identical composition targets that had not undergone this treatment. Pb composition in the film was modified by spin coating a layer of PbO on the top of the film before annealing.

Pt electrodes were DC diode sputtered onto the films using a shadow mask to produce 0.3mm diameter electrodes. After electrodes were deposited, the films were reprocessed in the RTP for 60s at 650°C to improve contact at the film/electrode interface. The bottom electrode is either the platinum surface of the substrate or a deposited layer of SrRuO₃ or LaSr_{0.5}Co_{0.5}O₃ between the film and the platinum. The bottom electrode was contacted

either by masking a portion of the substrate before deposition or by etching the PZT with 5% HF after deposition.

Geometry:	on-axis
Target-substrate distance:	5-7 cm
Laser fluence:	2-3 J/cm ²
Frequency:	10 Hz
Ambient gas:	40-60 mTorr 10% O3 in O

2.1.2.2 Fibers

PZT films were also deposited on both glass fibers and Pt wire. Deposition conditions are similar for fibers and flat substrates. Fibers were deposited at room temperature and 380°C to produce amorphous films which were annealed in the rapid thermal processor at 650°C for 60 seconds. They were suspended between two small alumina tubes 1/8" above the surface of the wafer thermocouple inside the RTP. This was done to prevent contact between the film and any part of the RTP.

2.2 Characterization

2.2.1 Structural Characterization

Films were characterized to find phase and microstructure information by several methods. The crystallographic phase was determined by x-ray diffraction (Scintag model SL-GLP). Both Θ-2Θ and glancing angle diffraction were used, with omega set at 12° for glancing angle patterns. This was done purposely to allow for substrate peaks to be included in the pattern for calibration of peak location. The Scintag has a Seifert Cu_{Ka} source and a solid state detector.

The thickness of the films was determined on a Tencor Alpha-Step 500 surface profiler. Clear edges were produced on the films for thickness measurements by masking the substrate during deposition.

Microstructural information was obtained by a combination of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM (ISI DS-130) was used to study the top surface of the films and fractured cross sections. All samples were sputter-coated with gold before examination in the SEM. This machine has a maximum usable magnification of ~100,000X.

Transmission electron microscopy was performed at University of California at Berkeley on a JEOL 200 CX. Samples were prepared by polishing the silicon substrate to a thickness of ~100µm on SiC paper. The sample was then embedded in beeswax. A small hole in the beeswax allowed for that portion to be etched in a solution of HF/HNO₃/acetic acid until only a thin layer of Si remains. The disk was then cold stage ion milled until a hole appeared. The edges of the hole were then examined in the TEM.

2.2.2 Electrical Characterization

The electrical properties of the films were examined through the use of a small probe station connected to a Radiant Technologies RT66A ferroelectrics tester in virtual ground mode for the examination of hysteresis behavior. For hysteresis measurements, a triangular waveform was generated and the voltage over an integrating capacitor is measured at a specified number of steps (usually 200) over the cycle of the wave. In a test cycle, five complete voltage cycles are applied. The hysteresis data is measured on the second cycle following a 100µs delay between the first and second applied wave.

The same probe station was used with an HP4275A LCR bridge for capacitance and loss measurements. These measurements were made with an applied 0.1V AC voltage at 100kHz.

Electrical properties of the films were measured as a function of stress. A stress rig which has been described in other publications (Shepard and Trolier-McKinstry, 1996) was used to generate biaxial tensile and compressive stresses on the order of ±150 MPa on the films while measuring capacitance behavior.

The edges of the wafer were placed between two vyton o-rings and clamped on top of a bored out aluminum round by an aluminum retention ring. This left an open cavity behind the wafer as shown in Figure 2.5. Stress was generated in the films by either filling the cavity with high gas pressures to cause the wafer to flex out (tensile stress) or by generating a vacuum to make the wafer flex in (compressive stress). The stress in the wafer was calculated using large deflection plate theory and published values of Young's modulus for PZT thin films (Tuchiya et al., 1996).



Figure 2.5 The stress apparatus (from Shepard et el., 1997)

RESULTS AND DISCUSSION

3.1 Effects of Growth Parameters on Microstructure

3.1.1 Microstructural Development in Quenched Growth Deposition

The films in this work were mainly grown at room temperature and post deposition crystallized in order to minimize problems with lead stoichiometry. The low temperature deposition process does, however, introduce additional problems associated with the limited number of mechanisms available for densification of the condensate at low temperature. Surface diffusion in particular is limited. To describe this, the effects of room temperature PLD growth on PZT thin films was studied from the perspective of the structure zone model.

When a thin film is grown at low temperature, voids are often incorporated due to the lack of surface mobility (Smith, 1995). This leads to a Z1 type microstructure as shown in Figure 3.1. It is characterized by amorphous or highly defected columns, often ~10's of nm wide separated by voids a few nm across. This type of low temperature/low surface diffusion growth is referred to as quenched growth. It is modeled as a ballistic deposition process because the only atomic action contributing to the structure of the films is that of the momentum of the arriving vapor.



Figure 3.1 Characteristic microstructures of films grown at T_s/T_m (Temperature of surface/Melting temperature of film material) so low that surface diffusion is negligible (Z1), T_s/T_m>0.3 (Z2), T_s/T_m > 0.5 (Z3), and energetically enhanced low temperature deposition (ZT) (Smith 1995)

When surface diffusion is negligible, several different factors can cause the observed void formation in Z1 type films, as illustrated in Figure 3.2. Z1 structure development is modeled as ballistic aggregation, which assumes that arriving atoms will settle in the crevices between nearby atoms to minimize energy associated with dangling bonds, as in Figure 3.2a. This aggregation causes self shadowing, which will result in different structure development depending on the arrival direction, ambient pressure, particle energy. etc. (Smith, 1995).

Figs 3.2b and 3.2c show deposition from a perpendicular direction at low enough pressures that particles are in the molecular flow regime. When atoms fill crevices such that overhangs form, the lower areas are shadowed from deposition. As the film grows, the atoms in the arriving vapor are attracted to the sides of the columns. When the film gets thick enough, the columns eventually meet to form a solid surface, and shadowed voids are left at the base of the film. This problem is enhanced if vapor is arriving from some direction other than normal to the substrate, as this increases self shadowing from columnar tilting towards the direction of deposition. Also, the mean free path length in the vapor

plays an important role. If it is much smaller than the columnar separation, voiding will be reduced.

