Ink Jet Printing of PZT Thin Films for MEMS

by

Stephen P. Bathurst

Bachelor of Science, Massachusetts Institute of Technology (2003)
Master of Science, Massachusetts Institute of Technology (2008)

Submitted to the Department of Mechanical Engineering
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Abstract

Of the readily available piezoelectric engineering materials perovskite phase lead zirconate
titanate (PZT) has the strongest mechanical to electrical coupling. PZT based devices have the
potential to have the highest performance. Due to the strong piezoelectric response and low
operating voltage, many groups have worked to integrate thin film PZT into a wide range of
microelectromechanical systems (MEMS) devices including: actuators, energy harvesters,
resonators, pressure sensors, pumps, nano-positioning stages, and MEMS switches. However,
processing of thin film PZT is not readily compatible with existing MEMS fabrication processes
and significant design constraints exist when integrating thin film PZT.

In recent years drop-on-demand (DOD) printing has been studied as a robust, flexible, and
inexpensive method of material deposition for MEMS. Direct printing enables the designer to
deposit a film based on a digital pattern file only eliminating the need for photolithography and
subsequent etching steps in the manufacturing process flow. There is a significant cost savings
due to a reduction in the material consumption during manufacturing and in chemical waste
produced. The result is a manufacturing process that is cleaner and cheaper than other
common deposition techniques.

The most compelling benefit of direct printing of PZT is that it provides a freedom of
geometry that eliminates many of the design constraints currently associated with PZT MEMS.
Since high quality thin films can be achieved with deposition control that is not possible with
spin coating, novel functionalities can be incorporated into PZT MEMS. Specifically, PZT printing
is able to deposit material over and around large out-of-plane features. In addition, the
thickness of thin film PZT can vary deterministically across a device or across a wafer.
A new manufacturing method for the deposition of PZT thin films based on ink jet printing has been developed and used to fabricate a piezoelectric micromachined ultrasonic transducer. A solvent system and processes parameters were established that enable the deposition of high quality PZT thin films. Substrate temperature and drop spacing for uniform deposition were determined and both multilayer and single layer PZT films were successfully deposited. Alignment within 10µm and a resolution limit of 30µm were demonstrated. The performance of a printed PZT based ultrasonic transducer was fit to established models to determine piezoelectric coupling and dielectric properties. The piezoelectric coupling coefficient, $d_{31}$, for printed PZT was between -75pC/N and -95pC/N. Impedance data at 1kHz provided the relative permittivity (750-890) and the dielectric loss tangent (2.4%-2.8%). The final printing process enabled the first digital deposition of thin film PZT and the printed PZT based pMUT confirmed the properties of the film are within the range required for a high performance piezoelectric MEMS devices.

Thesis Supervisor: Sang Gook Kim
Title: Professor of Mechanical Engineering
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I would like to sincerely thank all the people whose help and advice led to the successful completion of this work and who made my time at MIT fun and productive.

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I would also like to thank my committee members Prof. Jung-Hoon Chun and Prof. Martin Schmidt. I was lucky to have the opportunity to work with Prof. Chun on this project as well as many others over the last six years and I benefited greatly from his attention to detail and his expertise in droplet based manufacturing. Prof. Schmidt was instrumental in the creation of the digital fabrication research collaboration that began this work and the way he supported and challenged me throughout enabled me to stay clear on how my work may fit into the larger MEMS fabrication context. There is no doubt that the technical insights and high standards set by my committee encouraged me to raise my own expectations higher than I would have originally thought possible.

Thanks also to all the staff of the MTL that made my device fabrication possible. Especially Dennis Ward, Kurt Broderick, Donal Jamiesson, Eric Lim, Dave Terry, Bob Bicchieri and Dr. Vicky Diadiuk whose patience and guidance are the reason my transducers ultimately worked.

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Chapter 1: Introduction

Motivation

Of the readily available piezoelectric engineering materials perovskite phase lead zirconate titanate (PZT) has the strongest mechanical to electrical coupling and PZT based devices have the potential to have the highest performance. Due to the strong piezoelectric response and low operating voltage, many groups have worked to integrate thin film PZT into a wide range of microelectromechanical systems (MEMS) devices including: actuators, energy harvesters, resonators, pressure sensors, pumps, nano-positioning stages, and MEMS switches [1]-[3]. However, processing of thin film PZT is not readily compatible with existing MEMS fabrication processes and significant design constraints exist when integrating thin film PZT.

While some recent work has demonstrated novel ways of forming sol-gel based films, spin coating remains the dominant method of depositing thin film PZT for MEMS. Spin coating is not the best fabrication method for PZT based MEMS but it is currently the most easily integrated into a MEMS process flow. Not only is spin coating inherently wasteful of the expensive and difficult to manufacture sol, but it prevents the deposition of PZT films on or around out of plane features. PZT cracking and thinning occurs when PZT is spin coated over a step of only 2μm in height [4]. The sol-gel material is also very sensitive to other deposition parameters including humidity, particle contamination, and substrate material. As a result device yields are often low. Reliable deposition requires great care and often a good deal of experience processing PZT thin films. Consequently a flexible new approach is needed to easily and effectively deposit high quality PZT thin films for MEMS applications.

In recent years drop-on-demand (DOD) printing has been studied as a robust, flexible, and inexpensive method of material deposition for MEMS [5]. The benefits of DOD printing for MEMS make it an attractive deposition option. First, no mask or patterning is required. Direct printing enables the designer to deposit a film based on a digital pattern file only. This file can be generated in many ways, including from computer aided design (CAD) software, manually, or based on images. Digital deposition in this way eliminates the need for photolithography and subsequent etching steps in the manufacturing process flow. Furthermore the short cycle time required for pattern generation makes rapid prototyping possible and allows multiple design
iterations that were previously not possible in MEMS product development. A further advantage of direct printing is the cost savings due to a reduction in the material consumption during manufacturing and in chemical waste produced. The result is a manufacturing process that is cleaner and cheaper than other common deposition techniques.

Perhaps the most compelling benefit of direct printing of PZT is that it provides a freedom of geometry that eliminates many of the design constraints currently associated with PZT MEMS. Since high quality thin films can be achieved with deposition control that is not possible with spin coating, novel functionalities can be incorporated into PZT MEMS. Specifically, PZT printing is able to deposit material over and around large out-of-plane features. In addition, the thickness of thin film PZT can vary deterministically across a device or across a wafer. Thickness can be controlled from tens of nanometers for sol-gel based inks, all the way to very high aspect ratio features 100μm tall or thicker with particle based inks [6]. Together, these improvements enable a new geometry of device designs that were previously not possible with simple manufacturing processes. While it is unclear yet what novel devices this new manufacturing method will yield, it is possible that the precise deposition control achieved with PZT printing could have a significant impact on the way MEMS structures are designed in the future.

**Thesis Objective and Contribution**

The objective of this work was to develop a new PZT manufacturing process based on ink jet printing. That included ink development, printing process design, and finally film deposition and integration into MEMS test devices. Ink development required formulation of a solution that is chemically compatible with the sol-gel process and also has the viscosity, surface tension, and volatility needed for reliable inkjet printing. Models of the inkjet process were used in conjunction with knowledge of sol-gel chemistry to produce reliable and repeatable PZT material by printing. Ink jet process design focused on tuning the deposition conditions to achieve controllable uniform PZT thin films as well as developing the deposition patterns and alignment tools required to incorporate printed PZT into a MEMS process flow. Film coalesce and drying were extensively modeled and the conditions for uniform deposition were established. The effects of pattern design were investigated to ensure films were deposited and
dried as required. Also machine vision and alignment was integrated into the printing system enabling multi-layer film deposition. These efforts culminated in the fabrication of a printed PZT based ultrasonic transducer which demonstrated the effectiveness of the PZT printing process and also enable a full characterization of the properties of the printed PZT film. Dielectric and piezoelectric properties of the printed thin film were measured through device deflection test and complex impedance analysis. Ultimately the first full characterization of a printed PZT film is reported.

**Thesis Organization**

This thesis is organized to provide a full description of the manufacturing problem and requirements, ink and printing process design and modeling, and finally transducer design fabrication and results. Chapter 1 outlines goals and motivation as well as a basic description of the work completed. Chapter 2 provides a background on piezoelectricity and printing. Chapter 3 includes a full analysis of printing process design and modeling as well as a basic guide for printing process development. Chapter 4 gives the details of the PZT printing results including final ink chemistries and film geometry characterization. Chapter 5 focuses on the printed PZT based piezoelectric ultrasonic transducer including design, modeling, fabrication, testing, and ultimately details on the performance of the device and the PZT film are provided. Finally Chapter 6 is a summary and discussion of the PZT process results and the implications for future devices designs and process improvements.
Chapter 2: Background

Piezoelectricity and PZT

In the 1880’s Jacques and Pierre Curie discovered that in some materials there is a direct relationship between mechanical strain and electric field. This coupling, known as the piezoelectric effect, allows electrical/mechanical energy conversion in either direction. Mechanical strain within a piezoelectric material induces an electric field. This is commonly referred to as sensor mode operation. The application of an electric field causes mechanical deformation, known as actuation mode. Piezoelectric materials generally have low maximum strain (typically 0.1%) but high operating frequencies, high maximum force and are very efficient [7].

Polarization and Hysteresis

The electromechanical coupling in piezoelectric materials is caused by a spontaneous asymmetrical charge distribution in the base unit cell of a crystal structure. This charge distribution occurs when ions form a stable, non-center symmetric, structure that has a net charge imbalance, or polarity. When a piezoelectric material is strained, the crystal lattice deforms, and the normal polarization is exaggerated inducing an electric field. Spontaneous polarization is particularly strong in ABO$_3$ perovskite phase materials such as Barium Titanate (BaTiO$_3$), Lithium Niobate (LiNbO$_3$), and Lead Zirconate Titanate, or PZT (Pb(Zr,Ti))O$_3$. Figure 1 shows a typical tetragonal perovskite structure for a piezoelectric material.

