FABRICATION, MATERIALS, AND CHARACTERIZATION FOR
EFFICIENT MEMS POWER GENERATION

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Changes to the fabrication of lead zirconate titanate have been made to improve the processing efficiency and decrease the environmental hazards in the production of a piezoelectric thin film-based MEMS engine. Several trials of non-2-MOE-based solution deposition routes were attempted, finding an acetate-based hybrid sol-gel route to provide films of good quality with decreased processing times. Additionally, the incorporation of rapid thermal annealing (RTA) for crystallization of the sol-gel films is shown to be a practical replacement to the conventional furnace currently used in the PZT processing scheme. Viability of this route was determined through characterization of the structure (FESEM, AFM and XRD) and properties (dielectric constant, transverse piezoelectric coefficients, electromechanical response, and film stress).

Further improvements to the PZT thin film were investigated from studying the processing-structure-property relationship for various parameters, such as solution chemistry, dopant additions, and heat treatment. Three chemistries of sol-gel derived PZT were prepared, 32/68, 40/60, and 52/48. Increased piezoelectric response was obtained with 52/48 chemistry, showing a rhombohedral structure, which deviates from the tetragonal structures of the former
two chemistries. From doping the 32/68 and 52/48 chemistries with various amount of donor
dopant, niobium (0-7.8 mol% Nb), a strong change in the grain morphology from columnar to
equiaxed was observed as dopant concentration increased. Correlating these structure changes
with the measured properties show that columnar grains do not always lead to the best
combination of properties. Rather, the highest piezoelectric coefficients and dielectric constants
were observed for undoped and lightly doped Pb$_{1.1}$(Zr$_{0.52}$Ti$_{0.48}$)$_{1-x}$Nb$_x$O$_3$ where $x \leq 1.1$ mol% Nb.
The PZT chemistries that produced the lowest stresses were undoped 40/60 and 2.8 mol% Nb-
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CHAPTER ONE
MOTIVATION FOR THIN FILM PIEZOELECTRIC DEVELOPMENT

An ongoing project at Washington State University is working to incorporate piezoelectric thin films into MEMS devices for energy conversion. The P³ microengine is a MEMS-based device that uses a piezoelectric, lead zirconate titinate (PZT), to generate power. Historically, piezoelectric thin films have been used for ferroelectric applications, but more research continues to expand the use of the films into MEMS type devices.

1.1 BACKGROUND

The interest in using piezoelectrics in these applications revolves around the ability of these films to withstand the application of high loads while providing amenability to flexing structures. This has added benefits over other MEMS devices that employ electrostatic actuation and therefore have sliding or rotating parts creating friction and causing potential wear, such as the electrostatic comb drive pictured in Figure 1.1.1(a). To further contrast electrostatic and piezoelectric-based MEMS, from a design standpoint, they look radically different. Whereby electrostatic applications are typically fabricated using polysilicon, using both surface and bulk micromachining to create miniaturized systems, piezoelectric-based MEMS open an arena for creative design techniques that exploit the bending, flexing, or stretching necessary to produce charges, and vice versa. An example of a MEMS device that employs piezoelectric thin films is the micro pump featured in Figure 1.1.1(b). Another difference is that typically high forces are used to obtain low strains, making piezoelectric materials useful in sensitive
sensor and precise actuation devices. On the other hand, electrostatic devices are often characterized by high displacements and low forces. From these differences, piezoelectrics provide a new realm of MEMS design otherwise unavailable with traditional MEMS materials.

![Image of MEMS electrostatic comb drive produced using a 3-layer polysilicon surface micromachining process](image1)

![Image of MEMS micro pump made up of a set of 3 test membranes](image2)

Figure 1.1.1 Image of (a) MEMS electrostatic comb drive produced using a 3-layer polysilicon surface micromachining process [1] and (b) MEMS micro pump made up of a set of 3 test membranes. Each membrane is 0.10 x 0.04 x 0.003 mm in size [2].

In order to produce piezoelectric thin films, methods must be chosen to suit the fabrication and materials of the device. Solution deposition is one popular method that offers processing flexibility at low cost. In the case of the P³ engine produced at WSU, the route to obtaining PZT solutions involves the teratogenic and carcinogenic 2-methoxyethanol (2-MOE) commonly used in the production of PZT. However, a strong need exists for commercially viable deposition methods that maintain low costs and minimize environmental hazards while allowing engineering flexibility to tailor properties such as piezoelectric response and residual stresses.
Another key issue for integration of piezoelectric (and sol-gel derived) films into MEMS devices is decreasing the thermal budget. Two possibilities are offered, the first being to lower the overall processing temperature (ideally near 450°C) and the second being to limit the time at high temperatures (usually 600-700°C). By incorporating tools like the rapid thermal annealer (RTA), faster heating rates (40-80°C/s) can help to achieve crystallization in less time.

The goal of this work is to develop a new thin film deposition method for PZT that is compatible with the tools and equipment at WSU. In order to be successful, the processing route should be more efficient, less hazardous, and less expensive, while providing properties that are at least as good as if not better than the current 2-MOE route. Concurrently, while developing and characterizing new methods for obtaining piezoelectric thin films, it is hoped that a better understanding of the processing influences on the structure and the properties can be gained. Through the addition of dopants like niobium to the PZT system a means to compare processing changes with structure and, ultimately, properties can be obtained. By identifying the structural characteristics that enhance the properties, piezoelectric films can be tailored to meet the requirements of a given application.
1.2 REFERENCES


CHAPTER TWO

INTRODUCTION TO PROCESSING AND CHARACTERIZATION OF THIN FILM PIEZOELECTRICS

2.1 INTRODUCTION

Although the properties and structure of bulk lead zirconate titanate, Pb(ZrxTi1-x)O3 (PZT) have been widely studied and well established, there is much interest and consequently, much research into thin film PZT. PZT, a solid-solution ceramic, is a perovskite-type ferroelectric material known for excellent piezoelectric, dielectric and pyroelectric properties [1]. As a thin film, PZT has been widely exploited for current and potential use in such applications as nonvolatile memories (such as DRAMs and FeRAMs), decoupling capacitors, sensors (acoustic emission sensors, vibration monitors, chemical microsensors), piezoelectric micromotors, and micromachined ultrasonic transducers [2-4]. With the integration of PZT into such microelectronics and MEMS devices, like the P³ micro-heat engine, a more complete understanding of the thin film behavior, including nucleation and grain morphology and their effects on the properties is needed. Further insight is sought into the processing methods required to achieve structures with properties comparable to and exceeding those of the bulk material as well as possessing viability for integration into microelectronic fabrication schemes.

This chapter is intended as a review of 1) the general structure and properties of PZT films, 2) the basic processing methods currently available and utilized, and 3) the methods for testing and characterizing these thin films, particularly for structure and property optimization of the P³ microengine.
2.2 STRUCTURE AND PROPERTIES

The solid solution phase diagram for PZT is shown in Figure 2.2.1 [1]. It is well established that many of the properties (including piezoelectric, ferroelectric, and dielectric) are maximized at the morphotropic phase boundary (MPB), commonly identified at around 52/48 Zr:Ti ratio and associated with the coexistence of tetragonal and rhombohedral phases [1,5]. The peak in the properties is often explained by the existence of both phases making it possible to utilize the 14 domain orientation states in the poling process [5].

![Figure 2.1.1. PbZrO3-PbTiO3 solid solution phase diagram from Jaffe et al [1].](image)

It is generally recognized that the microstructure plays a significant role in the property behavior of these films. The basic crystal structure of PZT is of the perovskite-type (ABO$_3$) illustrated in Figure 2.1.2 (a), often the desired phase as opposed to the property-degrading, non-ferroelectric pyrochlore-type phase (A$_2$B$_2$O$_7$, e.g. Pb$_2$(Zr,Ti)$_2$O$_6$O$^-$), in Figure 2.1.2b. The pyrochlore phase arises due to lead deficiency and unequilibrated oxygen transport and is considered to be transient or metastable.
During the crystallization process, oxygen and Pb react readily form PbO. Not enough Pb will keep the oxygen gain greater than the oxygen loss allowing the metastable pyrochlore to stabilize. By adding excess lead (10-20%), the volatility of PbO can be compensated. Too much Pb will cause the oxygen loss to be greater than the gain, transforming the metastable pyrochlore to perovskite in a fine pyrochlore matrix. The latter case is the most common, although it is possible to achieve complete pyrochlore transformation to perovskite through an approximate balance between oxygen loss and gain.

Figure 2.1.2. Crystal lattice for (a) perovskite, space group Pm(-3)m (cubic) and (b) pyrochlore, space group Fd(-3)m (cubic) [6].

Since the reaction of Pb with the oxygen in the high temperature atmosphere is localized on the surface, the degree of second phase is often detected in thin films using general characterization methods like X-ray diffraction (XRD) and electron microscopy.
For a more detailed understanding of the pyrochlore formation, more sensitive surface characterization methods are needed. Griswold et al. were able to use glancing angle XRD to characterize the nucleation and phase transformations, finding the rate at which PZT transforms depends on the heating rate [7].

As mentioned above, the presence of pyrochlore, along with the grain morphology, can influence the properties of PZT. Tailoring these properties through influencing the microstructure can be achieved through various processing techniques. To better understand the processing-structure-property relationship in PZT, some of the common thin film deposition methods will be reviewed.

2.3 PROCESSING METHODS

The process of depositing PZT as a thin film involves many common practices adopted from bulk and thin film production techniques. Commonly, precursors are used in either in gaseous (CVD), solid (PVD), or liquid (solution deposition) form to react or combine to produce a thin film on a substrate.

2.3.1 Physical Vapor Deposition

By using a solid source and either heat, plasma, ion-beam, or laser to vaporize the solid, a solid thin film can be deposited onto a substrate. Although this technique has been used often in the production of metal films, a growing number of processes are being modified and developed to deposit ceramics, especially stoichiometric multicomponent films like PZT. Physical vapor deposition (PVD) techniques used in
ceramic processing include ion-beam, magnetron, and rf-diode sputtering; thermal, e-beam, and flash evaporation; and pulsed laser ablation.

Plasma sputtering deposition (PSD) is practical for both commercial and research environments, but often problems of thickness and compositional uniformity from using bulk targets plague the process [8]. Also, extreme sensitivity to deposition conditions and geometry result from the nature of the physical configuration. As is the case for general PZT processing, the formation of the perovskite phase is greatly influenced by the incorporation of Pb. With PSD, the type of system can influence the transport of Pb to the surface depending on the gas pressure [9, 10].

Another PVD method, ion-beam sputtering deposition (IBSD) uses multiple ion beams directed a single elemental target, e.g. Pb, Zr, and Ti for PZT, to counteract preferential sputtering of multicomponent oxides. Thus, control of the film stoichiometry stands out as this is an often a drawback for many vapor-based deposition processes. Although IBSD has lower deposition rates than PSD, some advantages include lower pressure during deposition and the production of smoother films [8].

Primarily still a research tool, pulsed laser ablation deposition (PLAD) is good for rapid exploration of novel chemistries and has been shown to produce single phase PZT at temperatures from 600-700°C [11]. It is most widely used for its ability to deposit a variety of ceramic films [12]. Exposing targets to an excimer laser beam creates a plume of material providing an evaporation source, transferring the target atoms to a heated substrate. This method is good for multicomponent system like PZT due to the accurate transfer of the target stoichiometry to the film in the case of oxides. Complexity arises in the spatial and time dynamic evolution of the ablated plume, and there are problems of
conformal and large-scale uniform coverage. For PZT, the presence of Pb may cause contamination problems during fabrication [11]. It is an expensive method due to equipment like laser and geometry-dependent chambers, and hence limited to research laboratories.

2.3.2 Chemical Vapor Deposition

Chemical vapor deposition (CVD) processes differ from PVD in that the deposition is due to chemical reactions of the precursor gases. Typically, this is a thermally driven process, using heat energy to activate the reactions. In the case of depositing PZT, a specific kind of CVD employed is metalorganic CVD (MOCVD) distinguished by the generally high volatility of the precursors permitting lower temperature processing [12]. Unlike PVD processes, stoichiometry in MOCVD is not such an issue due to the ability to precisely control the flows of the gaseous precursors, thus making it a suitable candidate for the preparation of PZT and other ferroelectric oxides films [12].

In many cases of CVD processing, the modification of using glow-discharge plasmas enables low-temperature deposition of films. Dey and Alluri discuss the use of plasma-enhanced MOCVD (PE-MOCVD) for PZT films combining the ability to achieve conformal coating, especially over device topography with low-temperature processing [13]. Some drawbacks include complex metal precursor selection, (typically metal alkoxides) and lower deposition temperatures. Further complexities arise from the precursor delivery technique. One proposed option called liquid-source injection produces a viable, albeit expensive, alternative technique for multicomponent systems [13-15]. Even with the decrease in processing temperature, the high costs override as a major drawback to using such methods.
2.3.3 Solution Deposition

One last method that is well known for inexpensive costs and relative ease is solution deposition. Of the processing methods available to produce thin PZT films, solution deposition stands out as the most adaptable and versatile as it can be used in the production of thin and thick films, tailoring to such parameters as chemistry and thickness fairly simply.