Four processes can assist in the reduction of voids in a quenched growth mode film (Smith, 1995). The first is low sticking coefficient, which is illustrated if Figure 3.2f. If particles do not to adhere immediately to the sides of the columns, it is more likely that they will reach the substrate. Two other methods arise from the arrival of energetic particles as in Figure 3.2g. An energetic particle can either cause a forward sputtering event due to impact with another particle, or use its own energy to move on the substrate once it has landed. This reduces self shadowing by sputtering the shadowing particles rather than sticking to them. One other method is local heating by impact, which causes local surface diffusion, however it is not as common as the two illustrated in Figure 3.2 f and g (Smith, 1995).



Figure 3.2 Processes of quenched growth structure development. a) ballistic aggregation b) overhang formation c) sideways attraction d) shadowing during deposition at an oblique angle Θ e) columns tilting towards direction of deposition f) void filling due to low sticking coefficient to sides of columns g) energetic particles filling voids due to enhanced mobility (left) and forward sputtering (right) (Smith 1995).

In films which are post deposition crystallized, such as those studied in this work, the structure zone model is not a complete description of the microstructure of the final film. It is, however, an indicator of the pre-crystallization morphology. This is important in this work, since significant shrinkage of the film during crystallization caused cracking in the films. This was believed to be due to the combination of the change in volume of a poorly densified amorphous film, and the difference in thermal expansion coefficient between the film and the substrate. Cracking prevented any type of electrical measurement of the films.

The deposition conditions can be modified to enhance as-deposited density in PLD in two ways, increasing energetic bombardment and increasing temperature. Bombardment can be enhanced by using low ambient pressures for deposition to allow for a higher arrival velocity of the ejected species (less thermalization in the gas phase). Higher velocity results in increased incidences of forward bombardment and impact mobility (higher mobility of energetic species landing on substrate). Both mechanisms assist adatoms in moving down the columns, filling voids. This helps to produce structures more like that of ZT than Z1. Reduced pressure is limited, however, by the amount of oxygen needed to achieve the correct stoichiometry, and resputtering caused by excessive bombardment. Bombardment can also be increased by increasing the energy density of ablation and by reducing the target to substrate distance. The second way to improve density is by depositing films at elevated temperature. This raises the T_s/T_m ratio, enhancing surface diffusion and producing morphologies closer to that of Z2. Choice of temperature to aid as-deposited density was balanced by the need to avoid crystallization of pyrochlore during deposition and loss of volatile Pb from the film.

3.1.2 Bombardment

The most common types of particles used for bombardment in sputter deposition techniques are ions extracted from a plasma by substrate bias, ions from ion guns, reflected high energy neutrals, and negative sputtered ions from a sputtering target or evaporation source (Mattox, 1988). With such sources, it is possible to control bombardment via biasing methods or independent plasma generation methods. This is convenient because bombardment can be controlled independently from factors such as ambient gas pressure, which are important for other reasons related to the quality of the film. In PLD the only source of energetic particles is the laser-target interaction. For a given energy density, it is reasonable to think of the laser-target interaction as a constant (Haglund, 1996). The number and energy of particles that are ejected from the target are similar (and at a maximum) during this interaction. As the particles move away from the target, interactions with the ambient gas result in thermalization, reducing particle energies. As the ambient pressure in the chamber or the distance over which the particle must travel increases, the likelihood of thermalization increases. Therefore, if the energy density is relatively constant, energetic bombardment in a PLD film can be controlled through modification of target to substrate distance and ambient pressure.

Based on past reports of growth of PZT by PLD (Ramesh et al., 1994, Krupanidhi et al., 1992), typical laser energy output, and system geometry considerations, the energy density of film growth was kept relatively constant, around 2.5 J/cm². The next two sections will detail the effects of varying pressure and target to substrate distance in this work.

3.1.2.1 Pressure

This section details the effects of background pressure on film quality. The data presented is for PZT 5A films, but similar microstructural variations were found in all compositions studied. Four distinct regimes of microstructure were found as a function of pressure. At 25 mtorr and below, it was very difficult to grow films successfully. On annealing, any films grown at or below 25mtorr of 10% O3 in O2 were found to crack and peel off of the substrate. A frequent cause of this type of behavior in thin films is the presence of a high residual stress produced during deposition from bombardment (Mattox, 1988). Generally, at high bombardment conditions, stress tends to be compressive due to the incorporation of gas atoms into the film and continual compression of already deposited species by atomic peening events. The amount of stress present in a deposited film is dependent on the amount of bombardment. Figure 3.3 shows a generalized plot of the residual stress in films vs. amount of bombardment. At low bombardment, the film is not fully dense and under tensile stress. As bombardment increases, atomic peening events and ambient gas molecule incorporation increase, causing compressive stress. If levels of bombardment are high enough, the compressive stress can be relieved somewhat by temperature increase and void formation.

The particles in PLD are generally in an energy range of 5-250eV(Leboef et al., 1996; Chrisey and Hubler, 1995), and are not enhanced by substrate bias. It would be difficult to achieve a high enough level of bombardment to be in a regime where stress relief (local heating and void formation) would occur. It is, therefore, concluded that the films are probably in compressive stress after deposition. This is supported by the fact that as deposition pressure increases (and bombardment decreases), cracking decreases (i.e. a film deposited at 50 mtorr would crack slightly in the center)



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Figure 3.3 Generalized residual stress in an as-deposited thin film as a function of bombardment



Figure 3.4 SEM micrographs of films grown at a) 50mtorr, b) 75mtorr, and c) 100mtorr in 10% O₃ in O₂ after post deposition annealing at 650°C for 60s.



Figure 3.5 Glancing angle XRD pattern of the films shown in Figure 3.4

At 40-50mtorr of 10% O₃ in O₂, films were found to have the best structural properties. An example of a 400nm thick film grown at 50 mtorr of 10% O₃ in O₂ at an energy density of 2.3 J/cm² and 6cm target-substrate distance is shown in Figure 3.4a. Small, densely packed grains of ~0.1 µm surface grain size were observed after a 60s/650°C anneal treatment, and only perovskite PZT was detected by x-ray measurements. The glancing angle XRD pattern is shown in Figure 3.5.

At 75 mtorr, films were found to have the best crystallinity following the 60s 650°C annealing conditions, but the microstructure that resulted under such growth conditions were poor. Figure 3.4b shows an SEM image of a film grown at 75mtorr of 10% O₃ in O₂ at an energy density of 2.3 J/cm² and 6cm target-substrate distance. It is evident that there

is a large percentage of intergranular porosity. Electrical property measurements on such a microstructure were not possible.