![Figure 1: Tetragonal form of perovskite crystal structure](image)

While piezoelectric materials can form single crystal structures, they are most commonly used in polycrystalline form. While each grain in the structure is polarized in a single
direction, due to the random arrangement of grains the net polarization of the bulk polycrystalline structure is neutral. In order to form a usable piezoelectric film the polarization of the grains must be aligned by a process known as poling. This is accomplished by applying a strong electric field, under elevated temperature for thicker films, which elongates each grain in the direction of the field. When the field is removed, and the temperature lowered, some permanent realignment of the grains remains. The bulk material is said to be poled, having a bulk net polarization in the direction of the applied field. One of the advantages of thin film piezoelectric devices (thickness $<1\sim2\mu m$) is that smaller voltages can completely polarize the film at room temperature. Often thin film devices are poled by the field applied during operation. For PZT, the electric field must be on the order of $10$ kV/cm in order to completely pole the structure, increasing the electric field beyond a critical level, between 40 and 100 kV/cm, results in dielectric breakdown of the film.

Due to deformation of the domains under an applied field, the polarization and deflection will lag behind the applied field. This leads to the hysteresis piezoelectric response shown in Figure 2.

![Figure 2: Typical hysteresis of a piezoelectric material in response to an applied electric field a) polarization, and b) strain [9].](image)

The y intercept for the polarization vs. field hysteresis plot is referred to as the remnant polarization. It represents the amount of polarization left over after the electric field is removed and is often used as an indicator of piezoelectric film performance.
Piezoelectric Performance

After polarization, when the applied field is small, the strain is roughly linearly proportional to the applied electric field. The constitutive relationship between electric field and strain of a piezoelectric device is represented as follows:

\[ S_i = s_{ij}^E \cdot T_j + d_{mi} \cdot E_m \]  
\[ D_m = d_{mi} \cdot T_i + \varepsilon_{mk}^T \cdot E_k \]

The matrices \( d \) and \( s^E \) contain the material’s piezoelectric and compliance constants, based on the directional convention shown in Figure 3, where directions 1 and 2 are in the plane of the piezoelectric material and direction 3 is normal to the film surface.

![Figure 3: Directional convention for piezoelectric materials][10]

Therefore, the \( d_{33} \) constant relates a material’s out of plane strain to a parallel voltage field, and \( d_{31} \) relates a material’s in-plane deflection to a perpendicular field. Orthogonal deflection in \( d_{31} \) mode is not a direct effect of piezoelectricity, but rather a result of the Poisson effect in the directions orthogonal to the applied field and induced strain. Values of \( d_{33} \) and \( d_{31} \) can vary widely based on grain size and crystal structure. Table 1 presents some reported constants for common piezoelectric materials. The relatively high values of \( d_{33}, d_{31} \) for PZT indicate that PZT based piezoelectric devices should provide improved performance over those based on other materials.

Table 1: Electro-mechanical coupling coefficients for MEMS devices made from common piezoelectric materials [11]-[17].

<table>
<thead>
<tr>
<th>Material</th>
<th>( d_{33} ) (\frac{m}{V}) (\cdot10^{-12})</th>
<th>( d_{31} ) (\frac{m}{V}) (\cdot10^{-12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum nitride (AIN)</td>
<td>3.9</td>
<td>-0.80</td>
</tr>
<tr>
<td>Lithium Niobate (LiNbO₃)</td>
<td>48.7</td>
<td>-2.6</td>
</tr>
<tr>
<td>Barium Titanate (BaTiO₃)</td>
<td>289</td>
<td>-111.2</td>
</tr>
<tr>
<td>Lead Zirconate Titanate (Pb(Zr,Ti))O₃</td>
<td>689</td>
<td>-150</td>
</tr>
</tbody>
</table>

---
PZT Processing Techniques

The promising properties of thin film PZT have motivated significant work towards developing reliable deposition methods and towards integrating those methods with established planar semiconductor manufacturing processes. The most basic requirements for the successful formation of a piezoelectric PZT thin film include: the deposition of lead, zirconium, and titanium in the correct stoichiometry, and the crystallization of the deposited material into a perovskite phase crystal. Previous work has also shown that controlling grain size is important to achieving a high remnant polarization and coercive field [13]. Finally, for integration into MEMS devices, the deposited film must be sufficiently uniform and patternable. The potential of PZT as an enabling material in MEMS manufacturing has led to many creative deposition and crystallization techniques that attempt to meet these requirements.

Previously demonstrated techniques for depositing high quality thin film PZT include: sputtering [15], laser ablation [19]-[20], chemical vapor deposition [21], and chemical solution deposition (CSD) processes [22]-[26]. Each of these processes has been shown to be capable of producing well crystallized PZT films. Table 2 indicates some processing conditions, as well as performance data for each of these deposition techniques.

<table>
<thead>
<tr>
<th>Method</th>
<th>Deposition Temp.* [°C]</th>
<th>Deposition Pressure [torr]</th>
<th>Energy Required</th>
<th>Process Complexity</th>
<th>Reported Remnant Polarization [µC/cm²]</th>
<th>Reported Coercive Field [kV/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sputtering</td>
<td>400-600</td>
<td>5·10⁻³ – 2·10⁻⁴</td>
<td>High</td>
<td>High</td>
<td>24</td>
<td>100</td>
</tr>
<tr>
<td>Laser Ablation</td>
<td>650-750</td>
<td>1·10⁻⁴ – 3·10⁻⁴</td>
<td>High</td>
<td>High</td>
<td>35</td>
<td>230</td>
</tr>
<tr>
<td>Chemical Vapor Deposition</td>
<td>400-800</td>
<td>1 - 760</td>
<td>High</td>
<td>Very High</td>
<td>24</td>
<td>96</td>
</tr>
<tr>
<td>Chemical Solution Deposition</td>
<td>Room Temp.</td>
<td>760</td>
<td>Low</td>
<td>Low</td>
<td>26</td>
<td>210</td>
</tr>
</tbody>
</table>

*Annealing may be required after deposition.

Chemical Solution based films have the most flexibility and are the least expensive of the PZT deposition processes [29]. CSD films are also highly uniform because the reactants can mix at the molecular level while in solution. As a result of these process and quality benefits,
solution based methods are currently the most commonly used methods for the deposition of PZT thin films. Sol gel based deposition, a subset of the CSD methods, is by far the most common single method of PZT deposition. A PZT sol is a colloidal suspension of Lead, Zirconium, and Titanium oxides (typically Lead Acetate (Pb(CH₃CO₂)₂·3H₂O), Zirconium-tetra-n-butoxide (Zr(n-OC₄H₉)₄) and Titanium-terta-iso-propoxide (Ti(i-OC₃H₇)₄)) in a solvent (typically 2-Methoxyethanol). This solution can be spun onto a flat surface and dried, causing the particles to precipitate into a condensed, gel-like, film. The metal-organic gel is then pyrolyzed into an amorphous stoichiometric mix of metallic molecules. This deposition can be repeated to build films up to several hundred nanometers thick. Finally, after the desired thickness is obtained, the film is annealed into the desired perovskite phase at around 650°C. Sol-gel deposition has proven to be the easiest, cheapest, and most flexible way to form very high quality PZT thin films.

**Spin Coating**

Since the reporting of a PZT sol-gel synthesis and processing method by Budd et. al. in 1985 [23] spin coating of solution based PZT has been the dominate method of forming perovskite phase PZT thin films. Although spin coating is generally an easy and inexpensive manufacturing method, it is not well suited to the deposition of PZT. The large volumetric contraction that occurs during the heat treatment of PZT films induces high residual stresses that make the brittle film highly prone to cracking and delamination, especially if the substrate has out of plane features (Figure 4). Furthermore PZT is a particularly stable ceramic oxide making patterning a challenge. Wet etching of PZT is most commonly achieved with buffered hydrofluoric acid. However PZT tends to etch along the grain boundaries which can lead to significant undercut and often leaves a metal-fluoride deposits that require a secondary etch for removal (Figure 5) [24],[25]. Reactive ion etching of PZT has also been demonstrated, but volatizing PZT requires high temperature and etch power and as a result selectivity with respect to photoresists is poor [26]. Despite extensive work to reduce the residual stress and facilitate patterning of spun cast PZT thin films, the constraints imposed by the process still result in limited design geometries for PZT based MEMS.
Figure 4: SEM images of poor step coverage of spin coated sol-gel PZT films [4].

(a) cracking  (b) thinning & high stress

Figure 5 Images of PZT devices that failed during wet etching. Failure occurred due to re-deposition of etch byproducts (a) or significant undercut (b).

Thermal Ink Jet Printing System

Thermal Ink Jet Technology (TIPS)

The droplet ejection controller used in this work was the thermal inkjet pico-fluidic system (TIPS). It was developed at HP for printing of functional materials and for use as a flexible development platform. While the design details of the controller and printer nozzles are proprietary technology owed by HP, a review of the basic concepts of thermal ink jet printing based on information available in the public domain is presented here.