The deposition is divided into two parts, the solution synthesis and the film deposition. Prepared solutions can be easily made in-house or commercially purchased. The various types of solutions are discussed further in Chapter 3. In addition, the solutions are often able to readily accommodate dopants. For depositing the solutions onto substrates, the basic process often involves some baking, or pyrolysis, and heat-treating, or crystallization, carried out at ~600-700°C in either a standard conventional furnace or a rapid thermal annealer (RTA) or processor (RTP). For the P³ and related research, PZT films are made via solution deposition for the reasons discussed above and further in Chapter 3.

2.4 TESTING AND CHARACTERIZATION

Once deposited, thin films must be characterized and tested to determine their viability in a given application. For the P³ microengine, the PZT films used in the membrane generator are examined using a variety of tools, including field emission scanning electron microscopy, atomic force microscopy, and x-ray diffraction. The former two methods can be carried out on fully patterned wafers (see Appendix A), but the latter must be done on dedicated samples of blanket films with no further processing.
beyond PZT deposition. In this research, the samples used for XRD were prepared on bulk Si wafers. A patterned top electrode and exposed bottom electrode are all that is needed for electrical measurements like capacitance and dielectric constant. For other testing, such as bulge testing and piezoelectric measurements, PZT films must be on thin Si membranes.

2.4.1 Field Emission Scanning Electron Microscopy

Scanning electron microscopy (SEM) is an invaluable tool in surface analysis. For imaging and observation of nm-µm scale PZT grains and grain morphology, both in cross-section and in plan-view, high resolution tools are necessary. Compared to a tungsten filament electron source that has a beam energy spread of 3 eV, field emission sources are improved to around 0.3 eV [16].

The field emission SEM (FESEM) used in this research (LEO 982) uses a Schottky-field emission gun (FEG), a beam booster, an electromagnetic multihole beam aperture changer, and a magnetic field lens. Crossover of the beam electrons is prevented through the design of the beam path. Overall, FEGs are regarded for high resolution, even at low electron probe energies through reduced chromatic aberration, improved beam brightness, and little beam energy spread. In this research, the LEO 982 was used specifically to characterize the grain morphology of 1-µm-thick PZT films. To do this, films on substrates were fractured and mounted vertically inside the FESEM chamber and an accelerating voltage between 2-4 keV was used to obtain images magnified as much as 50,000x. In some cases, the sample holder was tilted 15° to observe both the cross-section and the top surface.
2.4.2 Atomic Force Microscopy

Another tool for surface analysis is the atomic force microscope (AFM), which creates surface images on the atomic scale. The high resolution and direct interpretation of the sample makes it a useful tool in the characterization of PZT films. For this research, contact AFM (Park Autoprobe CP) was used in constant-force mode. Low voltage mode scans ranging in size from 1x1 µm\(^2\) to 7 x7 µm\(^2\) of PZT were collected. The size of the scan was dependent upon the surface grain size, i.e. if the grain size was determined to be under 100nm, the scan size was decreased to 1µm by 1µm so as to best resolve these grains. Using the AFM scan images obtained, the Heyn intercept method was utilized to measure the surface grain size [17]. Though the AFM is quick, requiring little sample preparation and can be conducted in ambient air, it is not a complete picture of the PZT microstructure, and thus more emphasis was placed on FESEM work for this research. On the other hand, AFM does offer the ability to measure surface roughness and film topography in a quantitative manner, and thus has further applications beyond the scope of this research.

2.4.3 X-Ray Diffraction

Analysis and measurement of the crystal structure of PZT films were conducted using X-ray diffraction (XRD). One goal of these tests was to ascertain the crystal structure through phase identification. Another goal was to measure the change in the lattice parameters as the processing and chemistry of the PZT varied. A Philips X’pert MPD System diffractometer was used with a Philips sealed ceramic tube as the X-ray source. Thin, dedicated PZT films approximately 1 µm thick were analyzed using CuK\(\alpha1\) radiation (\(\lambda = 1.5406\)Å). Symmetric 2\(\theta\)-\(\omega\) scan geometry was used with ‘normal’
powder type optics. The Si substrate was provided an internal d-spacing standard by aligning the sample on the Si (400) peak at \(2\theta = 69.130^\circ\) and, due to the strength of the peak, scanned separately. Additionally, a calibrated attenuator was inserted in the beam path when the count rate exceeded 250,000 counts per second to avoid overloading the detector.

Lattice parameters were obtained using, a cell refinement method (from data analysis program, MDI JADE v6.5.7) on several peaks determined to be from the PZT only, i.e. not from the Si or Pt peaks. Using this system, the only condition necessary for obtaining lattice parameters is a sample with a high degree of crystallinity so that a sufficient number of peaks may be resolved [18].

When analyzing the data for cell refinement, some complications arise. For instance, a sample of PZT with Zr:Ti ratio of 32:68 and doped with 5.5% niobium is assumed to be tetragonal, according to JCPDS card# 50-0346 (\(\text{Pb(Zr}_{0.44}\text{Ti}_{0.56})\text{O}_3\)). The peaks that emerge for the tetragonal structure are characterized by peak splitting of the (110) and (101) and the (220) and (202), thus, the cell refinement indexing can be done one of two ways: 1) where the \(c/a\) ratio is greater than one, or 2) where the \(c/a\) ratio is less than one. The reason for the two choices is based on the peak fitting to the card data, and the fact that the resolved peaks from the sample do not match up exactly with the card.

As shown in Figure 2.4.1 (a), if the first choice is assumed, then the peak fit for the (202) \(\mid (220)\) overlapped region is relatively good, but not for the (101) \(\mid (110)\) region. On the hand, if the second choice is assumed, the opposite is true, as shown in Figure 2.4.1 (b).
Figure 2.4.1. Cell refinement differences for indexing tetragonal PNZT (5.5/32/68).
Illustration of peak fitting for indexing choice where (a) fit is better in (202) | (220)
region, and (b) fit is better in (110) | (101) region [18].

For reporting of the lattice parameters, the first indexing choice was selected based on the
better fit at the higher angle peaks, i.e. (202) and (220), near the vicinity of the alignment
scan at 69.130º.

2.4.4 Dielectric Constant

To obtain the dielectric constant, it is necessary to measure the film capacitance.
By using an impedance analyzer (Agilent 9294A), the capacitance is measured at 300 Hz
(to match the frequency at which electromechanical testing was performed). Typically,
measurements for dielectric constant are made at 1kHz due to some frequency
dependence. Although the values measured at 300 Hz may not reflect absolute values,
they are relative to the dynamic testing done on the membranes, and therefore sufficient
for a relative comparison.

Capacitance (in nF), electrode area (mm$^2$), and thickness (measured using
profilometer (SPN Technologies), in µm) are used to calculate material permittivity, as
shown in Equation (1).

$$\varepsilon_T = \frac{C(F)d(m)}{A(m^2)}$$

(1)

Dividing by the permittivity of free space, $\varepsilon_o$ ($8.854 \times 10^{-12}$ F/m), the relative permittivity, $\varepsilon_r$, or dielectric constant is:

$$\varepsilon_r = \frac{\varepsilon_T}{\varepsilon_o}$$

(2)

2.4.5 Piezoelectric Response

With the growing interest in piezoelectrics for MEMS devices, there is more than
ever a need to accurately measure the piezoelectric response, i.e. the piezoelectric
coefficients. Two of the more common reported values are strain-based transverse
piezoelectric coefficient, or $-e_{31}$ (in C/m$^2$), and stress-based transverse and longitudinal
coefficients, $-d_{31}$ and $d_{33}$, respectively (in pC/N). Literature reports various methods to
measure piezoelectric coefficients, such as wafer flexure and cantilever method [19, 20].
For membranes, as in the case of the piezoelectric generators for the P$^3$ engine, two
methods can be used. One is an estimate of the lower-bound $e_{31}$ and can be obtained
from a figure of merit called specific voltage (further explained below) [21]. The other is
a method developed by Sullivan [22] called the rectangular membrane method (RMM), pictured schematically in Figure 2.4.2.

The RMM is desirable because it provides a way to measure $e_{31}$ and $d_{31}$ using piezoelectric films on membranes. Typically, the membrane generators are of a square geometry, but for RMM, rectangular membranes are fabricated using the same bulk micromachining methods (see Appendix A). Using a slightly modified mask, it is possible to produce wafers with both square and rectangle membranes so as to maximize possible testing. By using an integrating charge circuit that contains a reference capacitor (user selected), the membrane die is clamped to an acrylic holder, electrodes are connected to the integrating charge capacitor, and the membrane is statically bulged. A charge from the electrodes is measured off an oscilloscope for a given pressure. At this pressure, an interferogram is also taken to measure the strain at the center of the membrane.

![Figure 2.4.2. Schematic of RMM set-up used for measuring piezoelectric coefficients, developed by Sullivan [22.]](image-url)
2.4.6 Static and Dynamic Bulge Testing

Both mechanical and electromechanical characterization was carried out using a mechanical bulge tester. For a relative comparison of the film stress and compliance, static measurements were made from membranes held into place using an acrylic holder, and deflected using N₂ while capturing an image of the deflected membrane from a Michelson interferometer. By varying the pressure and recording the interferograms at each pressure, pressure-deflection data can be obtained.

For the electromechanical characterization, testing was conducted using a dynamic operation of the bulge tester whereby the pressure, deflection, and output of the piezoelectric membrane are recorded simultaneously. Using the data gathered (peak-to-peak output as a function of % strain) and knowing the PZT film thickness, a figure of merit called specific voltage, or peak-to-peak voltage per unit of biaxial strain at the center of the membrane per unit thickness was obtained [23].
2.5 REFERENCES


CHAPTER THREE

INCORPORATING AN ACETIC ACID SOLVENT INTO PZT DEPOSITION FOR THE P³ MICROENGINE

3.1 INTRODUCTION

Changing the precursor solvent for PZT synthesis inevitably will impact the materials properties, and, at the same time, incorporating that new solvent requires significant processing changes. In the current processing for the P³ microengine, PZT is synthesized using 2-methoxyethanol (2-MOE) as the solvent for the metal precursors. The objective of the following chapter is to describe the methods used in finding a replacement for the extremely hazardous 2-MOE while minimizing any property, structure, or performance degradation. As the processing varied, specifically the solution route, chemistry, and heat treatment, changes were observed in the structure (grain morphology and crystallography) and the properties (piezoelectric response and residual stress) of the film, consequently, impacting the overall generator performance.

When selecting the piezoelectric thin film for the P³, it is necessary the material not only provides the desired properties, but also is compatible with the microfabrication processing and capabilities currently in place at Washington State University. PZT was selected as the piezoelectric material based on its electroactive properties such as high electromechanical coupling coefficient \( k \sim 0.4-0.5 \), high dielectric permittivities \( \varepsilon \sim 100-2400 \), and low dielectric losses \[1, 2\]. In addition, many processing routes are available for depositing PZT as discussed in Chapter 2, but the low cost and processing flexibility offered from a solution deposition route make it one of the more attractive options.

Solution-derived PZT films offer many advantages over other methods, most notably superior stoichiometric control of complex mixed oxides \[3\]. Other advantages include
reproducible compositions and properties, acceptable processing temperatures, simple equipment, and low costs [4, 5]. Ways of depositing sol-gel films include spin-casting, dip-coating, and spraying. In this research all the PZT and dopant-modified PZT films were spin cast, similar to the processing of photoresist layers, and thus having the added benefit of incorporating easily into the microfabrication scheme currently in place for the P³ microengine (see Appendix A for the microfabrication protocol). One disadvantage with a sol-gel deposition method is obtaining uniform thickness over raised surface features, which is not a limiting factor for the P³.

Tuttle and Schwartz and Polla and Francis offer overviews of the variations in processing available “under the umbrella of solution deposition,” including the associated structure-property changes that may result [3,5]. Although much work has been done to identify the impact of various solution chemistries and precursors on the resultant structure and properties [6-14], some effects can be easily anticipated, such as changes in the microstructure from pyrolysis temperatures [8] and changes in the film stress that evolve from solvent evaporation and subsequent shrinkage [3].