Although the films were not dense, the crystallinity of films deposited at 75 mtorr were generally superior to those of other deposition pressures. Figure 3.5b shows the glancing angle XRD pattern of the film in Figure 3.4b. Notice that the peaks are significantly more intense than those of the 50 or 100 mtorr films. This was a common feature of films grown at 75mtorr.

Above 75 mtorr, film microstructures showed progressively higher levels of intergranular porosity with increasing deposition pressure. This can be seen in Figure 3.4c where the microstructure of a film deposited at 100mtorr of 10% O₃ in O₂ and crystallized at 650°C for 60s is shown. In Figure 3.5c the glancing angle x-ray pattern is shown.

Previously, pressure dependence of this sort has not been extensively explored in PZT films. This is probably due to the low pressure deposition regime used in this work. The ozone capability of the PLD system employed allowed for the use of pressures significantly lower than those used by most other researchers while still maintaining reasonable stoichiometry.

3.1.2.2 Target to Substrate Distance

Two scenarios were explored to test the effects of distance on film microstructure. The first involved changing the distance and pressure together. This was done to keep the substrate in approximately the same region of the plume. In the second data set, the pressure and energy density were kept constant while changing only the target to substrate distance. A schematic for each experiment is shown in Figure 3.6.

It is evident by studying the microstructures in Figure 3.7 that even if the substrate location relative to the plume is constant, but the pressure is increased, film density decreases.



Figure 3.6 Schematic for the plume-substrate relationship in a) varying distance only and b) varying pressure and distance together



Figure 3.7 Microstructures of annealed ~4000Å thick films deposited under varying distance and pressure: a) varying distance only at a pressure of 50 mtorr and b) varying pressure and distance together

The amount of density decrease (measured by the line intercept method) it slightly less than that of the increasing pressure only experiment (Figure 3.4). These data indicate that the effects of increased pressure are greater than those of increased distance between the substrate and plume. At increased pressures, the bombardment capabilities of PLD decrease.

In the experiment where only target to substrate distance was changed, the results are very similar to those observed as a function of background pressure alone. As the target to substrate distance is increased, the density of the film decreases. The amount of change is similar to that observed in films grown at increased pressure.

3.1.3 Temperature

3.1.3.1 Deposition Temperature

Depositing films at higher temperature was pursued to explore the effect of increasing T_s/T_m on film microstructure. The choice of temperature was made primarily based on stoichiometry considerations. PbO is known to become fairly volatile in films at about 500°C (Fox, 1992). Therefore, 500°C was set as the upper limit. Also of concern was the presence of pyrochlore or a lead deficient fluorite phase. It was found that if deposition was carried out at a temperature of 400°C, second phases would be present in as deposited films. This phase in indexed as pyrochlore in Figure 3.8, but it could be a lead deficient or defect fluorite material instead as observed in work by LeFevre et al. (1996). Figure 3.8 shows glancing angle x-ray diffraction patterns of two as-deposited films, one grown at 380°C and one grown at 400°C. It is evident that there is a crystalline second phase present in the 400°C film, and that the 380°C films is amorphous.



Figure 3.8 X-ray patterns of as-deposited films grown at 400°C and 380°C

Figure 3.9 shows x-ray patterns of films that were grown at 400°C and 380°C following crystallization at 650°C for 60 seconds. The x-ray data indicates that the phase present in the as deposited film remains in the 400°C film following the high temperature crystallization.



Figure 3.9 Glancing angle x-ray diffraction patterns of films deposited at 380°C and 400°C after a 650°C/60 second crystallization anneal

As even small amounts of second phase were found to significantly degrade the quality of the films in this study, it was preferable to avoid its formation. Therefore, most films were deposited at or below 380°C.

The effects of increased temperature on film microstructure was significant to the extent that it broadened the parameter window in which dense films could be deposited. In the previous sections, microstructural examination indicated that at room temperature the narrow deposition window of 40-60 mtorr of 10% O₃ in O₂, at a fluence of 2.0 to 2.5 J/cm², and 6-7cm target to substrate distance would yield dense films. Growing films at 380°C was found to increase the parameter window somewhat. Films deposited at pressures up to 100mtorr could be made dense enough to yield electrical measurements. However, the increased temperature did not yield films superior to those that could be grown at room temperature with careful parameter control. In addition, even for deposition below 400°C, the increased temperature led to a more frequent occurrence of second surface phases after crystallization.

Figure 3.10 shows the degradation of remanent and saturation polarization and dielectric constant with deposition pressure observed in films deposited at 380°C. Measurements were carried out at constant field to facilitate comparison. Remanent polarizations are low overall because low field strengths were used to minimize leakage in higher pressure deposited films.

Due to the lack of improvement in film quality and the increased complexity of deposition at elevated temperature, depositions were typically carried out at room temperature.




Figure 3.10 Variation in (a) remanent/saturation polarization and (b) capacitance and loss (for 4000Å thick films) with deposition pressure for films deposited at 380°C

3.1.3.2 Crystallization Temperature

Perovskite films could be grown from all of the PZT targets studied in this work. Figure 3.11 shows x-ray patterns of films grown in 50 mtorr of 10% O₃ in O₂ at a fluence of 2.5 J/cm² for each of the four compositions studied. All of these films were crystallized in a rapid thermal annealer at 650°C for 60s. It is evident that this crystallization temperature yields perovskite films for all compositions.

Room temperature films typically exhibited partial (100) preferred orientation, as is evident by the higher intensity of the 100 peak in the x-ray patterns as relative to the powder diffraction pattern (JCPDS card # 33-784). For clarity, limited angular ranges are presented here, but data was taken out to 60° for most of the scans presented. Some small amount of pyrochlore or fluorite phase may be present in the 5A film.



Figure 3.11 a)Glancing angle x-ray diffraction patterns of annealed PZT 8, PZT 5A, PLZT, and PZT 5700 films grown at 50 mtorr of 10% O₃ in O₂ and b) full x-ray scan of the PZT 8 film



Figure 3.11 (b)

The microstructure was found to change with crystallization temperature. Figures 3.12 and 3.13 show microstructures of films crystallized at 650°C, 700°C, and 750°C. In the 650°C film the surface microstructure is uniform and dense. The cross sectional image show a uniform microstructure throughout the thickness of the film which has noncolumnar microstructure with a 50-100nm surface grain size. The 700°C and 750°C films show what appears to be a surface layer that does not completely cover the film. In the cross-section, a grain boundary is observed in the middle of the film. A similar type of microstructure has been observed by LeFevre et al. (1996) for sol-gel PZT films with a layer of PbO deposited on top prior to crystallization. They found that for films with PbO layers, a grain boundary existed in the center of the film after crystallization. This might be due to a nucleation at the surface as well as the base of the film until they merge. Due to the observance of this type of microstructure, crystallization was kept to as low a temperature as possible. 650°C was found to be the most appropriate for forming phase pure perovskite films and attaining good microstructures.