The fundamental physics that govern droplet formation in a thermal ink jet printer are based on a rapid pressure increase, caused by the vaporization of a thin layer of ink on a resistive heater, which forces a droplet out through a nozzle. When a pulse of energy is applied to the restive heater, typically 15V-30V for 1-5μs, the heater quickly reaches a temperature greater than 330°C. This rapid temperature increase causes a thin, less than 100nm, layer of ink
to vaporize. The vaporization of a small amount of ink causes the internal pressure in the firing chamber to increase to approximately 125atm, which results in droplet ejection. During the thermal event, less than 0.3% of the ink in the firing chamber is heated, and therefore the temperature in bulk ink, when printing at full speed, generally does not rise more than 20°C. Relying on vaporization of the ink for droplet ejection results in a non-linear relationship between the applied thermal energy and the droplet size. Therefore, for a given heater size and nozzle geometry, a relatively narrow range of droplet sizes can be produced. This can be advantageous as it means that slight variations in the printing parameters will be less likely to affect the final printed dimensions. Different size droplets can be produced by using print heads with different nozzle and heater designs, each of which requires slightly different firing parameters. Thermal ink jet printers can commonly operate at frequencies greater than 20kHz and produce droplets that range from 1 pl – 300 pl in volume.

The TIPS controller (Figure 6) provided by HP integrates all of the functions of a full scale thermal ink jet printer into a hand held, or mountable platform. It provides the ability to control firing pulse parameters and an interface for the replaceable 0.5 ml ink reservoir and print head assembly. It also supplies a connection for regulation of the pressure inside the ink reservoir. A slight negative pressure is required during printing to prevent capillary action from drawing out the ink. Tips with different nozzle sizes and geometries supplied by HP allowed for varied droplet volumes and deposition energy. Finally the TIPS controller provides an interface for computer control and an input for a droplet deposition trigger.

![Figure 6: Thermal Ink Jet Pico-Liter System (TIPS) controller. Image courtesy of Hewlett-Packard.](image-url)
Integrated Printing System (POEM)

An integrated printing system for use with the TIPS controller (Figure 7) was also supplied by HP for this work. The Printing of Electronic Materials (POEM) system was developed as a tool to explore and expand the capabilities of thermal ink jet technology. It has been used to demonstrate the printing of many different materials useful for manufacturing electrical components and MEMS devices. This includes the successful deposition of sol-gel based solutions as well as nano-particle dispersions. It incorporates automated x and y semiconductor handling stages and a vision system for aligned droplet placement. Printing conditions are set by a digital power controller, a backpressure controller, and a heated vacuum platen. The entire system is controlled by proprietary control software developed by the HP imaging and printing group.

![Diagram of POEM system](image)

Figure 7: Printing of Electronic Materials (POEM) integrated printing system.

The POEM motion stages are Primatics PLG160 linear stages. They are powered by a ballscrew drive and the position is determined by a 1μm resolution linear encoder. The housing and mountings are aluminum, and all components are compatible with a class 10 clean room environment. With the installed encoder the stages are capable of accuracy ±7.0μm over the 400mm travel range, with repeatability of ±2μm. Motion control is carried out by a Galili DMC-1820 motion controller which interfaces with HP software as well as custom software.
developed in the Micro and Nano Systems Laboratory at MIT (MNSL) and MIT. The Galil motion controller has built-in functions for position and velocity control, as well as auxiliary digital outputs that can be used to trigger droplet ejection. Substrate alignment is accomplished with a CCD camera and video capture card. The video system is used, along with the motion control software, to determine the offset between the camera and the printer tip. Once this offset is established substrates can be aligned to the print head with approximately ±10.0 μm accuracy.

**Printer Control Software**

Software was developed in the MNSL to interface with the motion control card and place drops in a Cartesian coordinate system aligned to a substrate. The software accepts a text file containing sets of coordinates, each of which represents a droplet location. Alignment is accomplished based on the position of two alignment marks set by the user. The position of the two marks enables the calculation of the center of the substrate as well as the angular misalignment. Based on the location of the substrate an offset is determined for each droplet, and new droplet coordinate calculated. In this way all droplet locations are transferred into the substrate coordinate system and the device layer to be printed is aligned.

Tools were developed using Matlab® to facilitate the generation of input patterns based on certain user specified parameters. For example, starting and ending locations were used to generate close packed area coverage patterns. Droplet spacing and an edge offset were also variable parameters that could be specified by the user. Droplet spacing was generally used to control film uniformity, and the edge offset was used to ensure that, after spreading, the edge of the printed line was in the correct location as specified by the start and end points. The software was structured in this way so that the pattern generating code would closely represent the functional design intent. This allowed printing conditions to be changed without having to recreate the entire pattern manually. The result was the ability to rapidly generate new pattern files for a given droplet size and set of printing conditions, as long as the appropriate line edge offset and droplet spacing had been previously determined. Once the appropriate pattern is generated, and the substrate is aligned, a printed layer can be easily integrated into either a fully printed process flow or one which incorporates standard lithographically processed layers.
Chapter 3: Design and Modeling of a Sol-gel Ink and Printing Process

Introduction

To deposit high quality PZT thin films via drop-on-demand printing an ink must be formulated that is capable of producing the desired film properties and operating conditions must be established for the printing process. The process must provide reliable, repeatable, and controllable droplet and film formation as well as subsequent heat treatment. The final result should be the deterministic, uniform deposition of a thin ceramic film. To achieve this, the ink and process must perform well at all stages of deposition: droplet ejection, substrate impact, drop coalescence, drying, and finally crystallization. Each of these stages will be considered in detail to determine the ink properties and process parameters that are suitable for inkjet printing of sol-gel PZT.

There are many possible design parameters that may be used to achieve a continuous dense PZT film with strong piezoelectric coupling. Some of these parameters are ink properties such as concentration, viscosity, and volatility and some are process parameters like substrate temperature, drop volume, and deposition timing. The parameters of an ink and printing process are highly interdependent and the relationships between them are complex. This makes it almost impossible to prescribe a specific recipe for the best ink or process for a given material and often achieving good results takes a lot of experimentation. There are however, guidelines and boundaries that have been established for many basic ink and process properties that help ensure the quality of a deposited film and reduce the trial and error required. Several models have been proposed that help describe the basic physics of drop-on-demand printing and these serve as a starting point for such analysis. This chapter will attempt to summarize and extend this base of knowledge, and to provide a practical guide for ink and process design as it applies to sol-gel printing for micro-electromechanical systems.

Physical and Chemical Requirements of a Sol-gel Based Ink

Developing a sol-gel based drop-on-demand ink presents some unique challenges with respect to controlling both the physical properties of the ink and the sol-gel chemistry. Sol-gel solutions are made up of metal organic molecules that enable the dissolution of the desired
metals (in the case of PZT: lead, zirconium and titanium) in a compatible solvent. As the solvent dries, condensation polymerization of these molecules joins them together into a gel matrix the density and uniformity of which influences the quality of the final film. In order for a sol-gel ink to reliably deposit PZT it must have rheological properties that are compatible with drop-on-demand printing, but it must also enable control over the condensation reaction that forms the structure of the deposited film.

**Sol-gel PZT: Chemical Stability and Gel Formation**

The first sol-gel synthesis of PZT thin films was reported by Budd et. al. in 1985. While recent chemistry changes have been demonstrated that reduce the toxicity of the precursor, increase solution stability, and reduce the residual stress of the resulting film, most current PZT sol-gel techniques remain similar to the original process [30]. 2-methoxyethanol (2ME) is used as the primary solvent to dissolve the metal-organic precursors. 2ME (also known as methyl cellosolve) is often used in sol-gel synthesis because it readily dissolves many organic compounds, has good miscibility in variety of solvents, and it reduces the rate of precursor hydrolysis. Also, its boiling point of 125°C (at 1 atm) enables the removal of water by boiling (dehydration of the solution is also important for limiting hydrolysis of the precursors). Precisely controlled amounts of water may then be added to solution to achieve the hydrolysis levels required for bulk or thin film processing.

To form the PZT sol-gel, lead acetate is first reacted with titanium and zirconium isopropoxides in methoxyethanol to form PbTi(OR)₄ and PbZr(OR)₄ complex precursors. These precursors may then be mixed to achieve a range of different Zr/Ti ratios (Figure 8). Previous work has found that the highest piezoelectric coupling for PZT occurs at the phase boundary between its tetragonal and rhombohedral states [31]. This occurs at a ratio of Zr/Ti of 52/48. In addition, an excess of lead is often added to accommodate lead loss due to diffusion during heat treatment. All of the sol-gels used in this work were purchased from Mitsubishi Materials Corporation and while the exact synthesis route is undisclosed, they all have a Pb/Zr/Ti ratio of 118/52/48 and were likely manufactured by a processes closely related to that developed by Budd et. al.

1 In the chemical formulae for the precursors ‘OR’ refers to the alkoxy group of the molecule.
The key reactions that govern the grain size and crystal structure (and hence piezoelectric performance) of the final film are the hydrolysis and condensation reactions that form the bonds between the metals. In the presence of water the metal organic precursors ($M(OR)_x$) undergo a hydrolysis reaction:

$$M(OR)_x + H_2O \rightarrow MO(OR)_{x-1}(OH) + ROH$$  \hspace{1cm} (3)

The partially hydrolyzed molecule then condenses producing either water or alcohol and a higher molecular weight metal organic with a metal-oxygen-metal (M-O-M) bond.

$$2M(OR)_{x-1}(OH) \rightarrow M_2O(OR)_{2x-3}(OH) + ROH$$  \hspace{1cm} (4)

$$2M(OR)_{x-1}(OH) \rightarrow M_2O(OR)_{2x-2}(OH) + H_2O$$  \hspace{1cm} (5)

The process continues in this way, and the solvents and byproducts evaporate, eliminating much of the organic precursor molecules and forming a dense polymer matrix [30], [32]. It has been shown that the degree of hydrolysis and condensation of the precursor metal-organics significantly affects the density, texture, and grain size of the resulting ceramic film [33]. Furthermore, the molecular weight of the precursor directly influences the viscosity of the solution and high molecular weights can render the ink unsuitable for printing [34]. For these
reasons, controlling the hydrolysis reaction and limiting the absorption of water is a critical function of any sol-gel solution-based ink.