The deposition of PZT by solution deposition has three main steps: synthesis of a solution from metalorganic precursors, usually alkoxides; deposition onto the substrate; and heat treatment, or firing, of the film to achieve a dense, crystalline film. Within the synthesis component of solution deposition, the most common routes are reaction of metalorganics to form a gel, for example, using 2-MOE, as a solvent and reactant; metalorganic decomposition (MOD) of nonreactive precursors, using a solvent like xylene to dissolve the metalorganic compounds; and hybrid routes with some reaction involved, such as using acetic acid as a solvent and a chelating agent [3,5].
Previous work on the \( P^3 \) has been done to find an alternative route to the 2-MOE-based route currently in place, shown in Figure 3.1.1 (a) [15]. By employing a hybrid MOD route [16,17] presented in Figure 3.1.1 (b), not only can the teratogenic and carcinogenic 2-MOE solvent be eliminated from the laboratory, but also the solution’s sensitivity to water is decreased, facilitating easier processing [16,18].

\[
\begin{align*}
\text{Pb(OAc)}_2 \cdot 3\text{H}_2\text{O} & \quad \text{Add Zr (n-OPr)}_4 \\
\text{Add Ti(i-OPr)}_4 & \quad \text{Distill off water for 2 hours at 125°C} \\
\quad & \quad \text{Add 2-methoxyethanol} \\
\quad & \quad \text{Reflux for 3 hours at 110°C} \\
\quad & \quad \text{Distill off water for 2 hours at 125°C} \\
0.5\text{M Pb}_{1.1}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 & \\
\end{align*}
\]

\[
\begin{align*}
\text{Ti(i-OPr)}_4 & \quad \text{Combine with glacial acetic acid} \\
\quad & \quad \text{Combine with distilled H}_2\text{O} \\
\quad & \quad \text{Combine Zr(AcAc)}_4 \\
\quad & \quad \text{Combine with Pb(OAc)}_2 \cdot 3\text{H}_2\text{O} \\
\quad & \quad \text{Titanium Precursor Solution} \\
\quad & \quad \text{Add} \\
\quad & \quad \text{Age 1 day @ 60°C, freeze (-18°C)} \\
0.865\text{M Hybrid MOD Pb}_{1.1}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3 & \\
\end{align*}
\]

Figure 3.1.1. Flow chart synthesis route for (a) 2-MOE-based system from Budd et al [15], and (b) acetate-based hybrid MOD system from Wright and Francis [16].

3.2 EXPERIMENTAL DEVELOPMENT

3.2.1 Acetate-based Hybrid MOD Route

Although the initial results from experiments conducted by Eakins [17] showed there to be promise in the acetate-based hybrid MOD route, both in improving the processing time and the resultant properties, an error discovered in the calculations was found to alter the chemistry.
In calculating what was expected to be 40/60 PZT chemistry, the wrong formula weight was used was for the zirconium addition (zirconium (IV) 2,4-pentanedionate). Instead of synthesizing a 40/60 PZT chemistry with 10% excess lead, the actual chemistry was 31/69 PZT with 27% excess lead. The chemistry calculations were corrected to produce 40/60 PZT with 10% excess lead thin film samples using a stock solution concentration of 0.865M. The details of the calculation are given in the Appendix B.1. It was very difficult to achieve consistent and reliable films using this route, even after the chemistry was modified to 40/60 due to problems such as film cracking. Also, Wright and Francis determined aging to be an issue, and accounted for this by freezing and defrosting the solution, which adds another necessary step in the production of acetate-based hybrid MOD-derived films [16,17].

Some trial films were produced using the synthesis route presented by Wright and Francis pictured schematically in Figure 3.1.1.b. A dry N$_2$ glove box was used for all the additions of the precursors. Glacial acetic acid and titanium (IV) isopropoxide (or TIP, Ti(i-OPr)$_4$, 99.999%, Sigma-Aldrich) are first combined in a two-neck flask and stirred for 5 minutes without heat. Deionized water is then added to the solution, forming a white precipitate that requires about 30 minutes in an ultrasonic bath to dissolve. Zirconium acetylacetonate (or zirconium 2,4-pentanedionate, Zr(AcAc)$_4$, 98%, Sigma-Aldrich) and lead (III) acetate trihydrate (Pb(OAc)$_2$·3H$_2$O, 99+, A.C.S. Reagent, Sigma-Aldrich) are combined with the titanium precursor solution and refluxed for 30 minutes at 100°C. An accelerated aging of the solution is achieved by constantly stirring for 1 day at 60°C, adding H$_2$O$_2$, and then aging for an additional day. Aged solutions are then frozen (-18°C) to limit any further aging and thawed as needed for deposition.
Solutions are then coated onto annealed and platinized silicon substrates using the procedures outlined by Eakins [17]. This process is the result of many trials and had been optimized for use with this particular concentration (0.865M) and the equipment at WSU. The steps involve thawing the frozen PZT solution (by constantly stirring) 30 minutes prior to spin coating. Using a 0.2-µm filter, the substrates are coated and spun at 3000 rpm for 5 sec, with the acceleration and deceleration knob at 3 o’clock position. Pyrolysis is done after each layer at 400°C for 8 minutes, repeated between 2 and 3 more times before crystallization at 700°C for 20 minutes in a conventional furnace.

The acetate-based hybrid MOD route offers many advantages, such as greater thickness per layer (e.g. ~0.125µm vs. 0.083µm for 2-MOE) and ease of preparation (e.g. less complex and less time). On the other hand, the desire to further enhance the properties through the addition of dopants lead to the investigation of other non-2-MOE routes that could readily accommodate modifications made to the PZT system.

3.2.2 Diol-based Route

Originally developed for the production of lead titanate films, Phillips et al. devised a sol-gel system employing dihydroxy alcohols, like propanediol, as solvents [19]. Later, Tu and Milne modified this method to fabricate PZT (53/47) films using lead acetate trihydrate, titanium bisacetylacetonate, zirconium n-propoxide, 1,3-propanediol, and acetylacetone as shown in Figure 3.2.1 [20]. Further developments enabled the synthesis of niobium-doped films using a slightly modified version of the above route [18].
Following the route developed by Tu and Milne, a batch of 38/62 PZT was produced and coated onto plantinzed quarter wafer samples for initial viability. As the metal precursors are moisture sensitive, all additions were carried out in a N₂ glove box. Preparation of the solution involved mixing two separate solutions and later combining them for the final stock solution. The first is the lead solution produced by adding 20 mol% excess lead in a 1:5 molar ratio to 1,3-propanediol (or, 1,3-dihydroxypropanol, or trimethylene glycol, 98%, Sigma-Aldrich) in a two-necked flask and refluxed for 2 hours at 115°C. The lead solution is not moisture stable at this point and any exposure to air will cause a precipitate to form. The second solution contains the zirconium and titanium precursors. Zirconium (IV) n-propoxide solution (in 70 wt.% in 1-propanol, Sigma-Aldrich) is added in a 1:2 molar ratio to acetylacetone (or 2,4-pentanediione, ≥99%, Avocado/Sigma-Aldrich) to facilitate the exchange of alkoxy ligands by acetylacetonate.
groups [18]. When adding the zirconium to the acetylacetone, an orange precipitate forms, but
dissolves quickly upon refluxing for 30 minutes between 110-115ºC. Acetylacetone is used a
chelating agent to decrease the titanium and zirconium precursors sensitivity towards hyrolysis
[18]. This contributes to a relatively moisture-stable final solution. The solution is then cooled
to ~80ºC, titanium-(diisopropoxide) bis(2,4-pentanedione) solution (TIAA, or
diisoproxytitanium bis(acetylacetonate), 75 wt.% in 2-propanol, Sigma-Aldrich) is added in a
1:5 molar ratio with 1,3 propanediol, and then refluxed for 2 hours at 110-115ºC. At this point,
the two solutions, the lead and zirconium/titanium, are combined, refluxed for 1 hour at 110-
115ºC, and distilled at 115-120ºC to about 50ml, which corresponded to a 1M solution. After a
final reflux for 3 hours, the solution was cooled, and the concentration was adjusted to ~0.5M
using 1-propanol. Finally, the stock solution is transferred to a jar with a tight-fitting lid, and
ready for deposition.

To obtain thin films of diol-based PZT, the solution was filtered though a 0.2-µm
membrane filters onto an annealed platinized silicon substrate. Using a spin-coating system, the
standard practice is to deposit the film from the outside edges in towards the center of the wafer
so as to minimize the area that may be exposed to dust or other particles. The films were spun at
3000 rpm for 30 seconds followed by pyrolysis treatment onto a hot-plate fitted with a brass
plate for temperature uniformity at 350ºC for 1 minute. The number of layers was varied using
1,2, and 3 layers before crystallizing in a RTA at 700ºC for 30 s using a ~40ºC/s heating ramp.

3.2.3 Acetate-based Hybrid Sol-gel Route

Using the process developed by Lee and Lee [21] and adapted from Sayer et al. [22] the
following PZT chemistries were made using 10-20% excess lead: 32/68, 40/60, and 52/48. The
appeal of this method is that it can be used for both undoped and doped PZT chemistries, as
discussed further in Chapter 4. In addition, the process is relatively simple and straightforward, using the same metal precursors as currently used in the 2-MOE process, but with less toxic solvents such as acetic acid and n-propanol. The acetic acid acts as a stabilizer of the metal alkoxides with n-propoxide added for control of viscosity and improvement of wettability [13]. Figure 3.2.2 illustrates the flow diagram for preparation of the solutions. This route does not seem to fall classically into the description of sol-gel whereby a water/alcohol mixture is deliberately added in the final stage of synthesis to produce a polymeric-type sol [18]. For convenience and consistency, this method will be referred to as an acetate-based hybrid sol-gel route.

For the synthesis of the hybrid sol-gel solution, all mixing was carried out in a dry N$_2$ glove box to prevent any reaction of the moisture-sensitive precursors metal alkoxides, but once mixed, the system is reported to be stable for several months [21]. The basic procedure for solution synthesis, deposition, and heat treatment is given below. The film deposition process underwent many changes to the following processing variables: solution molarity, spin speed, pyrolysis temperature and time, number of layers deposited prior to crystallizing, and crystallization heating rates, hold temperature and hold time.
The zirconium (IV) n-propoxide solution (Zr(n-OPr)\textsubscript{4}, 70 wt.% in 1-propanol, Sigma-Aldrich) is added, followed by the titanium (IV) isopropoxide (Ti(i-OPr)\textsubscript{4}, 99.999%, Sigma-Aldrich). Acetic acid and n-propanol are added prior to the lead (II) acetate trihydrate (Pb(OAc)\textsubscript{2}·3H\textsubscript{2}O, 99+%, A.C.S. reagent, Sigma-Aldrich) addition. The lead powder is dissolved at ~92°C for 30 minutes and then cooled to room temperature before adding more acetic acid and n-propanol. If any dopant additions are required, they are added from a stock solution immediately before the final acetic acid/n-propanol addition.

All of the films were deposited using a multilayer process. Prior to deposition, the platinized silicon substrates were annealed at 650°C for 10 minutes using a conventional furnace with a vertical loading system. Each layer was spin-coated at 3000 or 4000 rpm for 30 seconds onto the annealed Pt substrates using a 0.2µm filter. The wafer was then transferred for pyrolysis to a digital hotplate fitted with a brass plate for heating uniformity [23] and a thermocouple for
accurate temperature readout. Pyrolysis was carried out at either 350°C or 300°C, and held for 1 or 3 minutes, respectively. In one trial, a pyrolysis temperature of 150°C was used for each layer to essentially bake out the solvents in accordance with the literature [21].

3.2.4 Crystallization

After pyrolysis the films must be fired at a temperature above the Curie temperature in order to crystallize the film. Two methods for heat treatment were used in this research: a traditional, conventional furnace, or a rapid thermal annealer (RTA, Total Fab Solutions Heatpulse 610). The latter greatly affects the heating rate, particularly the net rate oxygen is transported from the atmosphere to the film and vice versa. This method is sought after for improving the rapid formation of the perovskite phase. Using the RTA, two different heating rates were used in the production of PZT films as shown in Figure 3.2.3. Details of the operation of the RTA are provided in the Appendix C.

![Graph showing two experimental RTA thermal cycles](image)

Figure 3.2.3. Two experimental RTA thermal cycles used in the production of solution-derived PZT films.
3.2.5 Testing and Characterization

The structure of the films were examined by fracturing thin films for cross-section views of film morphology using secondary electron (SE) field emission scanning electron microscopy (LEO 982 FESEM). X-ray diffraction (Philips X’Pert MPD system) was used for crystal structure analysis, phase identification, and lattice parameter measurements. Additionally, atomic force microscopy in constant-force mode (AFM, Park Autoprobe CP) was used for plan-view grain size and phase analysis. Film thicknesses were measured using profilometry (SPN Technologies PHD profilometer). The stress of the films was qualitatively compared using pressure-deflection data obtained from static bulge testing. For quantitative comparison of the films, elastic modulus of the films was measured using dynamic stiffness nanoindentation (Hysitron Triboscope, corner cube tip) from established methods of Oliver and Pharr [24]. For the electro-mechanical characterization, gold top electrodes were deposited (see Appendix A), and capacitance was measured using an impedance analyzer (Aglient 9294A) at 300Hz from which the dielectric constant was calculated. As described in Chapter 2, dynamic bulge testing was used to test the film’s performance through a figure of merit called specific voltage. Also as described in Chapter 2, PZT films were deposited on rectangular membranes to directly measure the piezoelectric response.

3.3 RESULTS AND DISCUSSION

3.3.1 Defect Characterization

Before obtaining any data, it is imperative that the underlying Pt/Ti/SiO\textsubscript{2} films and Si substrate are of good quality, i.e. no defects or adhesion problems. Problems can result from pinhole formation in the SiO\textsubscript{2} that are visible under optical microscopy as pyramidal pits after
etching in EDP. These pinholes have been suggested as initiation sites for film peeling to occur (Figure 3.3.1). Other sources of defects can arise from the bottom electrode stack both in the Pt/Ti ratio, which was investigated by Eakins [17] and in the Pt adhesion measured using a tape test.