Figure 3.12 Surface microstructure of films crystallized at a) 650°C, b) 700°C, and c) 750°C. All films were deposited in 50 mtorr of 10%O₃ in O₂ at a 6 cm target to substrate distance.



Figure 3.13 Cross sectional microstructures of films crystallized at a) 650°C and b) 750°C

3.1.4 Effects of Curved Substrate

PZT films were deposited on fibers in two configurations: SiO₂ fibers of 125µm and 1mm were coated with layer of LSCO as a bottom electrode and then a layer of PZT, and platinum fibers of various diameters were coated only with a layer of PZT since the fiber could serve as a bottom electrode. Although direct electrical property measurements were not performed on the fibers, electrode layers were used on the glass fibers to prevent reactions and to more closely simulate a device configuration. All PZT films deposited on fibers were of the PZT-5A composition.

Figure 3.14 shows LSCO/PZT films grown on 125µm and 1mm SiO₂ fibers at room temperature. The micrographs clearly indicate a columnar microstructure in the films. However, surface microstructures indicate that the films have a low density.

Figure 3.15 shows scanning electron micrographs of a 125µm LSCO/PZT structure deposited at 380°C. It is clear that this film is significantly more dense than the film deposited at room temperature.



Figure 3.14 Scanning electron micrographs of LSCO/PZT structures deposited on (a) 1mm SiO₂ and (b) 125µm fibers at room temperature



Figure 3.14(b)



Figure 3.15 Scanning electron micrographs of an LSCO/PZT structure deposited on a 125 µm SiO₂ fiber at 380°C.

When surface microstructures are compared with those of flat films, the microstructure appears to be as dense as the 50 mtorr/6 cm structure, but with more surface roughness. Films with this type of microstructure should maintain reasonable piezoelectric d_{31} coefficients due to mechanical grain-grain contact.

Figure 3.16 shows scanning electron micrographs of surface microstructures for films deposited on Pt fibers of a) 0.5mm, b) 0.25mm, c) 0.125mm, and d) 0.05mm at 380°C. The film microstructure does not appear to change significantly in these films with radius of curvature, even at sizes as small as 0.05mm. This is reasonable given the large fiber diameter to film thickness ratio. The larger surface structures on the films are due to the surface roughness of the Pt fiber. A micrograph of a bare Pt fiber is shown in Figure 3.17. A large number of asperities are present on the surface of the fiber. These are approximately the same shape as many of the asperities on the film surfaces. Also, this type of surface structure is not observed in films grown on glass fibers, which have much less surface roughness.

It is concluded that although it is somewhat more difficult to produce dense microstructures on curved substrates (i.e. elevated temperatures are necessary), dense films can be produced down to a fiber radius of 0.05 mm if films are grown at a temperature of 380°C.



Figure 3.16 Surface microstructures for PZT films deposited on Pt fibers at 380°C



Figure 3.17 Surface of bare Pt fiber

3.1.5 TEM Microstructural Analysis

Figure 3.18 shows a cross sectional TEM image of a PZT film grown at 650°C (Courtesy of T. Sands and L. Tsakalakos, U.C. Berkeley). It can be observed that a columnar grain structure exists in the film, and that columns are 50-150 nm across the thickness. This is consistent with the observation of ~100 nm surface grain size structures in SEM investigations.

Figure 3.19 shows a plan view TEM picture of a PZT film deposited at room temperature and post deposition crystallized. What is visible in this microstructure are crystalline areas in an amorphous matrix. It is believed that the amorphous matrix resulted from excessive ion milling during TEM sample preparation. There are areas which exhibit



Figure 3.18 Cross-sectional TEM image of a PZT film grown at 650°C



Figure 3.19 Plan view of PZT-5A film grown at room temperature showing parallel bands of contrast

parallel bands of contrast. Unfortunately, it is unclear whether these are non-180° domain boundaries, damage from the ion milling process, or features associated with the Pt substrate. Electron diffraction was unclear, due to the excessive sample damage, but indicated a 60-80% likelihood of the presence of PZT in this area of the sample.

The population of ferroelectric domains in thin films has been shown to have a significant effect on the properties (Tuttle et al., 1995), where the density, size, and orientation of domains in films controls their contribution to the properties of the films. If compositional variation is eliminated, the two controlling factors for density, size and orientation of domains are grain size and stress at the transformation temperature. Films which are on a substrate of smaller thermal expansion coefficient experience a tensile stress when cooling through the transformation temperature, and those on a substrate of greater thermal expansion coefficient are in compression on cooling through the transition temperature. It has been found, as might be expected, that films in tensile stress during cooling have a higher population of *a* domains. It has been found that *c* domain oriented films have higher remanent polarizations and lower dielectric constants, while *a* domain films have higher dielectric constants and lower remanent polarizations. These differences have been found to be as extreme as 60μ C/cm² vs. 5μ C/cm² for similarly processed films with different orientations (Tuttle et al., 1996).

Grain size also has an effect on population of non-180° domains. It has been shown in bulk ceramics that domain size will decrease with decreased grain size (Cao and Randall, 1996, Arlt, 1990). For grain sizes between 1 and 10 µm, the domain size decreases as (grain size)^{1/2}. Cao and Randall (1996) have shown a departure from that relation for grains less than 1 µm and greater than 10 µm to higher domain densities. They have also shown that below 1µm, often only one or two sets of simple twin bands are observed per grain, as opposed to the more complicated cross-hatching type patterns observed in larger grains. They have observed domains in bulk samples for grains down to 100 nm.

Although the minimum grain size in which domains can be observed in films is unknown, Tuttle et al. (1996) has observed 90° domains in PZT with a 20/80 Zr/Ti ratio down to grain sizes of 60 nm in films deposited on Si substrates with RuO₂ electrodes. Although films closer to the 53/48 Zr/Ti ratio used in this work were examined by Tuttle et al. (1996), the grains of those films were larger than those of the 20/80 film. However, It was found that, excluding Zr:Ti ratio, in films of varying grain size (from 50 nm to 2.5 μ m), there were only very small increases in domain width with increasing grain size in that range. This indicates that the domain density throughout the film remained similar for films in the entire grain size range, although the number of domains per grain decreased.