There are two simple ways that an ink designer may ensure that the solvent system of a sol-gel ink is stable and hydrolysis is limited. First ensure that any ink additives are anhydrous and will not significantly alter the pH of the solution. Due to the fact that water initiates the hydrolysis reaction any water present in the solution can significantly increase the rate of condensation. Exposure to air must also be limited to prevent the absorption of water from the atmosphere. Similarly, altering the pH of the solution will affect the rate of hydrolysis reducing the density and deteriorating the compositional uniformity of the resulting gel. Second, through the addition of 2-ME the sensitivity of the precursor molecules to hydrolysis may be reduced. 2-ME and the metal precursors undergo an alcohol exchange reaction leaving the metal-organics with the less reactive 2-methoxyethoxy group. Since sol-gel inks generally require low concentrations, the addition of 2-ME as a dilutant can be an easy way to achieve chemical stability. Whatever the rheological requirements of a sol-gel ink system, the effects of solvents on the sensitive sol-gel chemistry should be of primary consideration when selecting ink additives.

Decapping and Concentration Limits

Reliable printing requires a stable meniscus at the printer nozzle and a jettable fluid in the firing chamber. When the printer is idle, however, these conditions deteriorate rapidly. Over time solvent evaporation causes the meniscus to breakdown and the solute concentration in the firing chamber to rise. Eventually the high concentration causes the ink at the nozzle to behave as a non-Newtonian fluid which makes firing a drop impossible. This breakdown of the solvent cap over the nozzle is called decapping and the time required to clog a nozzle due to evaporation is referred to as the decap time. Typically decap times are on the order of seconds but they can be much longer or shorter. Controlling the decap time through the balancing of ink volatility and concentration is therefore an important part of preventing clogging, and ensuring repeatable droplet formation.

Decapping can be particularly problematic when printing sol-gel based inks. There is a temperature rise in the firing chamber and ink reservoir during printing, especially when using a
thermal ink jet printer or a heated substrate. This temperature rise of roughly 15-30°C has the potential to speed up the condensation reaction of the metal-organic molecules and the resulting increase in the molecular weight of the solute materials which further decreases the decap time for sol-gel based inks.

The primary challenge associated with preventing decap arises from a process coupling between the long decap time, desirable for reliable printing, and the requirements relating to material deposition rate and film uniformity. Low volatility, dilute inks have long decap times and tend to form drops more reliably. However, dilute inks are restricted to relatively slow deposition rates and low volatility inks make controlling drop coalescence and drying difficult. As later sections discuss, the film formation and drying process governs the final morphology of the gel and hence the piezoelectric coupling of the printed device. Therefore the printing process must be designed to reduce this coupling as much as possible so that high volatility solutions can be used.

Process tools that have been implemented previously in drop-on-demand printing provide some examples of systems that can accommodate shorter ink decap times. One of these is the automatic priming system, present in most commercial printers, which can detect and repair clogs as they occur. Printers with the ability to automatically flush nozzles and recover from decap allow processing near clogging conditions without concern. Another common way to accommodate short decap times is to maintain a continuous flow of ink through the nozzle. So long as the time between drops is significantly smaller than the decap time, the meniscus will be constantly replenished and the concentration in the firing chamber will remain that of the bulk solution. Continuous printing is an easy and reliable way to prevent decapping but it can make deposition of sparse features difficult. Finally, drop-on-demand printers generally operate at a constant print head velocity, timing drop ejection to place the material in the desired location. This makes drop alignment more challenging but it allows for much faster printing and much shorter times between drops. While these process changes do not reduce the importance of considering decap during ink design they do provide additional flexibility with solvent volatility that can be used to achieve improved film uniformity and device performance.
A sophisticated printing process can reduce the process coupling and shorten the allowable decap time. However, it does not solve all the problems associated with decapping and fundamental process limits must still be considered. Inks with short decap times make printer setup and cleaning more difficult as they require careful nozzle priming and tend to clog very easily. They also limit the maximum distance between deposited drops as some inks with very short decap times may clog during travel between features. The maximum distance between features will roughly equal the decap time multiplied by the velocity of the printer. Finally, using an ink with a short decap time limits the range of acceptable substrate temperatures. The evaporation that drives decapping is very sensitive to substrate temperature and even a slight increase of 10-20°C can cause clogging. With these limitations in mind, the capabilities of the printer and the solution chemistry of the ink can be combined to create a process that meets the film formation and drying requirements while preventing decap related clogging.

Droplet Ejection

Once a stable fluid meniscus is achieved the next phase of drop-on-demand ink design is to ensure the formation of a stable ink drop. While the mechanisms for generating pressure pulses vary between printers, the fluid flows associated with the formation and separation of a fluid droplet are common. Droplet generation begins when a pressure wave deforms the meniscus at the nozzle causing the extrusion of a column of ink. A separated drop is then formed as this unstable ink column collapses. The balance of viscous and surface tension forces determine the volume and velocity of the fluid column and hence the dynamics of droplet formation. The inverse of the Ohnesorge number (commonly referred to as $Z$) is a dimensionless parameter relating viscous and surface tension forces that has been used successfully as a design parameter to control droplet formation dynamics [34]-[37].

$$Oh^{-1} = Z = \frac{\sqrt{\rho \gamma L}}{\eta} = \frac{Re}{\sqrt{We}}$$

Where $\eta$, $\rho$, $\gamma$, and $L$ are the fluid viscosity, density, surface tension, and a characteristic length scale respectively. In this case $L$ is taken as the radius of the printer nozzle. $Z$ may also be expressed in terms of the Reynolds number and the Weber number as shown. Previous work by J. E. Fromm and others has identified and modeled the primary physical mechanisms of droplet formation and has defined a working range for $Z$ of be between 1-10 for successful printing.
If $Z$ is less than 1, viscous forces will dominate the flow characteristics. Higher ejection pressures will be required and a low droplet velocity and short fluid column will result. If $Z$ is too low, droplet ejection is impossible. A high $Z$ value indicates small viscous forces relative to surface tension and a large fluid column will form before droplet separation. When the fluid column is large, Raleigh instabilities cause the formation of several drops the sizes and trajectories of which are erratic. Figure 9 is a plot of the design space for reliable drop formation; Figure 10 shows some examples of drops forming at different values of $Z$.

![Figure 9: Fluid properties for reliable drop formation in drop-on-demand printing, adapted from [38].](image)

The precision required for the successful printing of MEMS necessitates deterministic drop formation and placement. In general, keeping $Z$ below 8 is desirable to ensure the formation of single controllable drops that follow a repeatable trajectory. One challenge with the printing of sol-gel materials is that the solvents commonly used in sol-gel synthesis are relatively inviscid. Small viscous forces lead to the breakup of the drop into small, unpredictable, satellite drops. This is particularly problematic at large nozzle sizes, and makes repeatable printing difficult. Reliable printing of sol-gels therefore, usually requires the addition of a viscosity increasing additive such as 2-ethylhexanoic acid or 1,2 propanediol. However, some sol-gel spin coating solutions already have a viscosity modifier added to enable films of several hundred nanometers in a single coat. Therefore it is important to know the specific properties of the solvent system for each ink and to understand the balance between viscous and surface tension.
forces. Ensuring that the fluid properties of the ink are set correctly for the desired nozzle size is essential for precise control of any drop-on-demand deposition process.

![Image of droplet ejection for fluids with different Z values](image)

**Figure 10:** High speed images of droplet ejection for fluids with a range of Z values. High Z values eject rapidly and breakup into satellite drops, low Z values form single repeatable drops.

**Formation of a Uniform Thin Film**

The formation of a continuous and uniform gel, and hence final film, is critical to achieving high piezoelectric coupling in sol-gel PZT based MEMS. Any cracks or pinholes in the final film will provide a current leakage path between the electrodes and short the device. During heat treatment, as the organic gel matrix undergoes pyrolysis, the film experiences significant volumetric contraction (approximately 60%). This contraction, coupled with the residual stress resulting from heat treatment, causes cracks to form at any stress concentrations. Therefore the film must be highly uniform to distribute the stress uniformly and eliminate concentrations. As well as causing cracks, nonuniformity in the thickness of the film also directly reduces the overall piezoelectric coupling of the device. Any variation in the thickness of the PZT layer will result in a corresponding variation in the local electric field strength and hence the induced strain. The maximum operating voltage is constrained by the thinnest region of PZT and as a result the electric field in the thicker areas is relatively weaker. The effect is to significantly
reduce the overall strain induced in the PZT layer and the displacement-voltage coupling of the device.

Achieving a highly uniform thin film gel requires controlling the way drops coalesce and dry to ensure uniform deposition of the solute. This requires understanding then internal fluid flows within a drying drop or film and their influence on the final solute distribution. Also the way in which drops coalesce to form a film must be controlled to ensure the features of each drop do not aggregate into large scale non-uniformities. Understating the factors that determine the distribution of the metal-organic solutes and the velocity profile of the flows within the film provides the basis for a printing process that controls the final distribution of material on the substrate.

**Droplet Drying: The Coffee Stain Effect and Marangoni Flows**

The final morphology of an ink jet deposited film is determined primarily during drying. The internal fluid flows that occur as the film evaporates drive the solutes within the film and determine the distribution of solute after drying is complete. It has been widely observed that solutes tend to collect in a ring around the edges of a drop as solvent dries. This phenomenon is referred to as the coffee stain effect after the solute ring that forms when spilled coffee dries [39]. The non-uniform solute distribution that results from coffee stain effect is a particularly difficult challenge for drop-on-demand printing of uniform single layer films. Depending on the droplet spacing drops may form donut or scallop shaped non-uniformities and theses non-uniformities determine the scale of roughness in the final film (Figure 11).