![Image](https://example.com/image.png)

Figure 3.3.1. Optical micrographs of delaminated 32/68 film on poor oxide layers.

### 3.3.2 Solution Development

The diol-based route was abandoned as a viable alternative to the MOE-route based on the complexity and time-consuming nature of the synthesis process. Initial deposition trials yielded films with poor adhesion and or microcracking, the results of which are shown in Table 3.3.1. Cracked and delaminated films might be avoided through a lower crystallization temperature or a lower initial solution concentration, but persisting on this route appeared to offer little in the way of improvement especially since the process was longer to complete than the 2-MOE-based route. Although the diol-based system is extensively studied, and literature
reports a method for adding dopants, such as niobium, it was ultimately abandoned as a potential replacement for 2-MOE due to the complex and time consuming synthesis, requiring over 10 hours of processing.

Table 3.3.1. Results of deposition trials with ~0.5M diol-based (38/62) PZT sol with 20% excess lead.

<table>
<thead>
<tr>
<th>Spin speed/time (rpm/sec)</th>
<th>Pyrolysis temp/time (C/min)</th>
<th>No. of layers</th>
<th>Crystallization temp/time (C/min)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000/30</td>
<td>350/1</td>
<td>3</td>
<td>RTA fast ramp to 700/0.5</td>
<td>severe delamination</td>
</tr>
<tr>
<td>3000/30</td>
<td>350/1</td>
<td>2</td>
<td>RTA fast ramp to 700/0.5</td>
<td>severe delamination</td>
</tr>
<tr>
<td>3000/30</td>
<td>350/1</td>
<td>1 x 1</td>
<td>RTA fast ramp to 700/0.5</td>
<td>hazy appearance</td>
</tr>
</tbody>
</table>

For the acetate-based hybrid sol-gel route, the initial processing produced a high concentration solution (0.865M) so as to provide a comparison to the hybrid MOD route. Using literature and trial-and-error, the final molarity was adjusted to 0.4M, as used by Lee and Lee and Kwon et al [13, 21]. Initially a two-necked flask was used for refluxing but was later deemed to be less critical. Eventually the process was reduced to a one-bottle process, mixing the precursors in a closed system. The results of the multiple deposition trials are listed in Table 3.3.2. After lowering the final molarity, the quality of the film was judged according to amount of cracking, either on the macroscale, or microscale, the latter visible as a haziness over the film. For film adhesion, delamination occurred either subtly, in the form of localized peeling or severely, in the form of complete film delamination.
Table 3.3.2. Processing parameters and variations for deposition of acetate-based hybrid sol-gel PZT.

<table>
<thead>
<tr>
<th>chemistry (Nb/Zr/Ti)</th>
<th>% excess lead</th>
<th>molarity</th>
<th>spin speed/time (rpm/sec)</th>
<th>pyrolysis temp/time (C/min)</th>
<th>no. of layers</th>
<th>crystallization temp/time (C/min)</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.865</td>
<td>3000/30</td>
<td>300/5</td>
<td>3</td>
<td>700/30</td>
<td>film cracking</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.865</td>
<td>4000/30</td>
<td>300/5</td>
<td>3x3</td>
<td>700/30</td>
<td>cracking</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.865</td>
<td>4000/30</td>
<td>300/5</td>
<td>2x2</td>
<td>700/30</td>
<td>slight cracking</td>
</tr>
<tr>
<td>5.5/32/68*</td>
<td>25</td>
<td>0.865</td>
<td>4000/30</td>
<td>300/5</td>
<td>2</td>
<td>650/20</td>
<td>cracking, adhesion problems</td>
</tr>
<tr>
<td>5.5/32/68*</td>
<td>25</td>
<td>0.865</td>
<td>4000/30</td>
<td>150/4</td>
<td>2</td>
<td>650/10</td>
<td>severe delamination</td>
</tr>
<tr>
<td>5.5/32/68*</td>
<td>25</td>
<td>0.865</td>
<td>4000/30</td>
<td>150/2 + 300/5</td>
<td>2</td>
<td>700/20</td>
<td>cracked upon deposition of 2nd layer</td>
</tr>
<tr>
<td>2.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>300/5</td>
<td>3x3x2</td>
<td>700/20</td>
<td>hazy</td>
</tr>
<tr>
<td>2.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>300/5</td>
<td>3x3x3x3</td>
<td>650/10</td>
<td>light haze</td>
</tr>
<tr>
<td>2.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/3</td>
<td>3x3x3x3</td>
<td>650/10</td>
<td>light haze</td>
</tr>
<tr>
<td>2.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/3</td>
<td>4</td>
<td>650/10</td>
<td>film cracking</td>
</tr>
<tr>
<td>2.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>300/3</td>
<td>3x3x3</td>
<td>650/10</td>
<td>slight cracking on edges</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>300/3</td>
<td>3x3x3</td>
<td>650/10</td>
<td>fine</td>
</tr>
<tr>
<td>0/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>300/3</td>
<td>3x3x3</td>
<td>650/10</td>
<td>fine</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>300/3</td>
<td>3x3(x3)</td>
<td>650/10 (650/2)</td>
<td>fine</td>
</tr>
<tr>
<td>2.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>300/3</td>
<td>3x3x3</td>
<td>650/10</td>
<td>haziness at 2nd layer</td>
</tr>
<tr>
<td>0/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>300/3</td>
<td>3x3(x3)</td>
<td>650/10 (650/2)</td>
<td>some cracking</td>
</tr>
<tr>
<td>0/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>300/3</td>
<td>3x3(x3)</td>
<td>650/10 (650/2)</td>
<td>some cracking</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x3</td>
<td>650/10</td>
<td>good</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3</td>
<td>RTA-fast ramp to 650/0.5</td>
<td>delamination</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>2(x2)</td>
<td>RTA-slow ramp to 650/0.5</td>
<td>good</td>
</tr>
<tr>
<td>0/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3(x1)</td>
<td>RTA-slow ramp to 650/0.5</td>
<td>hazy</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x3</td>
<td>RTA-slow ramp to 650/0.5</td>
<td>good</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>2x2x2x2x2</td>
<td>RTA-slow ramp to 650/0.5</td>
<td>good</td>
</tr>
<tr>
<td>Temperature</td>
<td>Pressure</td>
<td>Base Pressure</td>
<td>Cycle 1</td>
<td>Cycle 2</td>
<td>Cycle 3</td>
<td>Cycle 4</td>
<td>Cycle 5</td>
</tr>
<tr>
<td>-------------</td>
<td>----------</td>
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<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>7.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>fine</td>
</tr>
<tr>
<td>7.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>wafer cracked during processing</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>fine</td>
</tr>
<tr>
<td>2.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>fine</td>
</tr>
<tr>
<td>2.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>hazy on edges</td>
</tr>
<tr>
<td>7.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>severe adhesion issues</td>
</tr>
<tr>
<td>7.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>adhesion problems/cracking; oxide pinholes</td>
</tr>
<tr>
<td>7.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>film cracking</td>
</tr>
<tr>
<td>7.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>650/10 (650/2)</td>
</tr>
<tr>
<td>0/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>650/10 (650/2)</td>
</tr>
<tr>
<td>2.8/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>fine</td>
</tr>
<tr>
<td>0/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>fine</td>
</tr>
<tr>
<td>5.5/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>film cracking</td>
</tr>
<tr>
<td>1.1/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>650/10 (650/2)</td>
</tr>
<tr>
<td>1.1/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>fine</td>
</tr>
<tr>
<td>1.1/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>good</td>
</tr>
<tr>
<td>0/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>cracking over membranes only</td>
</tr>
<tr>
<td>1.1/32/68</td>
<td>25</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>hazy on edges</td>
</tr>
<tr>
<td>0/40/60</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-slow ramp to 650/ 0.5</td>
<td>good</td>
</tr>
<tr>
<td>0/40/60</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3</td>
<td>RTA-fast ramp to 650/ 0.5</td>
<td>good</td>
</tr>
<tr>
<td>Zr/Ti Ratio</td>
<td>PEG wt%</td>
<td>Temp</td>
<td>Time</td>
<td>Chamber</td>
<td>RTA ramp to 650/ 0.5</td>
<td>Result</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>---------</td>
<td>------</td>
<td>------</td>
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<tr>
<td>0/50/60</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>wafer broke during pyrolysis</td>
<td></td>
</tr>
<tr>
<td>0/52/48</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>0.5/52/48</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>1.1/52/48</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>2.8/52/48</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>0/52/48</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>0.5/52/48</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>1.1/52/48</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>2.8/52/48</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>good</td>
<td></td>
</tr>
<tr>
<td>0/52/48</td>
<td>10</td>
<td>0.4</td>
<td>3000/30</td>
<td>350/1</td>
<td>3x3x2</td>
<td>good</td>
<td></td>
</tr>
</tbody>
</table>

*added 30wt%PEG
KEY: (_)=uncrystallized or partially crystallized

As referenced in Table 3.3.2, various chemistries of PZT and Nb-doped PZT were tested. The calculations used to determine the proper precursor amounts are detailed in the Appendix B, while the amounts are summarized in Table 3.3.3 for unmodified PZT films with Zr/Ti ratios of 32/68, 40/60, and 52/48. Based on the qualitative results from deposition trials of hybrid sol-gel acetate route, the final deposition flow chart was determined as shown in Figure 3.3.2. This represents the method for achieving the least film cracking and the most consistent results.
Table 3.3.3 Amount of metal precursors added for various chemistries of hybrid sol-gel chemistry

<table>
<thead>
<tr>
<th>Chemistry (Zr/Ti)</th>
<th>% excess lead</th>
<th>Zr(O-Pr)$_4$ solution (grams)</th>
<th>Ti(i-Pr)$_4$ (grams)</th>
<th>Pb(OAc)$_2$ 3H$_2$O (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32/68</td>
<td>20</td>
<td>2.62</td>
<td>3.41</td>
<td>8.35</td>
</tr>
<tr>
<td>40/60</td>
<td>10</td>
<td>3.74</td>
<td>3.41</td>
<td>8.35</td>
</tr>
<tr>
<td>52/48</td>
<td>10</td>
<td>4.87</td>
<td>2.73</td>
<td>8.35</td>
</tr>
</tbody>
</table>

**Figure 3.3.2. Deposition flow chart for acetate-based hybrid sol route.**

Films produced by the acetate-based route (0.4M solution) have a measured film thickness of ~1.1µm (for 9 layers or 0.12 µm/layer). This is a 50% increase in the thickness per
layer as that achieved with 0.5M 2-MOE-based route (0.08 µm/layer), making the production of ~1.0 µm PZT films possible in less layers, i.e. less time and fewer crystallization steps. The results of varying the chemistry were observed to effect the quality of the final film for the hybrid sol-gel acetate route as seen in Figure 3.3.3. All films were processed similarly on thin (2.3-µm) Si membranes with the 32/68 chemistry film showing through-films cracks in the PZT. Hence, electrical measurements were impossible to obtain as due to shorting. These cracks are an indication of stress-relief mechanism, implying the films were high stress prior to cracking. The 40/60 chemistry, on the other hand, was crack-free, and possible to measure electrical properties. A “wrinkled” appearance, however, is visible in the film, but only over membranes; the film over the bulk Si appears defect-free. The 52/48 film is completely defect-free.
Figure 3.3.3. Hybrid sol-gel acetate-based PZT deposited on membranes; (a) 32/68, (b) 40/60, and (c) 52/48. The side length of each Au electrode pad is 2mm.

Comparing the results of 32/68 films processed in the conventional furnace versus the RTA, the distinction between micro-cracking and macro-cracking is more evident, pictured in Figure 3.3.4. Both films were crystallized at 650°C, but the differences in the processing with the two heat treatments are the heating rates and the hold times. For the RTA fired film, the heating rate was done very slowly (~6°C/sec) since films with this chemistry fired at higher heating rates (~40°C/sec) showed severe delamination.
3.3.3 Structure

SE images taken using FESEM for 32/68 films in Figure 3.3.5 compare films annealed in (a) a conventional furnace with those in (b) an RTA using slow ramp. The latter sample was tilted 15° in the chamber and pictured in Figure 3.3.5 (c) to show the variations in surface grain structure that occur compared to that in the bulk of the film. Both films show a columnar structure, but the RTA-treated film appears to possess a surface structure that is incongruent with the underlying microstructure. Pyrochlore is barely visible on the surface, which is known to appear in micrographs as a fine-grained phase in Pb-deficient surface layers [25]. SE cross-sections for 40/60 and 52/48 chemistries are in Figure 3.3.6. Since part of the research goals is to link property values with structural changes, and not simply processing variations, the structure-property relationships are valid. Kwon et al. observed a difference in grain size for an acetate system versus 2-MOE for films processed similarly, thus showing that the precursor solution will impact the structure [13].
Figure 3.3.5. Cross-sectional SE images of undoped 32/68 PZT films, crystallized (a) in a conventional furnace for 10 min and (b) in an RTA for 30 sec hold using a slow ramp. (c) Sample is tilted 15 degrees to emphasize surface structure.
Figure 3.3.6. Cross-sectional SE images of acetate-based PZT with Zr/Ti ratio of (a) 40/60 crystallized in RTA using slow ramp and (b) using fast ramp; (c) 52/48 crystallized in RTA using slow ramp and (d) fast ramp to hold temperature of 650°C for 30 sec.