Due to the 50-150 nm grain sizes of the films in this work, it would be expected that non 180° domain patterns would be limited, existing as simple bands. Due to the fact that PZT films on coated silicon substrates are in tensile stress upon cooling through the Curie temperature, it would also be expected that there would be a larger population of a domains relative to c domains.

3.1.6 Summary of Microstructure

In summary, dense, perovskite films have been produced from all target compositions used in this work. For films on flat surfaces, room temperature deposition at conditions of 2.0-2.5 J/cm² energy density, 6-7 cm target to substrate distance, 40-60 mtorr 10% O₃ in O₂ ambient atmosphere, followed by a 650°C anneal for 60s in a rapid thermal annealer yielded dense, perovskite films with grain sizes on the order of 50-150 nm.

On curved surfaces of fibers down to 0.05 mm in diameter, PZT 5A films could be deposited which yielded dense, columnar microstructures. It is expected that good graingrain contact will facilitate the preservation of mechanical coupling throughout the thickness of the film. These films were produced under the same growth conditions as flat films with the exception of temperature. It was found that a temperature of 380°C was necessary to aid density.

In the TEM study, it is concluded that PZT grains are columnar in high temperature growth, and there may be non 180° domains present in some of the grains. It is expected that non 180° domains can exist in grains of this size. Based on thermal expansion coefficient differences in film and substrate, the film should exhibit a higher *a* domain population than *c* domain population.

3.2 Lead Stoichiometry

Pb stoichiometry has been the object of many studies for PZT films grown by PLD and other deposition techniques (Ma et al. 1996; LeFevre et al., 1996; Hau et al., 1995; Petersen and McNeil, 1992). Significant deviations from lead stoichiometry typically lead to the formation of second phases in the films (PbO for excess lead or pyrochlore for lead deficient). In addition, small variations in lead stoichiometry are expected to be important in this work because the property differences in hard and soft PZT are due to a difference in the concentration of Pb and O vacancies. If Pb stoichiometry cannot be appropriately maintained, lead vacancies and oxygen vacancies will result. The mobile oxygen vacancies could then form defect dipoles that are able to align with the poling field to pin domain walls. This, in turn, could minimize or overwhelm the effects of dopants on the defect chemistry, and hence, the softness, of the material.

It has been suggested by Hau et al. (1995) and Ma et al. (1996) that bombardment can affect on Pb stoichiometry. In a study of Pb composition vs. angular distance from the target surface normal (center of deposition), they found that Pb content was the lowest at the center of the film. This decrease in Pb concentration was attributed to a resputtering of Pb atoms by energetic Zr and Ti atoms during deposition. Ma et al. (1996) and Hau et al. (1995) showed that the lead content was ~25% lower at the center than at a point 20° away from the target surface normal for films deposited at a fluence of fluence of 4 J/cm² and a pressure of 0.1 mtorr. The % variation decreased significantly with increased pressure or decreased fluence, and was not observed at all at 200 mtorr/ 4J/cm². They concluded that the resputtering effect is significantly reduced with the addition of an oxygen ambient to the chamber, which is attributed to both the decreased sputtering coefficient of PbO vs. Pb, and the thermalization of energetic Zr and Ti species in the plume.

The films that had the best microstructures in this work were typically deposited at 40-50 mtorr of 10%O₃ in O₂, at fluences of 2.0 to 2.5 J/cm². These conditions are just inside the lower range of pressure/fluence combinations where Hau et al. (1995) observed decreased Pb concentrations in the center regions of their films. This is notable with respect to two observations found in the films in this work. First, cracking was frequently observed in the center regions of room temperature deposited films, and second, the highest remanent polarizations were generally observed at 7-12° from the center axis of deposition. As stated earlier, cracking can be due to residual compressive stress resulting from heavy bombardment during deposition. The same bombardment could cause resputtering of Pb from the center of the film, resulting in better stoichiometry in regions outside the center of the film. It should also be noted that when films were deposited at 380°C, the spatial variation in film properties was observed although cracking was suppressed. The reduction in cracking is likely to be due to a combination of increased surface mobility of the depositing species and a reduction in the temperature differential between growth and crystallization temperature, rather than a difference in bombardment.

To explore the Pb stoichiometry in the films in this work, PZT films were deposited on sapphire substrates and the composition was measured by energy dispersive spectroscopy (EDS) as a function of location in the films to see the trends in Pb content. A plot of the obtained data for an as-deposited film and the same film after annealing is shown in Figure 3.20. It is recognized this is not a quantitative measure of the Pb content, but should show whether there are large systematic variations across the wafer surface. This film was deposited at relatively low bombardment conditions of 60 mtorr 10% O₃ in O₂ ambient/6 cm target to substrate distance/2.3 J/cm² energy density.

The EDS was interpreted by the QUANTEX program which was programmed to calculate the composition of a collected spectrum in terms of oxide percent. This was done in an effort to eliminate the effects of thickness changes on the measurement of Pb content. Each spot on the surface of the film was measured 5 times, and the oxide percentages of Al₂O₃, PbO, TiO₂, and ZrO₂ were calculated. The PbO percentage in the film was then calculated by subtracting the amount of Al₂O₃ from the total amount, and calculating the %PbO relative to the amounts of ZrO₂ and TiO₂. The lines in the plot are generated as linear curve fits, to illustrate that the average amount of Pb is approximately the same for the annealed and unnannealed films.

This experiment was carried out with the purpose of detecting any systematic changes in Pb content across the surface of the sample. It can be observed that the data collected do not indicate a substantial change in relative lead content with angular position. It is expected from the observations of Ma et al. (1996) and Hau et al.(1995) that stoichiometric variations should be small for these bombardment conditions. It should be noted, though, that if a spatial variation in composition on the order of 1-3% was present in this film, it would not be detected by this technique.

A second important point from Figure 3.20 is that the data indicate that there is not a significant decrease in Pb content on annealing of the PZT film at 650°C for 60 seconds in a rapid thermal annealer. Thus, while there may be some lead volatilized from the film surface, there is no dramatic change in the stoichiometry.