![Image](a) ![Image](b)

**Figure 11:** The coffee stain effect causes outward solute flow in a single drop (a) and scallops for a set of lines (b) in drop-on-demand printed PZT.

If the printed film is made up of many thin layers this nonuniformity may be small. Furthermore, minimizing the coffee stain effect and printing highly uniform individual drops
does not guarantee that other factors will not introduce nonuniformities. In either case the coffee stain effect will determine the minimum achievable roughness and therefore understanding and controlling the causes of the coffee stain effect is critical to producing high quality thin films via drop-on-demand printing.

In 1997 Deegan et. al. identified evaporation driven capillary flow as the main cause of this outward solute movement [39]. They showed that if the contact line of a drying film is held fixed (a valid assumption for a wide range of droplet shapes and drying conditions) then the resulting surface evaporation and droplet geometry evolution requires an outward fluid flow. In other words, to maintain a fixed contact line position fluid from the interior of the drop must be constantly flowing outwards to replenish the evaporating solvent. Considering the pinned contact line assumption together with a generalized evaporative flux, the spherical nature of the droplet shape, and conservation of mass, an expression for the vertically averaged flow velocity may be determined [40]:

$$\bar{v}(r, t) = -\frac{1}{\rho r h(r, t)} \int_0^r dr \left( J_s(r, t) \sqrt{1 + \left( \frac{\delta h}{\delta r} \right)^2 + \rho \frac{\delta h}{\delta t}} \right)$$

(7)

Figure 12: a) Coordinate system and variable descriptions for drying conservation of mass equation b) Droplet geometries during drying as determined by the spherical cap and fixed contact line assumptions.

where $r$, $h(r, t)$, $t$, and $J_s(r, t)$ are the radial position within the drop, the drop height at that position, time, and the surface flux, respectively. The basis for solving Equation (7) and determining the solute distribution function is an understanding of the surface flux $J_s(r, t)$. Integrating the surface flux provides the drop volume change over time and hence the drop geometry over time. The difference in local vapor pressure across the surface of the drop, particularly at the drop edges, results in a surface flux that is both non-uniform and a strong function of the changing droplet geometry. Subsequent work by Deegan et. al. shows that the
surface evaporation flux of a sessile drop $J_s(r, t)$ is analytically analogous to the electrostatic potential of a charged conductor with a shape defined by two intersecting spheres. References provide a full derivation of the surface flux model [40]-[41] which results in the following expression:

$$J_s(r, t) \approx J(0, t) \left(1 - \left(\frac{r}{R}\right)^2\right)^{-\lambda(t)} \quad (8)$$

where $J(0, t)$ is the flux at $r = 0$ based on the vapor concentration gradient and solvent diffusivity, $R$ is the initial drop radius and $\lambda(t)$ is a flux uniformity parameter: $\lambda(t) = 0.5 - \frac{\theta(t)}{\pi}$, where $\theta(t)$ is the instantaneous contact angle.

![Profile of Evaporative Flux Through The Surface Of A Sessile Drop](image)

Figure 13: Non-uniform evaporative flux at the surface of a drying sessile drop. Result for water drying at 25°C and 38% humidity.

As Figure 13 shows, the evaporative flux increases at the drop edge due to a lower local vapor pressure. Combining Equations (7) and (8) an analytical expression for the time evolution of the solute concentration profile may be determined. The growth of the solute ring over time may be modeled based on the average flow velocity and estimates about the solute mass concentration at the edge of the drop ring may be made. However, as Deegan points out, this model of the flow does not fully describe the problem and a potentially significant portion of the solute mass flow is not captured.
Approximately 10% of the mass flow measured by Deegan is towards the droplet center and is not described through the evaporative driven flow analysis. In experiments with other solvent systems the mass flow not captured by the capillary flow model is even greater and in some cases the dominant flow is inward [42], [43]. Subsequent work has shown this inward flow of solute in a drying drop is a surface flow phenomenon caused by the Marangoni effect. The Marangoni effect refers to flow along an interface between two fluids (in this case the solvent and the atmosphere) that arises due to a surface tension gradient. If the solvent surface tension is higher in a particular region of the drop then surface flow in that direction will occur. In the case of a drying droplet a convective thermo-capillary flow is caused by the surface tension gradient that results from a non-uniform surface temperature [44]. For most liquids surface tension decreases with increasing temperature, therefore if one part of the droplet surface is warmer a surface tension gradient will be formed and surface flow will occur. The implications of this thermo-capillary convection are great for drop-on-demand printing as this flow can counter the evaporation driven flow and may be used to increase the uniformity of the final film.

Predicting the Marangoni flows within a drop as it dries begins with determining the exact temperature profile on the surface so that the surface tension gradient that drives the flow may be specified. If the temperature at the drop center is warmer than at the edge the Marangoni flow will be outward and the nonuniform coffee stain will increase. To use Marangoni flows to reverse the coffee stain effect the drop must be cooler at the center and warmer at the contact line.

![Figure 14: Notional streamlines for thermo-capillary convective (Marangoni) flow within a sessile drop when the drop edge is warmer than the drop center.](image)

One way to determine the surface temperature is to neglect heat transfer in the radial direction as a second order effect. Then the temperature at the surface of a drying sessile drop
is found by considering the 1D conduction of heat from the substrate up through the drop as well as the heat removed at the surface by evaporation [42]. The resulting temperature profile is:

\[ T(r, t) - T_{amb} = H_v J(r, t) \left[ 1 + \left( \frac{\partial h}{\partial r} \right)^2 \left( \frac{h(r, t)}{k_L} + \frac{h_S}{k_S} \right) \right] \]  

where \( T(r, t), T_{amb}, H_v, h, k_L, \) and \( k_S \) are the surface temperature, the ambient temperature, the latent heat of evaporation of the fluid, the substrate thickness, and the thermal conductivities of the fluid and substrate respectively. This result, combined with Equation (8), indicates that if heat loss due to evaporation dominates the contact line will be coolest due to the higher local evaporation rate (see Figure 13). Without heat flow from the substrate into the liquid, evaporation would completely determine the temperature profile within the drop and the Marangoni flow would be outward. If the substrate is sufficiently thermally conductive however, heat flow into the liquid from the substrate will dominate. In that case the temperature within the drop is largely dependent on the distance from the substrate, hence warmer liquid at the edge and cooler in the center. Thermodynamic analysis has recently shown the importance of heat conduction paths on the surface temperature of a drying drop. In 2007 Ristenpart et. al. reported that the drop is warmest at the contact line only if the thermal conductivity of the substrate is at least twice the thermal conductivity of the liquid [45]. In 2009 Xu et. al. included the impact of the substrate thickness on the heat flow and developed a criteria for ensuring the Marangoni flow is inward [46]:

\[ \frac{h_S k_L}{R k_S} < \frac{\sin(2\theta_c) - 4\lambda \tan \left( \frac{\theta_c}{2} \right)}{4\lambda + \sin^2 \theta_c} \]  

Equation (10) represents the balance between the nonuniformity of the evaporative driven cooling, which is a function of contact angle, and the nonuniformity of conductive heating, which is governed by the conductance of the substrate and liquid. When the inequality (10) is satisfied, the surface temperature is lowest in center and increases towards the drop edge and the Marangoni flow is inward.

Based on Equations (1) and (9) a full analytical solution for the velocity field \((U_z, U_r)\) may be calculated. The complete derivation is available in [42] and will not be repeated here, however
once the velocity field is known plotting streamlines gives a clear picture of the internal fluid flows and hence the final solute distribution. Figure 15 shows the streamlines that result under different levels of surface flow for a drop 2mm in diameter and 1mm in height. The degree of surface flow is determined by the Marangoni number (Ma) which is a function of previously mentioned fluid properties and $\alpha$ the thermal diffusivity:

$$Ma = \frac{dy R}{dT \eta \alpha} \cdot \Delta T$$

(11)

![Figure 15: Fluid flow streamlines in a drying sessile drop with (a) very little surface flow and (b) strong inward surface flow. Velocity profile was calculated based on knowledge of the drop surface temperature.](image)

Forming a uniform printed gel film is greatly simplified if the Marangoni flow is inward and balanced with the outward capillary flow of the coffee stain effect so as to provide uniform solute deposition. As demonstrated by this brief analysis, complete modeling of an ink drop drying can be cumbersome and complex. However, there are some practical results that can be applied to ink jet printing that enable the rapid tuning of inks and printing conditions to achieve controlled deposition. First the printing substrate should be thermally conductive enough to guarantee a uniform substrate temperature (at least twice the thermal conductivity of the ink). This ensures the surface tension gradient, and hence Marangoni flow, creates inward surface flow. Also, the printing environment must be free from particle contaminants. Surface particles in the printed film not only represent potential film defects, but can act as surfactants and reduce the surface tension gradient. In addition the geometry of the liquid drop should be controlled to maximize the temperature gradient. This requires the Bond number of the liquid be low enough ($Bo \ll 1$) that a spherical cap is formed. A thin flat film resulting from a higher Bond number would result in a relatively uniform evaporative flux and surface temperature.

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uniform surface temperate reduces the surface tension gradient and inward surface flow because the Marangoni number depends on a temperature difference; see (11). A more uniform surface temperate profile also occurs if the film is very flat due to a low contact angle \( \theta < 10 - 20^\circ \). As a result strong wetting is to be avoided to ensure a large evaporative flux and temperature gradient. Finally, aqueous solutions should be avoided in favor of other organic solvent based solutions. Water has consistently shown Marangoni flow velocities significantly lower than predicted. This reduction is most commonly attributed to surface contamination by surfactants but as yet this remains unproven. In any respect, other organic solvents show strong Marangoni flows and many have a higher temperature dependence on surface tension. Sol-gel solutions are non-aqueous and generally show strong inward flows for small drops printed on thermally conductive substrates.