The differences in XRD 2θ-ω scans for various heat treatments (i.e. heating rates) for 32/68, 40/60, and 52/48 are illustrated in Figure 3.3.7. The 32/68 and 40/60 chemistries are analyzed as tetragonal, as evidenced by the splitting of the (200), (210), (211) and (220) peaks. The lattice parameters from cell refinement analysis for the same data set are presented in Table 3.3.4, and indexed according to JCPDS card #50-0346 (Pb(Zr0.44Ti0.56)O3). For the tetragonal chemistries, there is a decrease in the tetragonality as the heating rate is increased, with the most tetragonal being the 32/68 conventionally annealed sample. Samples with 52/48 chemistry were indexed as cubic by peak selection, using the (100), (110), (111), (200), (210), (211), and (220)
peaks for cell refinement. For the rhombohedral samples very little change in the lattice parameter is observed with increasing heating rate.

Figure 3.3.7. XRD 2θ scans for various chemistries of acetate-based PZT with different heating rates.

Table 3.3.4. Lattice parameters for various chemistries of acetate-based PZT with different heating rates.

<table>
<thead>
<tr>
<th>Chemistry (Zr/Ti)</th>
<th>Heat treatment</th>
<th>c/a</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>32/68</td>
<td>Conv.</td>
<td>1.032</td>
<td>4.0065</td>
</tr>
<tr>
<td>32/68</td>
<td>RTA slow</td>
<td>1.027</td>
<td>4.0076</td>
</tr>
<tr>
<td>40/60</td>
<td>RTA slow</td>
<td>1.024</td>
<td>4.0184</td>
</tr>
<tr>
<td>40/60</td>
<td>RTA fast</td>
<td>1.020</td>
<td>4.0202</td>
</tr>
<tr>
<td>52/48</td>
<td>RTA slow</td>
<td>1.000</td>
<td>4.0674</td>
</tr>
<tr>
<td>52/48</td>
<td>RTA fast</td>
<td>1.000</td>
<td>4.0666</td>
</tr>
</tbody>
</table>
The presence of pyrochlore is detected from a peak at $2\theta \approx 29^\circ$ in the 40/60 sample annealed in the RTA using a slow heating rate. Although pyrochlore may not be evident in the XRD scans obtained, that is not to say that the films are pyrochlore-free since it often occurs at the surface, and not completely detected by $2\theta-\omega$ scan geometry used for these experiments.

### 3.3.4 Dielectric and Piezoelectric Response

The change in the dielectric constant as a function of Ti ratio for both acetate- and 2-MOE-based 40/60 and 52/48 are compared in Figure 3.3.8, presented along with the acetate-based 32/68 values. All values were obtained from an average capacitance for each film. The trend shows the dielectric constant to decrease as the Ti ratio increases, or, more likely, as the solution chemistry moves further away from the MPB. To obtain the dielectric constant, all that is needed is a top electrode and patterning to expose the bottom electrode. On the other hand, it is necessary to produce films on thin membranes to measure the piezoelectric coefficients, $e_{31}$ and $d_{31}$, which was challenging to obtain for the 32/68 chemistry since through-film cracking would often occur over the membranes. The film cracking was severe enough to short the capacitor and limit the property measurements obtained from such films. In contrast, 40/60 and 52/48 films were successfully deposited as crack free and subsequently used for bulge testing to measure $d_{31}$ and $e_{31}$ as shown in Figure 3.3.9 (a) and (b), respectively. For determination of $d_{31}$, an elastic modulus of the PZT was taken at 101 GPa, and the pressure used to test at was approximately 2 psi.
Figure 3.3.8. Change in dielectric constant with increasing Ti ratio for different sol-gel solvents.

Figure 3.3.9. Transverse piezoelectric coefficients, (a) $d_{31}$ and (b) $e_{31}$ as a function of Ti ratio for different solvents.
The highest values of $e_{31}$ and $d_{31}$ occur with the 52/48 acetate-based solution at $-12.0 \pm 1.7 \text{ C/m}^2$ and $-119.1 \pm 16.5 \text{ pC/N}$, respectively. This is an almost 20% and 30% increase in measured values of $e_{31}$ and $d_{31}$, respectively, over those for the 2-MOE-based system.

### 3.3.5 Film Stress

From static bulge testing, pressure deflection data were obtained for optimized processing of 40/60 and 52/48 acetate-based PZT films, i.e. comparing RTA (fast anneal) acetate with standard (conventional-furnace anneal) 2-MOE. The data are shown in Figure 3.3.10. Regardless of the solvent, 40/60 shows a more compliant film than the 52/48 chemistries.

It is important to distinguish the changes in the pressure-deflection curves as resulting from variations in the residual stress or from differences in the elastic modulus. To do this, measured elastic modulus values are used to model the residual stress, $\sigma_o$ from the following relationship in Equation (1) developed by Bonnotte et al [26]:

$$P(W_o) = \frac{c_1 \sigma_o t W_o}{a^2} + \frac{c_2 E_B t W_o^3}{a^4}$$

where $P$ is the pressure, $W_o$ is the maximum membrane deflection, $t$ is the membrane thickness, $a$ is half of the membrane side length, and $c_1$ and $c_2$ are two unitless constants that, for square membranes and an assumed Poisson’s ratio of 0.25, are 3.40 and 1.81, respectively. The biaxial modulus of the membrane, $E_B$, is a weighted average of all the layers in the film, or a composite film value, $E_{B,c}$ and determined using the following equation:

$$E_{B,c} = \frac{t_{Si}}{t_{total}} E_{Si} + \frac{t_{SiO_2}}{t_{total}} E_{SiO_2} + \frac{t_{Ti}}{t_{total}} E_{Ti} + \frac{t_{Pt}}{t_{total}} E_{Pt} + \frac{t_{PZT}}{t_{total}} E_{PZT} + \frac{t_{TiW}}{t_{total}} E_{TiW} + \frac{t_{Au}}{t_{total}} E_{Au}$$
The elastic modulus values for all the layers were assumed to be unchanging except for the PZT, which was measured using dynamic stiffness nanoindentation. The $E_{PZT}$ values were measured for 40/60 and 52/48 chemistry films. These results show the values to be very similar, indicating that the changes in the pressure-deflection curves are not due to changes in the elastic modulus of the films; rather, they are due to changes in residual stress.

Examining between the two solvent-routes for a given chemistry shows the acetate-based films to be comparable for 40/60, but slightly higher stress for 52/48. This is further illustrated in Table 3.3.5.

![Figure 3.3.10. Pressure-deflection curves for 40/60 and 52/48 chemistries of acetate- and 2-MOE-based PZT.](image)

**Table 3.3.5. Residual stress values for various chemistries and solvents.**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>2-MOE</th>
<th>Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry (Zr/Ti)</td>
<td>40/60</td>
<td>52/48</td>
</tr>
<tr>
<td>$\sigma_o$ (MPa)</td>
<td>66.9</td>
<td>93.4</td>
</tr>
</tbody>
</table>
3.3.6 Membrane generator performance

In order to provide a figure of merit for generator performance, dynamic bulge testing produces peak-peak output as a function of %membrane strain, plotted in Figure 3.3.11. Table 3.3.6 lists the average specific voltage for 40/60 and 52/48 acetate-based compared to 2-MOE based films. The data for the acetate-based films is an average of three samples of each, presented with the standard deviation in the table below. For just the acetate-based route alone, though the scatter is fairly large, the 40/60 chemistry appears to have a slightly lower specific voltage than that of the 52/48. Considering the results of the piezoelectric measurement, the increased voltage response with the rhombohedral film is to be expected. Comparing the specific voltages of different solvents for a given chemistry shows the acetate-based PZT to be slightly lower in the average value as Ti ratio is decreased. For the 2-MOE values, obtained from Olson, the difference is much larger [23]. These values were single measurements and have yet to be successfully reproduced, especially in the case of the high value for the 40/60 2-MOE chemistry. The discrepancy could be more a matter of structure than simply processing changes.
Figure 3.3.11. Specific voltage for 40/60 and 52/48 acetate-based PZT.

Table 3.3.6. Comparison of specific voltage and FOM for 2-MOE and acetate-based PZT with 40/60 and 52/48 chemistries. Acetate-based specific voltage values represent an average of three tests, shown with the standard deviation.

<table>
<thead>
<tr>
<th></th>
<th>2-MOE</th>
<th>Acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific voltage (V/ %ε·µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40/60</td>
<td>16.2</td>
<td>10.6±1.9</td>
</tr>
<tr>
<td>52/48</td>
<td>10.6</td>
<td>12.2±1.7</td>
</tr>
<tr>
<td>Muralt’s FOM</td>
<td>1.6</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>4.4</td>
</tr>
</tbody>
</table>
In addition to using specific voltage for a measure of the membrane generator performance, Muralt et al. have developed a figure of merit (FOM) for piezoelectric thin films in MEMS applications [27] that can also be applied for the P₃. Since both the power efficiency and the piezoelectric coefficient (proportional to the output force) need to be taken into consideration, the FOM goes as follows:

\[
FOM = \frac{(e_{31})^2}{\varepsilon_o \tan \delta}
\]

where \( e_{31} \) is the transverse piezoelectric coefficient, as discussed previously, \( \varepsilon_o \) is the relative permittivity, or dielectric constant, and \( \tan \delta \) is the dielectric loss tangent. Using the measured dielectric constants and piezoelectric coefficients, the FOM was calculated for 40/60 and 52/48 samples processed using both 2-MOE and acetate. A value of 0.03 was used for the dielectric loss tangent. The values, reported in Table 3.3.6, show that the acetate-based PZT has superior properties to the 2-MOE with the largest values present in the rhombohedral films.

3.4 SUMMARY AND CONCLUSIONS

Sol-gel-derived films of various chemistries were developed using different solvents to determine an adequate replacement for the 2-MOE-route used in the production of PZT films for the P₃ microengine. Using published sol-gel routes and various synthesis and deposition trials, a processing scheme has been developed for an acetate-based hybrid sol-gel route. This method not only eliminates the teratogenic and carcinogenic 2-MOE solvent, but also decreases some of the complexity in the solution synthesis. Compared to 2-MOE, the acetate-based system also improves the thermal budget, decreasing the annealing temperature by 50°C. In addition, by
incorporating an RTA (with fast ramping) for the crystallization of such films along with a 50% increase in the thickness per layer for the acetate-based system, the deposition time can be decreased, and thus, improving the processing efficiency for preparing 1-µm-thick PZT films.

From XRD, the crystal structures were confirmed for acetate-based films of various chemistries. Using cell refinement of identified peaks, it was observed that slower crystallization heating rates increases the tetragonality of the film. Measurements of the dielectric constant and the compliance of the films on thin Si-membranes show the acetate-based films to be comparable to 2-MOE films for a given chemistry. Maximum values of the piezoelectric coefficients, $e_{31}$ and $d_{31}$ were obtained for acetate-based 52/48 PZT films, showing a 20% and 30% increase, respectively, over those films prepared using 2-MOE.

Linking the PZT membrane compliance with the electrical properties the 40/60 chemistry has a lower compliance, but the dielectric and piezoelectric properties are considerably lower. On the other hand, for the less compliant 52/48, tremendous increases in piezoelectric and dielectric properties arise, with a gain in average specific voltage and piezoelectric FOM as well. Hence, a trade-off must be made between low stress and maximum output for an engine with a fixed pressure.
3.5 REFERENCES


CHAPTER FOUR
INFLUENCING PZT PROPERTIES AND STRUCTURE THROUGH NIOBIUM DOPING

4.1 INTRODUCTION

Doping can have a tremendous effect on the structure and properties of PZT films. Of the types of dopants added to the PZT system, two categories arise, donor-type and acceptor-type, depending on the effect the dopant has on the oxygen vacancies in the perovskite crystal (ABO₃). Acceptor-type, or “hard” dopants for PZT such as Fe³⁺, Al³⁺, Mn⁴⁺, and Mg²⁺ create charge deficient cations, while donor-type, or “soft” dopants include La³⁺, Nd³⁺, Ta⁵⁺, and Nb⁵⁺ add an excess charge cation. Both types can substitute onto the A-site or B-site of the perovskite cell.

Donor dopants are known to improve the elastic compliance, electrical resistivity, and dielectric constant [1]. Much of the research into the donor-type Nb-doped PZT thin films has focused on the ferroelectric properties and the hysteresis characteristics [2-12]. In general, the Nb additions produce polarization hysteresis loops with low coercive fields and large remanent polarizations.

More relevant to the P³ engine is the reported changes Nb induces in the dielectric properties and piezoelectric response of PZT thin films. Also changes in the film stress are expected to have a considerable impact on the performance of PZT-based membrane generator. Regarding the literature of dielectric films, results are not consistent for PZT films, especially when obtained through different processing methods. Haccart et al have shown that small additions of Nb (up to 2 at%) will increase the dielectric constant in sputtered PZT films, but further additions will cause a decrease [13]. Durruthy et al have
confirmed similar effects for sintered films [14]. Conversely, others report a different
effect for sol-gel-derived films [9,10]. Using a 2-MOE-based route, Klissurska et al
observed a dependence of the dielectric constant with the annealing temperature, showing
for films annealed at 650°C the dielectric constant remains constant with increased Nb
doping. On the other hand, films annealed at 600°C showed a marked decrease in
dielectric constant with Nb doping [9]. For diol-based sol-gel films, a similar decrease in
the in the dielectric constant with increased Nb doping was observed [10].