Figure 3.20 Plot of Pb content as measured by EDS as a function of location on the film surface for a PZT film deposited under moderate bombardment conditions before and after annealing

To further explore Pb stoichiometry in the films in this work, sol-gel PbO coatings were used in an attempt to minimize Pb vaporization from the surface of the film. Also, growth of films from Pb enriched targets were attempted. A PZT 5A target was packed in a powder filled crucible (20% PbO/80% PbZrO₃) and soaked at 1000°C for three hours. EDS measurements indicated approximately an 8% increase in Pb content, accompanied by a change in the color of the ceramic from pale yellow to bright orange. Neither technique yielded films with superior properties to those of films grown with the non-Pb enriched targets.

3.3 Electrical Properties

3.3.1 Electrical Properties of Bulk Compositions

Targets used for film growth were Piezokinetics PZT 5A and PZT 8 soft and hard compositions respectively, PZT 5700 (a 5H) from Channel Industries, Inc., and a PLZT from TRS Ceramics, Inc.. The properties of the four compositions in the bulk are listed in Table 3.1 and the compositions of each target are in Table 3.2.

Table 3.1 Target Properties				
Property	PZT-8	PZT-5A	PLZT	5700 (5H)
dielectric constant	1000	1700	4000	3200
tan δ at 1KHz	0.004	0.015	0.025	0.02
d33 (pm/V)	225	400	790	550
Curie temperature	320°C	350°C	185°C	190°C
kp (coupling factor)	0.5	0.6	0.68	0.62

Table 3.2 Target Compositions		
Target	Weight% dopant	
PZT-5A*	2.5%BaO, 0.97% Nb2O5	
PZT-8*	0.43% Fe2O3, 1.68% SrO,	
	0.12% Al ₂ O ₃ , 0.10% NiO	
ZT 5700* 3.94% Nb, 0.2%La, 0		
PLZT	12% La	

* determined by ICP, error is ±5% of measured value

3.3.2 Hysteresis Behavior

3.3.2.1 PZT-8 and PZT-5A films

Electrical properties were studied for PZT films of all compositions on flat substrates. Properties for PZT-8 (hard) and PZT 5A (soft) films were found to be similar. Typical hysteresis loops for PZT-8 and PZT-5A films are shown in Figure 3.21. Both compositions show similar coercive field and remanent polarization values. The dielectric constants of these films ranged between 1000 and 1500 with no trend of higher or lower values based on composition. The loss tangent, however, was found generally to be lower for PZT-5A films than for PZT-8 films. For the two films in Figure 3.21, the loss tangents were 0.01 and 0.03 for soft and hard compositions, respectively.

The observance of similar coercive fields is notable because it is a prime indicator of domain wall mobility. Thus, the domain walls appear to have comparable mobility in the hard and soft composition films. The increased loss tangent in hard composition films also is consistent with this conclusion. In bulk hard and soft PZT ceramics, the loss is higher in soft PZT due to the contribution of domain wall motion, and lower in hard PZT because the walls are pinned (Jaffe et al., 1971). The trend seen in these films is the opposite. If the contribution of domain walls were similar in both cases, other contributions must be considered to explain the differences. Since conduction in undoped PZT is generally p-type (Moulson and Herbert, 1990), hard (acceptor) doped materials would be expected to exhibit increased conduction due to an increase in hole concentration. Soft PZT on the other hand, which is donor doped, should exhibit a reduced amount of conduction due to suppression of carriers from electron-hole recombination (Moulson and Herbert, 1990). It is unlikely that the dopants would vaporize during deposition, due to the significantly lower volatility of Fe and Nb relative to PbO (Lide, 1993). As a result, it is concluded that the the

dopants are incorporated into the films, and that coercive field is a better measure of the wall mobility than tan δ in thin films.



Figure 3.21. Hysteresis loops for PZT 8 and 5A thin films

3.3.2.2 Other Compositions

Although films of good microstructure and phase have been obtained, PZT 5700 and PLZT compositions did not yield exceptional electrical properties. Figure 3.22 shows a typical hysteresis loop obtained for PLZT film which had dielectric constant of 800 and

loss value of 0.04. The remanent polarization and dielectric constant are lower than those obtained for 8 and 5A compositions, although the coercive field appears to be similar. The loss, on the other hand is somewhat higher. The reasons for this observance are not known for certain. Due to the higher loss in these films, the Pb stoichiometry and dopant incorporation are more questionable than in the 5A and 8 compositions.



Figure 3.22 Plot of PLZT hysteresis loop shown overlaying the PZT 8 and 5A loops for comparison

In an effort to determine what mechanisms are responsible for the similar electrical behavior in our films, biaxial stress experiments were carried out. Figure 3.23 shows a plot of normalized capacitance vs. in-plane stress for bulk PZT 5A and PZT 4 (a hard PZT), and an undoped sol-gel film.



Figure 3.23 Effects of applied biaxial compression the capacitance of bulk PZT 5A and 4 ceramics, and an undoped sol-gel film (bulk data from Brown, 1961, thin film data from Shepard et al., 1996)

In looking at the results of these experiments, two things are worth remembering. First, the magnitude and direction of the change in dielectric constant, and second, that soft PZT was more affected by stress than hard PZT. Although the return curves are not shown on this plot, the following observations were made: hard PZT (PZT 4) showed a 46% reduction in properties for 400MPa of applied biaxial compression (sum of the principle stresses), with a nearly full recovery of its original properties on the removal of stress, and PZT 5A showed a 57% reduction in properties for 400 MPa (sum of the principle stresses of applied biaxial compression), with a recovery to only ~75% of its original properties. Similarly, large changes in properties were observed under uniaxial stress (Zhang et al., 1996). In those studies, changes of this magnitude were attributed in large part to ferroelastic reorientation.

It follows that as non-180° domain walls are more mobile in soft PZT, these compositions would be more strongly affected by stress than a hard composition where such walls are not as mobile. In addition, in soft PZT there is little restoring force to cause the domains to return to their original configuration when the stress is released.

Thin films are found to behave differently under applied biaxial stress than bulk ceramics. The results for the undoped sol-gel film obtained by Shepard et al. (1996), also in Figure 3.23, show small, reversible changes in the opposite direction to those obtained in bulk ceramics.

Figure 3.24 shows the results of biaxially applied compressive (4a) and tensile (4b) stress on both hard and soft composition PZT thin films. In all cases, the changes ranged between 2-7% of the total unstressed properties and are essentially reversible. The amount of change and reversibility were essentially the same within experimental error (i.e., film to film variability) for each composition. The direction of change is also opposite to that observed in bulk ceramics. This leads to the conclusion that it is difficult to force the movement of non-180° domain walls in these films by the application of a mechanical stress. It also supports the observation that the non-180° domain walls in films of all three compositions are pinned, and therefore are not able to contribute to the dielectric properties.