The most important design parameter for controlling the balance between the Marangoni flow and the coffee stain effect is the substrate temperature. Several results have indicated an increase in substrate temperature also increases the outward flow of solute in a drying drop [47], [48]. It is likely this is a result of rapid evaporation cooling the contact line and driving the temperature gradient towards outward flow. The model of Marangoni flows presented thus far assumes conduction paths dominate the temperature profile which requires:

\[
\frac{h_s}{k_s} \ll \frac{T_0}{H \cdot J(0,t)}
\]  

(12)

Where \( T_0 \) is the temperature just under the substrate. If the temperature of the substrate is increased this condition no longer holds and the previous analysis of surface temperature is not valid. Instead a more complex analysis is required that considers the effects of increased substrate temperature in detail. Such analysis should include both a 2 dimensional analysis of the convective and conductive heat transfer as well as the effects of elevated temperature on the vapor saturation and diffusion of the solvent vapor. Thankfully, uniform printing may be achieved without completing the full thermodynamic analysis of the impact of substrate temperature.

Achieving uniform printed thin films requires only that inward and outward internal flows be in balance. When designing an ink solvent system the simplified 1 dimensional analysis presented may be used to ensure a strong inward flow at room temperature. Then as the
temperature of the substrate is raised, and the outward flow begins to increase, an optimum temperature for minimizing surface roughness will be reached. This temperate balances the evaporation driven flow and the surface tension flow so as to provide the highs achievable film uniformity. As long as the various preconditions for inward Marangoni flow are satisfied, substrate temperature control provides the final adjustment that enables uniform thin films.

**Extension to Lines and Films**

The study of single drops is important for determining initial deposition parameters and ensuring uniform deposition is achievable. Forming a uniform line or film however requires additional analysis of the effects of droplet coalescence on the morphology of the deposited gel. Many factors contribute to the behavior of the drops as they coalesce including: substrate temperature, drop spacing, time between drops, and the volatility and concentration of the ink. If the drops dry rapidly, or are spaced far enough apart, there will be little to no coalescence and each drop will dry as predicted by the drying models in the previous sections. If the droplets dry very slowly, or are placed rapidly and close together, they will join together in a liquid film before drying. The drying of fully coalesced films may be modeled similarly to the single drop case with geometry modified to match that of the joined drops. Neither of these cases however, produces particularly uniform films. It is in between these two extremes, when drying and coalescence occur at similar rates, that uniform films are formed.

Previous work from Soltman and Subramanian has shown the effects droplet spacing, timing, and temperature have on the morphology of printed polymer lines when drying and coalesce are occurring simultaneously [47]. Their results indicate drop spacing must be no more than about 1-1.5 times the radius of a single drop. Greater spacing will prevent complete coalescence and a scalloped morphology will result. If the drops are placed very close together solute can build up and an unstable bulging of the line may occur. The spacing that determines the onset of these morphologies also depends on the drop drying time and hence substrate temperature. Uniform coalescence requires the drying time be longer than the deposition period. Drops must be deposited fast enough to prevent the ‘stacked coin’ morphology that results from the buildup of individual drying events. Generally drop spacing and deposition
frequency can be used to achieve uniform lines with a range of temperatures leaving temperature as a design parameter that may be used to control the internal fluid flows.

The study of single lines, like that of individual drops, represents a controllable special case that enables the tuning of printing parameters. Deposition of a two dimensional film however, requires consideration of how sets of lines interact and coalesce as well as the starting and ending morphologies of the printed line. In general, when drops are spaced appropriately to achieve uniform lines, the spacing and time between neighboring lines can be used to control the overall film uniformity until ultimately some minimum finite periodic nonuniformity associated with the interfaces between printed lines is reached. There is also a nonuniformity associated with the beginning and end of each printed line that must be considered. The start of each new line is slightly thinner and there is a buildup of solute at the end of the line. The likely cause is a nonuniform liquid meniscus formed at the leading edge of a printed line as the droplets coalesce and the print head moves. Considering the coalescence of two drops during printing, the first drop has experienced some drying before the second drop is deposited. Therefore when the drops coalesce the resulting liquid shape is slightly thicker in the direction of printing. The reason for the thin regions at the start of each line is that this nonuniform meniscus is still forming as the first drops join and taking with it some amount of solute material. Similarly when the printed line ends the drying of liquid deposits an excess of material and the ends of lines are slightly thicker. This nonuniformity is apparent in two dimensional films as well as lines and results in a thin starting edge and a thicker edge in the direction of printing (Figure 16).
Deposition frequency, drying time, feature size and drop spacing all contribute to the two dimension uniformity of a printed film. However, these parameters are generally used to ensure the process is well tuned for uniformity of printed drops and lines. Once that is accomplished, one way to influence the final film uniformity is using the deposition pattern. The deposition pattern includes the location and order of deposited drops and it also has a direct impact on the large scale morphology of the deposited film. For example, one simple way to remove the nonuniformity at the ends of printed lines is to make multiple passes, printing the lines of each pass in different directions (Figure 17, center). The overlapping passes will have non-uniformities in different regions the sum of which will improve end uniformity. Depending on the shape of the area, and its size relative to the non-uniform end regions, the type and orientation of the pattern should be chosen so as to maintain a constant time between depositions of neighboring lines. This time influences the degree to which lines coalesce and may be easily tuned for patterns where it is constant. To that end serpentine and spiral designs should be avoided as the time between neighboring lines is a function of position and is difficult to control. If printed drops and lines are uniform and the time between neighboring drops is constant, then the process may be easily tuned by adjusting the printer velocity until a uniform film is achieved.

Sometimes meeting all of the requirements to form a highly uniform film is not possible. Ink chemistry may be constrained or the shape of a feature may make designing a pattern for
uniform film deposition difficult. Significant non-uniformities can be eliminated if they are randomly distributed and many layers are built up on top of each other (Figure 17, right). With enough layers, individual non-uniformities average out and a more uniform aggregate film may be formed. Printing a feature with a well-defined boundary and thickness that also has randomly distributed nonuniformity can be challenging. A good way of achieving randomize solute distribution is to make sure that each drop is completely dry before placing another drop nearby. Limiting coalescence limits the scale of thickness nonuniformity to that of a single drop and prevents non-uniformities from building up. Depending on the process time for each layer, this slow solute aggregation can be time consuming. However if process rate is not a concern this method can provide an easy way to achieve highly uniform films without having to fully characterize the printing process.

![Figure 17: Images of printing patterns for achieving improved two dimensional uniformity; single layer pattern (left), multi-pass pattern (center), and randomized pattern (right).](image)

Achieving a uniformly deposited sol-gel film requires understanding of the solute distribution that each drop produces, but the way in which drops join together and dry is what ultimately determines the overall thickness profile. Patterns should ensure that neighboring films have the same printing distance between them and therefore the same time to coalesce. This is true both for drops forming lines and for lines forming two dimensional films. The speed of the printer may then be used to increase or decrease the coalescence time until uniformity is
achieved. When uniform coalescence is not possible, many layers may be overlaid to achieve a uniform aggregate film. Whatever the method, each pattern design must primarily focus on ensuring the film formation process occurs in repeatable well-understood way and that it may be controlled.

**Pattern Resolution**

Dimensional tolerance is a fundamental measure of the capability of any manufacturing process. In general printing processes have very good thickness and line edge control, but relatively poor feature resolution as compared with lithographic processes. The thickness of a printed film may be controlled using ink concentration and layering and as such can be controlled to within tens of nanometers. Achieving a very sharp line edge with variation less than one micron is possible after tuning drop coalescence to prevent scalloping. In plane feature resolution however is constrained due to a practical limit to the size of drops that can be controllable deposited. Very small drops cannot be easily controlled in air as they carry very little energy and their trajectories may be altered by local air currents. Drops less than approximately one micron in diameter form an aerosol in air and have highly unpredictable trajectories. Practically, reliable and deterministic droplet placement limits the minimum drop volume to approximately 1pl (d≈12.5µm) which corresponded to a minimum feature size of ≈30µm (25 degree contact angle).

This resolution limit applies for solution deposited onto flat substrates with a constant surface energy. In which case the film morphology is determined by the impact, coalescence, and drying events for which the physics are relatively well understood and resolution limits may be predicted. There are ways however to modify the substrate to constrain the deposited ink, either physically or using surface energy. Understanding the dimensional accuracy of several methods of film deposition including process limitations and what parameters can be used for morphology control enables the substrate to be used as a tool to improved quality and helps integrate the printed film into a MEMS process flow.

**Drop Impact and Shape**

The size and shape of a drop printed onto an unyielding non-porous surface is determined by the both the dynamics of the impact event and substrate wetting. As a drop contacts an
unyielding surface the kinetic energy of the drop is transferred to a combination of three primary absorption mechanisms: increasing surface energy as the droplet shape deforms, viscous dissipation, and ejection of sub-drops or splashing. Each of these mechanisms affects the amount of spreading that occurs immediately after impact. Once the impact energy has been dissipated (0.1-1ms after impact) the surface drop will have a diameter determined by the contact angle of the fluid/substrate pair which may be bigger or smaller than the dynamically determined diameter. Understanding and modeling this energy dissipation and subsequent wetting is required to determine the final drop diameter on the substrate.

The trajectories of ejected sub-drops are unpredictable and as should be eliminated whenever possible. These drops form when instabilities that develop in the water sheet during spreading overcome the ability of viscosity and surface tension to maintain a coherent drop. They are affected by many factors including: surface roughness, temperature, droplet radius, and impact speed. A parameter that considers the relative effects of surface tension, viscosity, and inertia has become widely accepted as predictive of the onset of splashing:

\[ K = \frac{We^{1/2} Re^{1/4}}{ } \]  

(13)

If \( K \) is above some critical value \( K_c \) which depends on surface roughness and temperature then splashing will occur [49]. For ink jetted drops on a smooth substrate \( K_c \approx 100 \).