Although less work is published in the area of Nb effects on piezoelectric response,
the data that is reported is much more consistent. Jaffe et al. report 60% increase in $d_{33}$
and an 80% increase in $-d_{31}$ by doping 52/48 PZT with 2 mol% Nb [1]. This corresponds
well with other work finding that a general increase in either $d_{33}$, $-d_{31}$, or $-e_{31}$ occurs
with small (1-2%) Nb additions [7,12-14].

Worthwhile to note is the change in the film stress from initially tensile when
undoped to low tensile stresses, or even to low compressive stresses with small additions
of Nb for sol-gel derived PZT films [15]. Most of these property changes result from
processing variations on the structure. Linking these property changes to the chemistry
modifications is not complete without an analysis of the structure and the microstructure.
Changes in the structure, including the nucleation behavior of perovskite and lead-
deficient pyrochlore can have tremendous impact on the electrical and mechanical film
behavior. Small amounts of pyrochlore can be enough to degrade properties and cause
especially large changes in the dielectric character [16]. Typically, it is observed as a
fine grain phase in a matrix of larger perovskite grains. Although using XRD can help to
identify phases in thin films, the presence of pyrochlore may not be reflected in the data,
therefore requiring the need for examining the microstructure either by AFM, SEM, or TEM. Much of the inconsistency on the reported property values of Nb-doped PZT thin films can be attributed to the occurrence of surface pyrochlore, which has been suggested to act as a separate capacitive layer creating, effectively, two capacitors in series [9]. Hence, it is necessary to investigate the surface characteristics of the films along with the bulk, or transverse section, to properly characterize the microstructure and grain morphology.

Since the purpose of this experimental research is two-fold, 1) to improve the piezoelectric response, and, ideally, the overall performance of the piezoelectric material within the P3 engine, and 2) to understand the influence of Nb on the processing-structure-properties relationship of PZT, the effects of Nb doping were investigated on two different Zr/Ti ratios, 52/48 and 32/68. The former ratio was chosen based on the results of a previous study shown in Figure 3.3.9 that determined the piezoelectric response was higher with a Zr/Ti ratio of 52/48 compared to that of a 40/60 ratio (-12.0 C/m² compared to –7.7 C/m², respectively).

In order to systematically determine the structure and property changes that result from introducing Nb, a reliable processing route is required that will allow for easy incorporation of dopants. The benefits of using solution-based deposition, discussed in Chapter 2, offer good control over stoichiometry and film thickness, low processing temperatures, and the ease of incorporating Nb. Therefore, it is the method used in this research.
4.2 EXPERIMENTAL PROCEDURE

4.2.1 Solution Development

Nb-doped- and undoped-PZT films (32/68 and 52/48) were prepared from a hybrid acetate-based solution route adapted from Lee and Lee [11] and pictured in Figure 4.2.1. The solution was made using the following precursors: zirconium (IV) n-propoxide solution in 70wt% 1-propanol (Sigma-Aldrich), titanium (IV) isopropoxide (99.999%, Sigma-Aldrich), and lead (III) acetate tryhydrate (99+%, Sigma-Aldrich). Glacial acetic acid (HOAc) and n-propanol were used as the solvents. Niobium (0, 0.5, 1.1, 2.8, 5.5, and 7.8 mol%) was added to the solution from a stock solution made from niobium (V) ethoxide (99.95%, Sigma-Aldrich), which is extremely unstable in air, and 2,4-pentanedionate (or, acetylacetonate, 99%, Avocado). Once made, the niobium stock solution is relatively stable for up to 3 months. More complete details of the niobium-modified acetate-based hybrid synthesis route are provided in Chapter 3 and in the Appendix B.
Depending on the defect compensation mechanism, the amount of lead can vary slightly. In all cases, excess lead (10-25%) was added to account for the volatilization during heat treatments. As explored by Klissurska et al [5,9], two charge compensation scenarios can occur. The first assumes that the incorporation of Nb$^{5+}$ occurs on the B-sites, and the charge compensation for the extra positive charges occurs through creation of A-site vacancies. As a consequence, the amount of Pb is modified for this through the following stoichiometry:
\[ \text{Pb}_{1.1-\chi/2}(\text{Zr}_y\text{Ti}_{1-y})_{1-\chi}\text{Nb}_\chi\text{O}_3 \]

The other case assumes that the Nb is incorporated through the creation on B-site vacancies. Thus, making no corrections, and the amount of Pb will increase with the amount of Nb added as given by the stoichiometry:

\[ \text{Pb}_{1.1}(\text{Zr}_y\text{Ti}_{1-y})_{1-\chi}\text{Nb}_\chi\text{O}_3 \] [6, 9].

For all the chemistries made in this experiment, the latter stoichiometry was used. Barlingay and Dey concluded that donors are compensated by B-site vacancy (V_{Ti}^{\text{'''}}), likely due to the increased activity of lead [6].

Niobium-doped and undoped PZT thin films were prepared on Pt/Ti/SiO_2/Si substrates after a heat treatment of 650ºC for 10 minutes in a conventional furnace. For the P^3 engine, it is desired that the films be tested and characterized on thin (2.3\,\mu m) Si membranes and undergo bulk micromachining processing. (See Appendix A for further substrate processing details.) Films were prepared through a multiple-layer spin-on technique as shown in Figure 4.2.1 above using 0.4M precursor solutions. The solutions were filtered through a 0.2-\mu m filter onto the substrates and spun at 3000rpm for 30 seconds using a commercial spin-coater. Two different pyrolysis conditions were used, 300ºC for 3 minutes and 350ºC for 1 minute.

### 4.2.2 Heat Treatment

Employing a multilayer process whereby after several spin-coated and pyrolyzed layers, in this case three, the films were annealed, or crystallized, in either a conventional furnace with a vertical loading system or in a rapid thermal annealer, or RTA (Total Fab Solutions Heatpulse 610) using a SiC susceptor. In addition to studying the effects of
niobium, processing parameters such as heating rates and hold times were investigated.

The various conditions used are listed in Table 4.2.1.

<table>
<thead>
<tr>
<th>Designation</th>
<th>Temperature (°C)</th>
<th>Time</th>
<th>Furnace type</th>
<th>Heating rate (°C/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>conv</td>
<td>650</td>
<td>10 min</td>
<td>conventional</td>
<td>3</td>
</tr>
<tr>
<td>conv-2 min</td>
<td>650</td>
<td>2 min - last anneal only</td>
<td>conventional</td>
<td>3</td>
</tr>
<tr>
<td>RTA-slow</td>
<td>650</td>
<td>30 s</td>
<td>RTA</td>
<td>6</td>
</tr>
<tr>
<td>RTA-fast</td>
<td>650</td>
<td>30 s</td>
<td>RTA</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 4.2.1. Processing variations for PNZT films.

4.2.3 Testing and Characterization

Film properties were measured using a variety of tools. Field emission scanning electron microscopy (LEO 982 FESEM) was used to obtain secondary electron (SE) images for investigating the grain size and morphology of films in cross-section and at a 15° tilt. Atomic force microscopy (AFM, Park Autoprobe CP) in constant-force mode was used to image the surface of the films in plan-view. The Heyn intercept method was used to determine the grain size from the AFM images. For phase analysis and unit cell parameters, a Philips X’pert MPD system with CuKα radiation was used to obtain 2θ-ω scans. Cell refinement of different diffraction peaks (as described in Chapter 2) was used to determine the lattice parameters. Film thickness was measured using profilometry (SPN Technologies PHD profilometer).

For electrical measurements and membrane characterization, Au top electrodes were sputtered onto the films according to the processing detailed in Appendix A. Capacitance was measured using an impedance analyzer (Agilent 9294A Precision...
Impedance Analyzer) at 300 Hz, and used to calculate the dielectric constant. The
piezoelectric properties (\(d_{31}\) and \(e_{31}\)) were measured using a rectangular membrane
method as described in Chapter 2. The compliance of the films was measured with static
bulge testing to obtain pressure-deflection curves. Using nanoindentation (Hysitron
Triboscope) methods established by Oliver and Pharr [17], the elastic modulus of films
was determined. Residual stress was modeled from pressure-deflection curves using the
measured elastic modulus according to relationship developed by Bonnotte et al. [18] and
discussed in Chapter 3. Dynamic bulge testing was employed for a relative comparison
of the overall performance of the membrane generators in a figure of merit called specific
voltage. Details of the bulge testing are available in Chapter 2. Since there are often
some slight variations that occur across the wafers, random multiple (2-3) membranes
were tested.

4.3 RESULTS AND DISCUSSION

4.3.1 Structure

Employing the deposition method for 0.4M precursor solution, the total film
thickness was measured ~1.1 µm (for 9 layers, or 0.12 µm/layer). Two different Zr/Ti
ratios were studied, the tetragonal 32/68 and the MBP chemistry 52/48. Plan-view
images (such as AFM) are a sufficient means of obtaining grain size measurements, but
this should be confirmed with cross-sectional views to be certain that the grains on the
surface are representative of those in the bulk of the film. Figure 4.3.1 shows 15º tilted
SE images of 32/68 PNZT where Nb ranged from 0-7.8% to illustrate the discrepancies
that can arise due to surface effects. For the films doped \(\geq 2.8\) %Nb, the grains are
representative, but for those doped <2.8%Nb, the tilted images show that the surface grains vary in size from those in the bulk. For example, in the undoped 32/68 sample, the grain size on the surface appears to be comparable to that of the 5.5%Nb-doped sample, but when examining the cross-sections, the grain morphologies range from columnar to equiaxed, respectively.
Figure 4.3.1. SE images (tilted 15°) of 32/68 PZT films Nb-doped with (a) 0, (b) 1.1, (c) 2.8, (d) 5.5, and (e) 7.8 mol%. All films were annealed in an RTA (slow ramp). The scale bar in (a) applies to all the micrographs.

Keeping in mind the differences in grain structure, the results of grain size (as measured from AFM images pictured in Figure 4.3.2) as a function of Nb concentration and heat treatment is presented in Figure 4.3.3. Speaking only with regard to the surface grain character of these films, a pronounced increase in grain size occurs for those films crystallized in the RTA. Only a slight increase is observed for films crystallized for 10 minutes in a conventional furnace. Almost no change is seen for the films crystallized for 2 minutes (on the last crystallization only) in a conventional furnace, but this can be expected, as the films are still somewhat amorphous on the top layer as visible, for example, in Figure 4.3.4 j. A complete illustration of the cross-sections of films heat-treated at 650°C using both RTA (slow ramp) and conventional furnace (2 and 10 min) is given in Figure 4.3.4.
Figure 4.3.2. AFM images of 32/68 PNZT films doped with Nb (a) undoped, conventional, 10 min., (b) undoped, conventional, 2 min., (c) 2.8%, conventional, 2 min., (d) 5.5%, conventional, 10 min., (e) 5.5%, conventional, 2 min., (f) 2.8%, RTA, slow ramp, (g) 5.5%, RTA, slow ramp, (h) 7.8%, RTA, slow ramp.

Figure 4.3.3. Surface grain size as a function of Nb concentration.

Much of the structural characterization discrepancy referred to previously surrounds the effect Nb has on the grain size. Some authors report a decrease in grain
size with increasing niobium concentrations [10,11,14,19]. Kurchina and Milne observed
the surface microstructure of Nb-modified films finding that for low Nb concentrations
(2%) the grain size decreased, while for higher Nb levels, the grains were harder to
resolve likely due to the fine-grained pyrochlore grains concentrated in the surface [10].
Although others have reported the opposite effect, an increase in grain size with
increasing Nb concentration, most conclude that the Nb does influence the pyrochlore
stability, potentially inhibiting perovskite nucleation [8,9].