(a)



Figure 3.24 Normalized capacitance vs. applied pressure for a) biaxial compression and b) biaxial tension. Open symbols represent application of stress, filled symbols represent removal of stress

3.3.4 Summary of Electrical Properties

Several groups have now shown that non 180° domains are generally not mobile in undoped PZT films (Shepard et al., 1996; Tuttle et al., 1995). One of the foci of this work was to attempt to free the domain walls as is done in bulk materials, by donor doping to make soft PZT films. The electrical properties observed in our soft composition films do not suggest the expected increase in domain wall mobility. PZT 8, a hard composition, and PZT 5A, a moderately soft composition have shown nearly identical dielectric constants, remanent polarization and coercive field values. Softer compositions, a PZT 5700 and heavily doped PLZT composition, have not been fabricated with comparable properties. The reasons for the departure from bulk behavior is believed to be associated with four major factors: residual stress in the films, grain size, dopant distribution, and preparationrelated defects.

From the thermal expansion coefficient difference between the substrate and film material, it is known that PZT films on Si substrates are in a state of ~100MPa residual tensile stress (Tuttle et al., 1995). This has two effects on the final domain structure of the film. First, the film is in tensile stress as it cools through the transformation temperature, which should cause significantly more *a* domains to form than *c* domains. Second, once the film is completely cooled, the domains could be held in place by this stress. To achieve any mobility in the domain walls, the effects of the residual stress must first be overcome.

To explore this effect, the behavior of the films in this work as a function of stress was explored. While bulk materials show large decreases in properties with applied compressive stress (Brown, 1961), films in this work have shown an order of magnitude smaller change in the opposite direction. This implies that the overall residual stress is not the only factor in pinning the domains. Another factor that could cause our films to behave similarly is grain size. The number of domain variants per grain has been reported to decrease with decreasing grain size (Cao and Randall, 1996, Tuttle et al., 1996, Arlt, 1985). Twin domains have been observed, however, in grains down to a size of 100nm in bulk materials (Cao and Randall, 1996) and 50nm (Tuttle et al., 1996) in thin films. What is generally observed is that below 1µm, instead of complicated cross hatched patterns, domains form as bands spanning the entire diameter of the grain. Also, as the grain size approached 50 nm, non-180° domain walls are only seen in some, rather than all, of the grains (Cao and Randall, 1996, Tuttle et al., 1996).

The grains in our films have been found to have lateral grain sizes of 50-150 nm. By TEM we have seen what could possibly be interpreted as a domain structure in selected grains. From what is known about domain structures in films, and the grains size of our films, it is postulated that there are domains present in at least some of our grains. Our similar electrical properties have indicated that doping has no effect on the switchability of non-180° domains present in the film.

The third and fourth factors that would affect electrical properties of our films are dopant distribution and defects introduced by the deposition process. Both are related to the number and type of defects present in the films. Specifically, in order to obtain soft PZT films, it is important that the defects generated by dopant incorporation control the electrical properties, as the difference between hard and soft PZT are generated by a purposeful incorporation of point defects into the structure. If dopants are incorporated into the grain boundaries rather than the grains, the grains will effectively be undoped, causing the behavior of the films to be hard. Accordingly, if there are more defects incorporated into the film during processing (e.g. a significant loss of Pb or a significant population of dislocations or voids) than by dopants added to the film, the preparationinduced defects will likely control the electrical properties rather than the incorporated dopants. It is believed that the dopants are incorporated into the films due to the lower loss observed in soft films.

Pb stoichiometry remains as only a partially answered question. It is well known that accurate, quantitative composition analysis is difficult in thin films. Measured film properties indicate low loss values, strong remanent polarization values, and high dielectric constants. Films are also perovskite with little to no trace of second phases. As PZT is known to have high conductivity losses and second, lead deficient phases when Pb deficient, this would support the idea that the films in this work are of approximately correct stoichiometry. It is difficult to detect whether a surface layer of Pb deficient material exists in the films. However, growing films from Pb enriched targets and coating with PbO solution before annealing yielded no improvement in properties. This is a subject which should be studied further.

SUMMARY AND CONCLUSIONS

The microstructure of PZT films has been explored for films deposited under various conditions. It was found that perovskite PZT films with good microstructural and electrical properties could be grown at room temperature. Dense microstructures were observed with a grain size of approximately 50-150 nm. Given the ability to tailor the microstructure via the deposition conditions, it should be possible to control the piezoelectric anisotropy (i.e., the d₃₃/d₃₁ ratio) in thin films. Also notable is the fact that films deposited using this technique were able to incorporate complex doping schemes without the appearance of large amounts of second phases.

A fiber rotator was fabricated to allow deposition of PZT films on fibers. A microstructural study of films on fibers of varying diameter was carried out. It was found that films could be deposited on fibers down to 0.05 mm in diameter with dense surface microstructures. Cross sectional microstructures of PZT on 125 µm SiO₂ fibers showed a dense, columnar microstructure throughout the thickness of the film. This is important for the maintenance of grain-grain mechanical coupling in films on fibers of small diameter. It is significant that dense microstructures are observed on a 125µm fiber because that is an important thickness for fiber-optic modulator devices.

Because Pb stoichiometry is a factor of great importance, stoichiometry by EDS was measured as a function of substrate position before and after annealing. It was found that under moderate bombardment conditions, Pb stoichiometry did not vary over the surface of a wafer, and also did not decrease significantly after annealing. Films grown from Pb enriched targets and annealed with a PbO surface layer deposited on top were not found to have improved properties as compared to the films grown from stoichiometric targets. Electrical properties of PZT films with different compositions were compared to explore whether or not properties of soft PZT could be achieved in a thin film. Both PZT 5A and PZT 8 compositions showed similar coercive field and remanent polarization values. In addition, both types of films show small reversible changes to applied tensile and compressive biaxial stress. The dielectric constants did not show a strong dependence on the doping, but the loss tangents were found to be lower for soft compositions. These observations are contrary to what is observed in bulk materials. The reasons behind this are thought to be mainly a function of the effects of composition, film microstructure, and substrate considerations on the mobility of domain walls in the film.