Once splashing is eliminated the behavior of the fluid after impact is well understood and may be modeled and predicted. One such model, developed by Pasandideh-Fard et al. [50], predicts the maximum diameter during spreading based on fluid properties and impact conditions:

\[ \zeta = \frac{d_{max}}{d} = \frac{We + 12}{3(1 - \cos(\theta)) + 4\left(\frac{We}{\sqrt{Re}}\right)} \]  

(14)

where \( d_{max} \) is the maximum diameter of the impacting drop, \( d \) is the diameter of the drop before impact, and \( \theta \) is the contact angle of the fluid with the substrate.

After the impact energy has been absorbed and the drop is at rest its shape is determined by the balance between surface tension and gravitational forces. Surface tension pulls the liquid into a spherical shape while the minimization of gravitational potential holds the liquid as flat as possible against the substrate. The Bond number, \( Bo \), indicates the balance between
surface tension and gravitational forces and combined with knowledge of the wetting conditions it can be used to determine the exact final shape of the fluid on the substrate.

\[ Bo = \frac{pgL^2}{\sigma} \]  

(15)

Where \( \rho, g, L \) and \( \sigma \) are the fluid density, acceleration due to gravity, a characteristic length scale, and the surface tension of the fluid respectively. If the Bond number is much less than one, surface tension forces dominate and the droplet will form a spherical cap the shape of which may be exactly determined by the fluid volume and contact angle:

\[ d_c = \left( \frac{48 \pi V}{\beta^3 (3\beta^2 + 1)} \right)^{1/3} \]  

(16)

Where \( d_c \) is the drop diameter as determined by capillary forces, \( V \) is the drop volume, and \( \beta \) is a ratio of the cap radius to height determined by the contact angle:

\[ \beta = \frac{r}{h} = \frac{1+\sin(90-\theta)}{1-\sin(90-\theta)} \]

If the Bond number is higher, a wide flat film will form with surface tension based curvature only present at the film edges. A single printed drop will likely have a very low Bond number (\( Bo < 0.01 \)) but as many printed drops coalesce the characteristic length increases and gravity begins to play a larger role. Features a few millimeters in size will begin to flatten rather than remain spherical. Typically drying occurs fast enough to prevent drops coalescing into liquid features on this scale but not always. Much of the analysis presented here is based on a spherical drop geometry, and while certain specific high Bond number cases are addressed it is generally safe to assume the forces in the small volumes of liquid used in drop-on-demand printing (0.5-300pl) will be dominated by surface tension.

These two models can be used to find the size of the surface drop during and after impact however, for a given drop size and velocity, it is the speed at which the drop dries that determines which regime the process is operating in and ultimately the diameter on the surface. If the drop dries quickly the resolution limit will be determined by the impact event. The spreading ratio for a printed drop can easily be 1.5-2 or even higher. Therefore significant resolution improvement is possible by reducing the drop impact velocity. Minimizing the drop ejection energy and impact velocity is an important part of tuning a printing process. The minimum ejection energy for any ink may be found easily via experimentation. The appropriate printing energy is slightly higher (~10%). If the drop drying time is longer, substrate wetting will
determine the final drop diameter. In general strongly wetting substrates should be avoided, plasma or silane treatment can be used if surface modification if needed. Determining which physics is setting the drop diameter enables resolution optimization and, if the drop trying time can be changed, moving between regimes can be used to control resolution.

Another measure of the performance of a printing process is the line edge sharpness. Films formed in a single pass can have very uniform edges if the drop spacing sufficiently reduced. The step of a single layer film can also be very sharp if the drying process is well controlled. The edge resolution for multi-layer films will be limited by the accuracy and repeatability of the drop placement system. Alignment between the printer nozzle and the substrate can introduce significant error and it is best not to change this alignment between layers if possible. It is also important to ensure the print head is as close to the substrate as possible (<1mm) when depositing multi-layer films. Drop interactions with the air make trajectories that are too long unpredictable and unrepeatable. Controlling the drop velocity and wetting conditions, as well as setting the drop spacing correctly and properly aligning of layers, are all required to reach the resolution limit of ink jet technology for drop-on-demand printing.

Process engineers must decide how to fit the requirements of the pattern to the capabilities of the ink and process. If low concentration inks are acceptable then smaller drop volumes can be used but this may require the alignment of multiple layers. If a narrow line is to be printed the drop spacing should be large, if the pattern is a wide film then very tight drop spacing with wide but uniform lines may be desirable. It is important to measure the drop spreading for each new ink or set of processing conditions. This spreading tends to be consistent for a given set of conditions and can be incorporated into pattern design automatically. Whatever the goal of a particular film geometry, understanding the process by which films and lines are formed as well as the parameters that control them provide the basis for interpreting printed results and making successful process changes.

High Resolution Printing

For many MEMS devices a spot size of >30µm microns is acceptable, for geometries that require higher resolution however some techniques for constraining the fluid flow during spreading have been developed. Some recent results indicate that it may be possible to use a
pre-patterned or treated substrate surface to constrain the ink boundaries and decrease the effective minimum feature size [51],[52]. The geometry of a printed drop may either be influenced directly, through micro-molding or printing over pre-released structures, or indirectly by controlling the surface energy of the substrate which can guide the liquid film. Some of these techniques require photo lithographic patterning of the substrate and all of them add additional complexity to a sensitive process. However, for those devices where small feature size is important, using these methods maintains ink jet printing as a viable deposition tool.

Physically constraining the ink is the simplest and most reliable way to achieve high resolution printed geometry. With a lithographically patterned sacrificial mold, printed material can be deposited into or over very narrow features, effectively reducing the minimum feature size to that of the lithographic process. Printing can also be used to coat a MEMS device after release so that excess printed material is collected in a sacrificial region around the device. This can allow release to be moved forward in the process flow and enable new device geometries or material flexibility. The need to include lithography in the process can eliminate some of the benefits of printing. However the flexibility as well as the low cost of printing can sometimes make a process with both drop-on-demand deposition and lithography the best choice.

Another way to improve printed resolution is through the modification of surface energy of the substrate. If the printing surface includes a fluidphilic region and a fluidphobic region any drops printed on the interface will experience a surface tension force toward the stronger wetting fluidphilic side (Figure 18). The force on the drop can be calculated based on the contact angles of the two regions (17). The substrate surface energy may be controlled using photolithographically patterned polymer layers, plasma treatment, or printing of surface energy modifying solutions. Recent work has also shown the potential of Nanoimprinted self-assembled monolayer (SAM) templating to be a rapid and flexible way of modifying substrate surface energy [52]. With surface modification, the minimum printed feature size can be reduced to 5-15μm and in extreme examples features of less than 100nm have been reported [53].
Figure 18: Free body diagram of a droplet at the hydrophobic and hydrophilic surface interface. Figure courtesy of Heon Ju Lee, Micro and Nano Systems Lab, MIT.

\[ F = 2 \int_0^{\pi/2} \left[ \sigma_{LG} (\cos \theta_A - \cos \theta_B) \right] \cos \theta \, Rd\theta \]  \hspace{1cm} (17)

The many ways of controlling the resolution of a drop-on-demand process makes printing a manufacturing option for nearly all MEMS devices. Practically however, the advantages provided by drop-on-demand printing are diminished significantly as the minimum feature size is pushed below the fundamental \( \approx 30 \mu m \) limit. Including a mold or surface energy pattern adds a nonstandard process step which can be difficult to achieve repeatably at scale. Furthermore, if lithography is used to create the mold or pattern it is important to ensure that the same single lithographic step cannot be used to pattern the deposited film directly. Using lithography combined with printing doesn’t make sense if lithography will work alone. High resolution printing is best used in cases where the film deposition is difficult with standard techniques. Such as coating out of plane or released features or when several different materials or thicknesses are needed. When features are greater than \( \approx 30 \mu m \) however, printing is most often faster and less costly than standard MEMS manufacturing processes with the additional advantage of adding flexibility to design geometry. While for some devices it is possible to conceive a fully printed process flow, an alternative is to print only those layers for which for the resolution requirement is not strict. The result is to bring down the process time and overall device cost while maintaining the dimensional accuracy for those layers where it is important. Whatever the process flow, including printing requires trading off resolution against the
benefits provided which is ultimately a design choice that must always be made in a device specific context.

**Conclusion**

Designing a drop-on-demand printing process requires satisfying many different goals using a large set of available parameters. Achieving the desired chemical compatibility, resolution, uniformity, and other performance requirements necessitates a detailed understanding of the relationships between these requirements and the available process parameters. Often changing one process variable will affect the quality of the printed film in multiple ways. For some MEMS devices it is unclear whether an acceptable process can be developed. This chapter outlines some ways in which success can be predicted, if not guaranteed. Furthermore, while significant experimentation is still required to create a new printing process, these models help outline a procedure by which a new ink and process and be quickly developed and tested without significant iteration. The details provided here for reference may go beyond what is generally required for some processes. Each process presents unique challenges however, and in each case a different piece of the drop-on-demand printing model may be needed.