From examining the cross-sectional SE images of doped 32/68 PZT films, the
greater the Nb concentration, the less columnar the grains become as seen in Figure 4.3.4.
For a given heat treatment the change in grain morphology can be attributed to inhibiting
columnar grain growth via the stabilization of pyrochlore or slowing the heterogeneous
nucleation of perovskite at the Pt/PZT and PZT/PZT interfaces. It is also important to
note that the cross-section samples were prepared from fracturing and some of the
differences in the images may be artifacts of the fracture method rather than arising from
intrinsic differences between samples.
Figure 4.3.4. Cross-sectional SE images of $x/32/68$ PNZT with various heat treatments; (a) $x=0$, conventional furnace, 2 min., (b) $x=0$, conventional furnace, 10 min., (c) $x=0$, RTA, (d) $x=1.1$, conventional, 2 min., (e) $x=1.1$, conventional, 10 min., (f) $x=1.1$, RTA, (g) $x=2.8$, conventional, 2 min., (h) $x=2.8$, conventional, 10 min., (i) $x=2.8$, RTA, (j) $x=5.5$, conventional, 2 min., (k) $x=5.5$, conventional, 10 min., (l) $x=5.5$, RTA, (m) $x=7.8$, conventional, 2 min., (n) $x=7.8$, conventional, 10 min., (o) $x=7.8$, RTA. Scale bar for (a) applies to all films annealed in the conventional furnace for 2 min. All others have the same scale bar as (b) and (c).
Figure 4.3.5 gives the results for the XRD 20-ω scans for 32/68, with a notable change in the tetragonality (c/a) as a function of the Nb concentration as given in Table 4.3.1. The most tetragonal films are those without any dopant for the conventional furnace-processed film, although the undoped RTA-treated sample is relatively high for the RTA set. For those samples annealed in the RTA, just a small amount of Nb (1.1-2.8%) increases the tetragonality. For samples crystallized for only 2 minutes on the last heat treatment, a dramatic change occurs between undoped versus 5.5% Nb-doped samples in the form of extra peaks arising at 20 ≈29, 34, 50 and 59.5° as illustrated in Figure 4.3.6. These extra peaks may indicate transient pyrochlore phase (corresponding to (222), (400), (440) and (622) peaks identified by JCPDS card #40-0828, Pb₂Nb₂O₇) that has yet to transform upon further heat treatment. From this, the conclusion is made that the 5.5% sample annealed in the RTA shown in Figure 4.3.5 is fully crystallized, i.e. pyrochlore transformed to perovskite, evident by the lack of extra peaks. This is confirmed from results of Griswold et al that used glancing angle XRD to show that PZT transformation to perovskite needs a minimum ramp rate of 50°C/s to complete the transformation [20].
Figure 4.3.5. XRD 2θ-ω scans for 32/68 PNZT with Nb=0-7.8% for RTA-treated films and Nb=0 and 5.5% for conventional furnace-treated films.

Table 4.3.1. Lattice parameters based on cell refinement for tetragonal PNZT (32/68) films with Nb=0-7.8 mol% and heat-treated in conventional furnace and RTA using slow ramp.

<table>
<thead>
<tr>
<th>Nb (mol%)</th>
<th>Heat treatment</th>
<th>c/a</th>
<th>a (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>conv</td>
<td>1.032</td>
<td>4.0065</td>
<td>4.1365</td>
</tr>
<tr>
<td>5.5</td>
<td>conv</td>
<td>1.020</td>
<td>4.0155</td>
<td>4.0973</td>
</tr>
<tr>
<td>0</td>
<td>RTA</td>
<td>1.027</td>
<td>4.0076</td>
<td>4.1169</td>
</tr>
<tr>
<td>1.1</td>
<td>RTA</td>
<td>1.028</td>
<td>4.0085</td>
<td>4.1227</td>
</tr>
<tr>
<td>2.8</td>
<td>RTA</td>
<td>1.028</td>
<td>4.0080</td>
<td>4.1215</td>
</tr>
<tr>
<td>5.5</td>
<td>RTA</td>
<td>1.020</td>
<td>4.0138</td>
<td>4.0924</td>
</tr>
<tr>
<td>7.8</td>
<td>RTA</td>
<td>1.021</td>
<td>4.0109</td>
<td>4.0949</td>
</tr>
</tbody>
</table>
Figure 4.3.6. XRD for undoped and 5.5% Nb-doped 32/68 PZT crystallized in conventional furnace for 2 min for the last three layers. Extra peaks emerge for doped sample.

For 52/48 PZT, the structure is rhombohedral evident by the absence of peak splitting in Figure 4.3.7 (a). Similar peaks to those in the 2 minute-annealed 5.5/32/68 sample from Figure 4.3.6 arise for increased Nb concentrations in the 52/48 system, as displayed in a closer view in Figure 4.3.7 (b). This could indicate an increased stability of transient pyrochlore, possibly remedied by longer crystallization hold times as the amount of Nb is increased. Unlike the 32/68 films, which were annealed using the slow ramp in the RTA, the 52/48 samples were crystallized according to the fast ramp. Table 4.3.2 lists the lattice parameter for 52/48 doped samples, showing very little change for increasing Nb concentrations. All cell refinement, i.e. lattice parameters, for the rhombohedral films were indexed according to a cubic structure. Further characterization of the rhombohedral cell distortion could be made from measuring the angle, $\alpha$. 

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Figure 4.3.7. XRD for undoped 52/48 at two different heating rates and doped 52/48 using fast ramp for (a) full 2θ-ω scans and (b) close up of region where peak at 2θ≈29° and 34° becomes more defined as Nb increases.
Table 4.3.2. Lattice parameters based on cell refinement for rhombohedral (c/a =1) PNZT (52/48) films with Nb=0-2.8mol% and RTA heat-treated in using fast and slow ramps.

<table>
<thead>
<tr>
<th>Nb (mol%)</th>
<th>Heat treatment</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>RTA slow</td>
<td>4.0674</td>
</tr>
<tr>
<td>0</td>
<td>RTA fast</td>
<td>4.0666</td>
</tr>
<tr>
<td>0.5</td>
<td>RTA fast</td>
<td>4.0665</td>
</tr>
<tr>
<td>1.1</td>
<td>RTA fast</td>
<td>4.0655</td>
</tr>
<tr>
<td>2.8</td>
<td>RTA fast</td>
<td>4.0600</td>
</tr>
</tbody>
</table>

Figure 4.3.8. Cross-sectional SE images of 52/48 PNZT films doped with (a) 0%Nb, (b) 0.5%Nb, (c) 1.1%Nb, and (d) 2.8%Nb. All films were heat treated in RTA using fast ramp. The scale bar in (a) applies to all images.
4.3.2 Dielectric and Piezoelectric Response

Measured capacitance and thickness values were used to calculate the relative permittivity, or dielectric constant. Results for various Nb concentrations of both 32/68 and 52/48 chemistries are plotted in Figure 4.3.9, showing an increase for small Nb dopant levels, i.e. 0.5 and 1.1 mol% for 52/48 and 32/68, respectively.

For piezoelectric coefficient measurements, more attention was given to the MPB composition, which shows above a 50% increase in the value of $e_{31}$ over the tetragonal, 32/68 chemistry. (See Figure 3.3.9.) For calculating the value of $d_{31}$, the elastic modulus of the PZT used was 101 GPa. Much like the data for dielectric constant, a similar rise was observed (Figure 4.3.10) for the piezoelectric coefficients, showing the maximum $e_{31}$ value at 1.1% (for 52/48 and 32/68, with $-12.2\pm0.8 \text{ pC/N}$ and $-1.90\pm0.03 \text{ pC/N}$, respectively. It appears that the maximum $d_{31}$ is obtained for the undoped 52/48 samples ($-119\pm16.5 \text{ C/m}^2$), but doping with 1.1% does not change much ($-111.6\pm6.9 \text{ C/m}^2$). The scatter in the data arises from testing of multiple membranes taken from different areas of the wafer. Based on reports that identify 1-2% Nb as producing the highest piezoelectric coefficients, the possibility for further increasing the piezoelectric coefficients through doping can be done by adding Nb additions from 1.2-2% [7,12-14].
Figure 4.3.9. Dielectric constant as a function of Nb concentration for 32/68 and 52/48 PZT films.

Figure 4.3.10. Piezoelectric coefficients (a) $d_{31}$ and (b) $e_{31}$ coefficients for Nb-doped 32/68 and 52/48 films.

### 4.3.3 Film Stress

Film stress is important in an application like the P³ engine where maximizing the strain for a given pressure can increase the voltage output. Pressure-deflection data for Nb-doped 32/68 and 52/48 is reported in Figure 4.3.11 (a) and (b), respectively. Elastic
modulus was determined for the complete set of doped 32/68 and 52/48 film samples. By applying the model developed by Bonnotte et al. [18], the residual stress can be determined as listed in Table 4.3.3. For both the tertagonal and rhombohedral films, a decrease in the residual stress is seen with Nb additions of 2.8 mol%. Figure 4.3.12 is a comparison of the compliance between two membranes tested using the same batch of PNZT (5.5/32/68), but deposited at different times to demonstrate the effect of solution aging on the film stress. For the sample aged 25 days, there is an observed increase in compliance.
Figure 4.3.11. Pressure deflection results for Nb-doped (a) 32/68 and (b) 52/48 PZT films.

Table 4.3.3. Average residual stress values for composite films based on pressure-deflection and PZT elastic modulus of 70 GPa.

<table>
<thead>
<tr>
<th>Zr/Ti ratio</th>
<th>Nb (mol %)</th>
<th>Average $\sigma_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>52/48</td>
<td>0</td>
<td>111.2</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>93.7</td>
</tr>
<tr>
<td></td>
<td>1.1</td>
<td>88.7</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>58.4</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>106.85</td>
</tr>
<tr>
<td>32/68</td>
<td>1.1</td>
<td>111.2</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>93.7</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>88.7</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>58.4</td>
</tr>
<tr>
<td></td>
<td>106.85</td>
<td>106.85</td>
</tr>
</tbody>
</table>
Figure 4.3.12. Aging study of 5.5%Nb-doped PZT, pyrolyzed at 350°C/1 min and crystallized using RTA-slow ramp for 30 s hold time.

4.3.4 Membrane Generator Performance

Comparing the dynamic bulge testing results for 2.8 and 5.5 mol% Nb-doped 32/68 in Figure 4.3.13 (a), specific voltage decreases for the higher doping level. Furthermore, there is a similar aging effect in the data shown in Figure 4.3.13 (b) as observed for the pressure-deflection curves in the 5.5% PNZT film. The specific voltage is greater for those films deposited with solution that has undergone little aging. Figure 4.3.14 shows the specific voltage for doped samples (0-2.8% Nb) of 52/48. Though a change in the output of PZT on membranes is expected for donor doping from other observed property changes, only slight changes are recorded for the rhombohedral films, presented in Table 4.3.4.
Figure 4.3.13. (a) Specific voltage for 32/68 doped films and (b) effect of aging PNZT solution on 5.5% PNZT for 1 day or 2 mos.

Figure 4.3.14. Specific voltage for 52/48 PNZT with Nb=0-2.8 mol%.
Table 4.3.4. Comparison of specific voltage for various Nb-doped PZT chemistries.

<table>
<thead>
<tr>
<th>Chemistry (Nb/Zr/Ti)</th>
<th>2.8/32/68</th>
<th>5.5/32/68</th>
<th>5.5/32/68 aged</th>
<th>0/52/48</th>
<th>0.5/52/48</th>
<th>1.1/52/48</th>
<th>2.8/52/48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific voltage (V/%ε·µm)</td>
<td>12.2</td>
<td>7.6±0.4</td>
<td>5.4±0.7</td>
<td>12.2±1.7</td>
<td>12.2±1.6</td>
<td>12.4±1.1</td>
<td>11.6±&lt;0.01</td>
</tr>
</tbody>
</table>

Additionally, as discussed in Chapter 3, another means to assess the performance of the membrane generator exists. Developed by Muralt for piezoelectric thin films in MEMS devices [21], the figure of merit \((FOM)\) considers both the transverse strain-based piezoelectric coefficient and the dielectric constant. Since the \(e_{31}\) values for the 32/68 doped films are significantly lower than those for the 52/48, only the latter values are listed in Table 4.3.5. Much like the observed change in piezoelectric coefficients with dopant concentration, the \(FOM\) ranges from a low value for 2.8% Nb to a high at 1.1% Nb. From this it can be determined that there is a very tight range of Nb additions (at low concentrations) that will optimize the piezoelectric response in the P³ micro engine.

Table 4.2.5. Figure of merit for 52/48 PZT films with varying amounts of dopants.

<table>
<thead>
<tr>
<th>Amount of Nb (mol %)</th>
<th>0</th>
<th>0.5</th>
<th>1.1</th>
<th>2.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muralt’s FOM</td>
<td>4.4</td>
<td>3.3</td>
<td>4.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>
4.4 SUMMARY AND CONCLUSIONS

Sol-gel derived PZT films of two chemistries, 32/68 and 52/48, were successfully doped with varying amounts of Nb (0-7.8%). Property changes occur in the dielectric character, the piezoelectric response, the specific voltage, and the film stress as Nb content changes. The best electrical properties were observed for the MPB chemistry (52/48), which was anticipated from the literature [1]. However, donor doping with 1.1% Nb was shown to only slightly increase the $e_{31}$ from the undoped 52/48 by 1.6%.

From a structural perspective, Nb appears to affect the grain morphology of PZT films, decreasing columnar growth indicating a decrease in the perovskite nucleation with increasing Nb. Although pyrochlore was not explicitly identified in micrographs or XRD data of fully annealed 32/68, the presence of a different surface structure especially in the case of Nb <1.1% indicates some surface reorientation or other interaction with the atmosphere during heat treatment. Crystallization hold times are shown to be important in the transformation of transient pyrochlore, particularly for conventional furnace annealing. Using the RTA (with a slow heating rate) for 32/68 films with variable Nb concentration offers fully crystallized, single-phase films. On the other hand, using the faster heating rate (while maintaining consistent hold times) in conjunction with 52/48 donor-doped films produced films with increasing pyrochlore with Nb concentration. This likely confirms the role of Nb as a pyrochlore stabilizer.