Explorations of the effects of four major factors on domain wall mobility were made, and a partial explanation of the observed phenomenon has been proposed. Residual stress, grain size, dopant distribution, and deposition generated defects are all though to have a role in inhibiting non-180° domain wall mobility. The specific cause has not yet been determined, but the following observations have been made:

PZT films on Si substrates are in a state of ~100MPa residual tensile stress.
Relieving this stress by the application of ~142MPa of compressive stress did not cause any significant change in the properties of a hard, soft, and very soft composition films.
Therefore, if the residual stress limits domain wall contributions to the properties, it is not the only factor. It is also possible that local stresses are more important than the global stress state.

 Dielectric loss levels are observed to be lower in soft compositions than in hard compositions. This indicated that dopants are indeed incorporated into the films.

 The Pb concentration is observed to stay relatively constant before and after the annealing treatment employed in this work. Also, significant amounts of second phases are not observed in the films, suggesting that the average stoichiometry is reasonable. Domains have been observed in films and bulk materials with similar grain sizes as those in our films. TEM on these films is inconclusive, but does suggest a possible domain structure in some grains. It is likely that some depression in properties is occurring due to the reduced number of domains relative to a material with larger grains, but non-180° domains should be present in some concentration in the film. It is clear that the non-180° domain walls which are present do not significantly affect the properties.

Finally, the focus of this thesis was twofold. The first objective was to determine the effects of substrate curvature on the microstructure of PZT thin films. Dense films have been deposited on fibers with diameters down to 0.05mm. Cross sectional microstructures indicate good grain-grain contact throughout the thickness of the film. The second objective of this thesis was to determine whether or not the properties of soft PZT could be achieved in a thin film. To date, it has not been possible to produce PZT films with soft properties.

FUTURE WORK

5.1 Fibers

It has been determined that grain-grain contact is good in films deposited on curved substrates down to diameters of 0.05mm. The electrical properties of these films need to be explored. It would be useful to have a measure of the piezoelectric anisotropy and how it changes for different microstructures. A good method by which to perform electrical measurements on fibers of this type needs to be established, and then a comprehensive set of measurements of electrical and electromechanical properties vs. substrate curvature should be undertaken. This will give a better overall picture of how useful PZT films will be for fiber modulator device applications.

5.2 Electrical Properties of Hard and Soft Composition Films

5.2.1 Electrodes

Significant trouble was encountered with metallization in the films in this work. Sputtered Pt electrodes were found to make poor contact with the film until annealed at 650°C for 60s after deposition. Even with an anneal treatment, often there was significant difficulty in finding acceptable electrodes on a film. Contact was generally improved with the use of a Ti layer between the Pt and the PZT, but an anneal treatment was still necessary for reliable contact. Oxide electrodes presented another set of curious behaviors. If a layer of LSCO or SrRuO₃ was deposited on the Pt coated Si substrate, cracking which occurred during annealing of films deposited directly on Pt was suppressed. The reduction of cracking as well in the PZT film deposited on sapphire supports the idea that oxide-oxide adhesion is better than oxide-metal. Efforts to integrate oxide electrodes into PZT capacitor structures and understand that differences in interaction between oxides, Ti, Pt, and Au, should be undertaken.

5.2.2 Further Exploration of Present Work

The contributions of several factors to the property difference (or lack thereof) of hard and soft composition films are still unknown. Continued work in this area is important to contribute to a full understanding of the mechanisms controlling the electrical properties of these films. If a complete explanation can be made, the factors which are presently preventing soft properties may be surmountable, such that soft films could be fabricated.

5.2.2.1 Higher Doping Levels

The improvement of condiitons for depositing films with higher doping levels is of utmost importance in further exploring the effects of dopants on the properties of PZT films. Generally speaking, in fine grained bulk materials, higher doping levels are necessary to generate soft properties (Hackenberger, 1997). The only soft composition films deposited in this work with consistently good properties were from the PZT 5A target, which is only moderately soft. A systematic study of the properties of PZT films vs. increasing dopant percentage in the target should be carried out. At the same time, increasing levels of excess lead should be used to allow deposition of films at high temperature. At high temperature, highly oriented films could be formed. The lower angle grain boundaries which will form in this kind of deposition process could be advantageous to non-180° domain formation. In low temperature deposition, voids or areas of lower density, second phases, and defects are formed in much more significant quantities than in high temperature deposition with the appropriate stoichiometry corrections. Cao and Randall (1996) observed several instances of domains with uniform coupling across grain boundaries, suggesting that grain-grain interactions were important in the formation of domains in fine grained materials. Facilitating grain grain interactions may promote the formation of larger numbers of domains, resulting in a greater population of domain walls. Once they are present in more significant quantities, it may be possible to make them mobile.

By adding steadily increasing levels of dopants, the effects of processing-induced defects might also be semi-quantifiable. If a level of doping exists where dopant defects outnumber processing-induced defects, then the approximate level of processing-induced defects might be extracted.

5.2.2.2 Different Stress States

The effects of stress on the behavior of PZT films could be further explored by changing the equilibrium stress state in as-processed PZT films. This could be accomplished by using substrates with different thermal expansion coefficients. MgO and sapphire, for instance, have a larger thermal expansion coefficients than PZT, and should result in the formation of films under residual compressive stress. This should result in films with a higher population of *c* domains than *a* domains. Comparison of films in residual tensile and compressive stress to films on PZT substrates (or another material of

identical thermal expansion coefficient) would give a good indication of what the effects of each type of stress are on the properties of the films.

5.2.3 Understanding of PLD Specifics and New PLD Methods for PZT

Films prepared by pulsed laser deposition has proven that PLD is a somewhat more complex deposition technique than once thought. To truly optimize deposition of PZT by PLD, more understanding of the mechanisms behind Pb sticking coefficient and resputtering, stress formation during deposition, and angular dependence of properties is necessary. A study of the specific plume components for various oxygen pressures, including species and energy distribution would be helpful in understanding some of the phenomenon observed in this work. It is thought that a combination of particle energy during deposition and thickness of the deposited film are responsible for the cracking observed during annealing. However, the suppression of cracking with the use of an oxide electrode between the PZT and Pt layers and the observation that when bombardment conditions were low enough to prevent cracking, good electrical properties could not be obtained indicate that there are more factors involved in explaining this phenomenon. A thorough understanding of plume dynamics might facilitate an understanding of some of these observations.

As well, good areas in the films in this work were often found in areas where laser interaction with plume species had occured. An interesting addition to the understanding of plume species and dynamics would be the use of multiple laser techniques to change the species distribution and energies to enhance deposition of high quality films.
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