Correlating the properties to the structure in order to determine what type of structure gives the best properties, it has been observed that various properties scale differently. For instance, in the 32/68 samples the most compliant film was observed for 2.8% Nb-doping, which possessed a more equiaxed grain structure. This film also had
the highest specific voltage and only slightly lower piezoelectric coefficients. On the other hand 2.8/32/68 had by far, the lowest dielectric constant. To say that columnar structures lead to the best overall properties is a bit of a misnomer. Columnar grains, which form due to heterogeneous nucleation at the interfaces, have been shown to exhibit better electrical fatigue and polarization than equiaxed grains [22, 23]. The overall contribution of grain structure to the performance of the P³ engine may be more convoluted than originally thought. Variations in electrical properties are also suggested to be linked to preferred orientation in thin films, signifying different stress levels in the films that together with changes in the relative alignment of the polar axes could help explain differences not easily resolved or explained using the microstructural analysis techniques applied in this research [24].
4.5 REFERENCES


CHAPTER FIVE

CONCLUSION

5.1 SOLUTION DEPOSITION

Through the work presented it has been shown that an alternative route to preparing PZT films for the P³ microengine can be accomplished without compromise to the properties. Implementing an acetate-based method that uses acetic acid and n-propanol solvents instead of 2-MOE is successful in producing comparable dielectric properties and pressure-deflection characteristics. In the case of piezoelectric coefficients, e₃₁ and d₃₁, the properties are improved. Time to process is significantly quicker and easier through the following changes:

- Synthesis of the solution is less complicated and takes less time,
- Deposition of acetate-based PZT produces 50% thicker layers, decreasing the time it takes to deposit a multilayer film, and
- Crystallization using the RTA streamlines the process, decreasing the time needed for heat treatments.

The process is also safer through eliminating the use of 2-MOE, replacing it with a non-toxic solvent like acetic acid. The metal precursors used remain the same. Another supplement to the acetic acid-based route is the improvement in the thermal budget by heat treating at 50°C lower temperature than needed with 2-MOE.
5.2 STRUCTURE AND PROPERTIES

From investigating the structural changes that occur from processing variations (solution synthesis, chemistry, dopant additions, and crystallization parameters, like heating rates and hold times), preliminary correlations can be made between the structure and the properties. Using this information a new generation of tailoring piezoelectric materials for devices can be gained whereby the properties are achieved through adjusting the structure.

If comparing only the structure with the processing, vital information about the crystallization development is missing. For instance, by changing the chemistry of the precursor solution from 40/60 (tetragonal) to 52/48 (rhombohedral) an increase of over 50% is observed for both transverse piezoelectric coefficients, $e_{31}$ and $d_{31}$. On the other hand, an increase in the film stress is observed with the 52/48. Simply from the processing-structure information, a trade-off appears to exist between high piezoelectric response and increased compliance.

By doping with niobium, a change in the properties was invoked via a change in the structure. With increased amounts of niobium, the grain morphology changed from columnar to equiaxed, allowing a comparison between the enhanced properties gained with doping and accompanying microstructural changes. What was observed was little proof that columnar grains lead to best overall properties. For the dielectric effect, a relatively high value was obtained from a structure with mostly columnar grains (1.1/32/68). As the film was doped further (2.8%Nb), the grains grew larger and more equiaxed and the dielectric constant dropped. Interestingly, the dielectric constant was not highest for the undoped film that possessed the greatest qualitative degree of
columnar grains. Rather, the highest overall value for the 32/68 chemistry was observed for the heaviest doped (5.5% Nb) and, hence, most equiaxed film. From this, it becomes apparent that there are some further structural changes occurring that convolute the structure-property relationship.

Comparing some of the other property changes with the structure it appears that a complete columnar structure is not needed to optimize the piezoelectric response and the film stress. Considering the case for the 32/68 chemistry again, the most compliant film (with 2.8 mol% Nb added) possesses a mostly equiaxed grain structure, but this also produces lower $e_{31}$ and $d_{31}$ values. The higher $e_{31}$ and $d_{31}$ values are produced using films that show less compliance and more columnar grains. Therefore, a compromise must be struck between optimizing for piezoelectric properties and film stress. From this research, the potential to improve the output as well as decrease the residual stress through the addition of Nb does exist, ultimately leading to enhanced performance of the P³ micro engine.
APPENDIX A

STANDARD FABRICATION PROTOCOL FOR PRODUCTION OF MEMBRANE GENERATORS

- High temperature oxidation (wet) at 1050°C

- Oxide etch in 10:1 BOE

- Boron diffusion at 800°C for ~3.6 hrs

- Low temperature (sacrificial) oxidation (wet) at 850°C

- Oxide etch in 10:1 BOE

- Low temperature oxidation (wet) at 850°C

- Pattern oxide using positive photolithography and etch in 10:1 BOE

- Etch Si in EDP for ~6 hrs

Si (100)

SiO₂

oxide etch

boron doping

oxide etch

oxide etch

oxide etch
Pt/Ti bottom electrode deposition (DC magnetron sputtering)

Pre-anneal Pt (650°C for 10 min) and PZT deposition via sol-gel

Au/TiW top electrode deposition (DC magnetron sputtering)

Pattern top electrode using positive photolithography and TFA Au etch and H₂O₂; pattern PZT and etch to expose bottom electrode
APPENDIX B.1
CORRECTION TO ACETATE-BASED HYBRID MOD CALCULATIONS

For 50mL of 0.865M solution:

Amount of titanium(IV)isopropoxide (TIP): 4.43g / 284.26 g/mol = 0.01558 mols Ti

Amount of zirconium(IV)2,4-pentanedionate: 3.40g / 487.66 g/mol = 0.006972 mols Zr*

Amount of Lead(III)Acetate trihydrate: 10.83g / 379.33 g/mol = 0.02855 mols Pb

Mol ratio of Ti: 0.01558 / (0.01558 + 0.006982) = 0.69

Mol ratio of Zr: 0.006982 / (0.01558 + 0.006982) = 0.31

Mol ratio of Pb: 0.02855 / (0.01558 + 0.006982) = 1.27

Thus, the actual chemistry of PZT was: \( \text{Pb}_{1.27}(\text{Zr}_{0.31}\text{Ti}_{0.69})\text{O}_3 \)

*In initial calculations instead of using the formula weight for Zr(AcAc) of 487.66 g/mol, the formula weight of Zr(n-OPr)$_4$ of 327.58 was used.
APPENDIX B.2
ACETATE-BASED PZT AND PNZT SYNTHESIS PROCEDURE

For 50-ml batch 0.4M solution:

Notes: Use a clean pipett for all liquid additions. Properly dispose of the pipett when finished.
Refer to Table 3.3.3 for amounts of precursors to add depending on desired chemistry (i.e. 32/68, 40/60, 52/48). If niobium is to be added, it is highly recommended that the stock solution be made at least one day in advance. The procedure for making the Nb stock solution is given below.

1. Turn on hot plate with a thermometer in the oil bath to ~92°C.
2. While the oil is heating, clean a 100-ml jar with a screw cap and place in oven to dehydrate. Considering that the precursors are moisture sensitive, it is very important that the glassware be clean and dry before making the solution.
3. Once the oil bath temperature has reached the correct temperature (about 2 hours), place the jar with screw cap and a magnetic stir bar into the load lock of the glove box.
4. Evacuate the load lock to 10mmHg and backfill with N₂ three times.
5. Using the gloves on the box, open the internal load lock door and place the jar, cap, and stir bar inside the glove box. Close the load lock door.
6. With the uncapped jar (with magnetic stir bar inside) placed on the digital scale, zero it and weight out the required amount (see Table 3.3.3) of zirconium (IV) n-propoxide solution.
7. Add the required amount of titanium (IV) isopropoxide (see Table 3.3.3).
8. Add 5ml HOAc (5.24g)
9. Add 5ml 1-propanol (4.02g)
10. Using the metal scoop, add required amount of lead (II) acetate trihydrate (see Table 3.3.3).

11. Close the cap tightly and place jar in load lock.

12. Remove jar from load lock and secure bottle over oil bath using rubber-coated clamps. Once in place, raise oil bath above the level of the liquid in the jar, noting the temperature, using continuous stirring.

13. After approximately 30 minutes (the lead should dissolve during the first 5-10 minutes) physically lower the oil bath and adjust the temperature to 60°C. Allow the solution in the jar to cool until the bath is at 60°C (~90 minutes).

14. With oil bath temperature at 60°C, wipe the excess oil off the outside of the jar and place back into the load lock and repeat steps 4-5.

15. Uncap the jar and place on the digital scale.

16. If niobium is to be added, measure of the correct amount of stock solution and pipet into the jar.

17. Add 10ml HOAc (10.49g).

18. Add 10ml 1-propanol (8.04g).

19. Replace the cap, repeating steps 11-12.

20. Allow the solution to stir at 60°C for 12-24 hours. This step ensures complete mixing.

Steps for making Niobium stock solution:

Note: Similar to the other metal precursors, the niobium ethoxide is extremely unstable in moisture, so care must be taken to avoid contact with air or moisture. Once the stock solution is complete, it is relatively stable in air, but storage in the glove box is recommended. The solution
will be a bright orange-red color and will last ~2-3 months. New solution should be made when
the old solution begins to lighten in color and thicken.

1. Turn hot plate with a thermometer in the oil bath to ~70°C.

2. Once the oil bath temperature has reached the correct temperature (about 2 hours), place
   50ml-single-necked flask, glass stopper, and a magnetic stir bar into the load lock of the
glove box.

3. Evacuate the load lock to 10mmHg and backfill with N₂ three times.

4. Using the gloves on the box, open the internal load lock door and place the flask, stopper,
   and stir bar inside the glove box. Close the load lock door.

5. Place magnetic bar inside flask and set on cork stand on the digital scale.

6. Add 5g Nb(OEt)₅.

7. Add 15ml (or 14.625g) 2,4-pentanedione.

8. Replace stopper and place flask in load lock.

9. Remove from load lock and place rubber clamps and tighten around neck of flask.

10. Raise heated oil bath and react for 30 min.

11. Lower oil bath and cool. Store solution in glove box for future use.
Basic operation of the RTA (Total Fab Solutions Heatpulse 610 RTP) requires training from the clean room manager. Once approved, the procedure is as follows:

1. Verify that the main cooling water at the fumehood is on. If off, turn two turns on.
2. Check pyrometer cooler is on and set to 17.0°C
3. Verify that fusebox power supply switch is on. If it is off, it may or may not be padlocked. Consult the clean room manager before continuing. This is a possible indication that the equipment is down.
4. On the RTA front panel, verify the position of the following switches.
   - TEMP MON set to T.C.
   - LAMP CONTROL set to AUTO
   - EMISSIVITY thumbwheel set to 50
5. Verify compressed air regulator is set to 20 psi.
6. Turn on the N₂ supply valve.
7. Turn on the RTA power supply on the front panel. A green indicator light will illuminate.
8. If off, turn on the computer and/or monitor (it is not necessary to shut down the computer when finished, only turn the monitor off).
9. Open the HEATPULSE 610 software
   - Click on RTP CONTROL PAGES
   - Click on RUN PROCESS
10. Set the **purge mfc set point, slm** to **0.0** and verify that the **over temp setpoint** is set to **1200**.

11. Select the proper pyrometer calibration program from the drop down menu. Always, do a test run first to be certain the program is working correctly.

12. Slowly, pull down on the door handle and slide open the drawer to the RTA. The default position is with a bare Si dummy wafer loaded in the drawer.

13. If using the SiC susceptor (recommended), load a dummy wafer (polished side down) in the recessed area and replace susceptor cover. Load the susceptor in the drawer. If not using the susceptor, *be certain* that a dummy wafer is placed on the quartz holder inside the RTA. *Do not run the RTA without either a wafer or the susceptor loaded!*

14. Slowly, close the drawer and lock the handle securely in place.

15. Select the appropriate recipe name, i.e. **650_30sec_pyr.txt**

16. Click on the **start** button, holding it down for 2-3 seconds to ensure that the program started. Watch the program run until the end. If anything goes wrong with the program, hit **stop** immediately.

17. When the program is complete, i.e. the **control temperature** readout is below 30°C, a window will appear prompting the user to continue with the **next wafer** or **store data**. The data is stored as a Word Pad file.

18. Allow the wafer to cool for a complete 5 minutes before opening the drawer. After 5 minutes, slowly open the drawer and verify that the susceptor (or wafer) and the quartzware is cool. Remove the susceptor (or bare wafer) using wafer tweezers. Store the dummy wafer in the wafer box provided.

19. Once the test run is complete, repeat steps 12-18 with the wafer to be processed.
20. To shut down, wait at least ten minutes after the last run, then replace the dummy wafer in the drawer. Replace the susceptor into its plastic sleeve.

21. Exit the **HEATPULSE 610** software.

22. Turn off the \( \text{N}_2 \) supply valve.

23. Turn off the RTA power supply switch on the front panel.

24. Turn off the pyrometer cooler power.

25. Leave the following on:

   - Main power fusebox,
   - Cooling water at fumehood, and
   - Compressed air supply (at 20 psi).