It is useful to outline the basic steps of drop-on-demand ink and process development. Both to serve as a guide during development and to ensure that if process changes are needed the effects on already fixed design parameters will be minimized. The first step of any ink development should be to ensure all solvents are compatible chemically with the process material. Any solvent or surfactant used in an ink must be checked for its effects on solution stability. The next consideration is drop formation which is controlled by the balance between surface tension and viscosity of the solvent blend. Fixing the surface tension and viscosity can impact both the spreading behavior and volatility of the ink, however in general the set of available solvents is large enough to provide options that minimize such effects. At this stage of ink development the resolution limit of the process should also be set. Resolution is a function of substrate temperature, impact energy, and contact angle but it is primarily controlled by drop size which in turn is limited by ink concentration. For this reason the resolution of the process must be decided during ink development to be sure the ink will work well with the desired nozzle size.
Once the ink is developed the process must be tuned for uniform deposition. This begins with establishing the conditions for inward Marangoni flow at room temperature which requires the solvent blend have a negative and large surface tension to temperature coefficient (common for most fluids) and is free from surfactants. The substrate must also be thermally conductive enough that conduction dominates the heat flow into the drying drop. The temperature for deposition is then set experimentally based on single drop uniformity. At this point the drop spacing required to achieve uniform lines may be determined. Finally a deposition pattern is developed that extends the uniform film in two dimensions through controlling line spacing and deposition rate. Following these steps does not guarantee that a printing process will meet device performance requirements but it does ensure that the printed layer will approach the fundamental physical limits of drop-on-demand deposition with minimally iteration and experimentation.

As the modeling and design considerations in this chapter demonstrate, there can be significant upfront work required in order to achieve the film quality required for high performance MEMS. Process engineers may be reluctant to invest the time and effort to develop such a process when the current tools can sometimes provide a similar result, albeit with additional cost and effort during processing. The process development investments made in standard VLSI processes means that research and development in MEMS is more likely to utilize those tools. However, the low cost and flexibility of printing makes it a growing part of the MEMS engineers’ process set. Consider that current commercial printing processes are capable of producing a 4 color, 4”x6” photo with a pixel size of $=30\mu m$ in 13 seconds at a cost of $0.25. If those metrics are extended to a MEMS process it may be possible to print a 16 layer pattern on an 8” wafer in 2min at a cost below $2. Importantly, this cost and rate are volume independent and may be achieved for one device or thousands [54]. The current state of printed MEMS process development may require upfront work for any new printed material or device. However, continued research and a growing material set means that printing may soon compete with VLSI process as a development and a manufacturing tool.
Chapter 4: Printing Process Results

Introduction

The primary goal of this research was to develop a manufacturing method for the deposition of thin film PZT based on printing. Throughout this work changes in sol-gel chemistry, printer capability, and device design necessitated the development of several drop-on-demand inks and associated processing conditions. The data presented here resulted from a development process similar to that outlined in Chapter 3, beginning with solution chemistry and drop formation and moving to uniformity optimization and device integration. Initially development was based largely on experimentation and expert advice. Many process parameters were investigated for their effect on film quality [55]-[59]. However, as models and design analysis built an understanding of the process physics new chemistries and processing conditions were incorporated to improve printing performance. Determining more precisely which process parameters could best be used to satisfy each printing requirement ultimately lead to the more rigorous process development strategy proposed in Chapter 3.

As the models and procedures outline in Chapter 3 were created the process development cycle was streamlined. New inks were synthesized and printed successfully with little or no prior optimization. Not all the experiments detailed here were conducted in the order most desirable for efficient printing process development. Nevertheless, the data are presented in a sequence that provides structure and clarity to the printing process development. Furthermore, following this experimental sequence helps ensure that as each process parameter is fixed it will not adversely affect the printing requirements addressed later. This chapter describes this experimental process sequence as applied to the printing of thin film PZT. Ultimately, these results led to a set of solution chemistries and processing conditions that provide high quality PZT films designed for a range of thickness and resolution requirements.

Physical and Chemical Requirements of a Sol-gel Based Ink

A Jettable PZT Sol-Gel Ink

The starting point for the formulation of a PZT ink for this research was two commercially available sol-gel solutions purchased from Mitsubishi Chemical Corp. One sol-gel was based on
2-methoxyethanol (Mitsubishi Chemicals ID: A6) and the other was based on 1-butanol and 1,2-propanediol (Mitsubishi Chemicals ID: E1). As purchased the solutions are designed for spin coating and while they provide a reliable source of precursor material they do not make good drop-on-demand inks. The base solvents evaporate slowly which adversely affects both the process rate and uniformity after drying (discussed in detail in the next section). Also, the concentrations of spin coating solutions are too high to be printed reliably. Printing for this research was carried out with a HP thermal ink jet printer which is normally limited to a weight concentration of a few percent. The A6 and E1 sol-gel are both 15% (wt) metal-organics and required significant dilution to jet from small nozzles. As solvents were added to dilute the ink the balance of viscosity and surface tension was also controlled to ensure reliable drop formation for the specified nozzle size. The measured viscosities of the A6 and E1 sol-gels were 1.7 and 8.8 mPa-sec respectively, the target viscosity for the inks in this research was approximately 2 mPa-sec. Finally, the chemical compatibility of the solvents was confirmed by measuring the extent of the condensation polymerization reaction over time.

A high concentration ink can prevent drop formation by reducing the decap time and causing the solution to behave as a non-Newtonian fluid. The acceptable concentration limit depends both on the molecular weight of the solutes and the sizes of the nozzle and firing chamber. Due to the low molecular weight of the metal-organics in the PZT, sol-gel printing of relatively high concentrations is possible provided that condensation polymerization does not occur. PZT ink development began with a characterization of the concentration limits for different drop volumes. Anhydrous 2-methoxyethanol was used as the primary solvent with 4% wt of 2-ethylhexanionic acid added. EHA is a common drop-on-demand ink additive. It has a high boiling point (226°C) and adding a small amount of EHA improves nozzle health and increases decap time. Five solutions of PZT sol-gel were primed and printed through a range of seven nozzle sizes between 10pl and 220pl. The smallest drop size to print reliably for approximately 1 hour over a 40°C substrate for each solution was considered the size limit for that concentration (Table 3).
Table 3: Maximum allowable metal-organic concentrations for reliable printing.

<table>
<thead>
<tr>
<th>Nominal Drop Volume (pl)</th>
<th>Nozzle radius (µm)</th>
<th>Maximum Acceptable Concentration (% wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>80</td>
<td>24</td>
<td>4.7</td>
</tr>
<tr>
<td>35</td>
<td>24</td>
<td>2.3</td>
</tr>
<tr>
<td>20</td>
<td>12.5</td>
<td>1.5</td>
</tr>
<tr>
<td>10</td>
<td>8.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

This result provides a guideline for sol-gel metal-organic concentration limits for thermal ink jet printing. It should be noted that the concentration limits for piezoelectric printers will be higher. Regardless of the printing method, identifying the concentration limits enables the formulation of an ink with the right amount of solute material for a given drop volume and resolution limit.

As the stock sol-gel solution was diluted the viscosity and surface tension of the resulting ink were estimated to ensure that the inverse Ohnesorge number, Z, was within the jettable range. The balance of viscous and surface tension forces determines the jettability of the ink. Z is a dimensionless parameter relating viscous and surface tension forces that has been used successfully as a design parameter to control droplet formation dynamics. Z should be between 1-10 for successful printing. Jettability however, does not guarantee controllable drop formation. High speed video and still images were ultimately used to confirm the formation of single, stable drops. The first attempts to print sol-gel material, based on the as purchased solution without modification, gave an indication of how the Z value would need to be reduced (Figure 19). In order to jet solutions of this concentration large nozzles sizes were used (r=30µm) and while jetting was possible drop control was poor and a large erratic stream of ink resulted. It is clear that Z (~20) is too high for the stock solution at this nozzle size. However, this nozzle is too large for MEMS scale features and reducing the nozzle size also reduces the value of Z. As the nozzle radius was reduced from 30µm to 8.5µm the mix of solvents used to reduce the concentration was adjusted to control the viscosity. The viscosities of the inks were adjusted between 1.8 and 2.2mPa·s to achieve a successively reducing Z value. This required increasing the viscosity of the A6 solution by 15%-20% and reducing the viscosity of E1 solution by approximately 80%. High and low viscosity solvents compatible with sol-gel chemistry were
used as viscosity modifiers. The inks were diluted with 2-methoxyethanol and 2-propanol based
on the film drying requirements (see next section), however for stable drop formation 2-
propanol is preferred as it has a low surface tension which also reduces $Z$.

![Printing test of as purchased Mitsubishi sol-gel; 180pl nominal drop volume; 30μm nozzle radius; $Z \approx 20$.](image)

A useful way to estimate the effects of solvents on drop formation is to plot the fluid
properties on a viscosity-surface tension plot. If a fluid density and printer nozzle size is
assumed, lines can be overlaid that show the value of $Z$ and the impact of particular solvents
can be visually estimated (Figure 20, Table 4).

![Fluid properties of sol-gel ink solvents and their influence on drop formation. The $Z$ values
1 are plotted (dotted lines) assuming a density of 0.96 g/cm$^3$ and a nozzle radius of 8.5μm.](image)
Table 4: Fluid properties of Mitsubishi sol-gels A1 and E6 and solvents used in sol-gel ink preparation.

<table>
<thead>
<tr>
<th></th>
<th>Viscosity [mPa-s]</th>
<th>Surface Tension [dyn/cm]</th>
<th>Density [g/cm³]</th>
<th>Z (r = 8.5μm) []</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-A1 (A1)</td>
<td>1.7*</td>
<td>30.84**</td>
<td>1.14*</td>
<td>10.2</td>
</tr>
<tr>
<td>PZT-E6 (E6)</td>
<td>8.8*</td>
<td>24.93†</td>
<td>0.90*</td>
<td>1.6</td>
</tr>
<tr>
<td>2-methoxyethanol (2-ME)</td>
<td>1.54</td>
<td>30.84</td>
<td>0.96</td>
<td>10.3</td>
</tr>
<tr>
<td>1-butanol (1-Bu)</td>
<td>2.80</td>
<td>24.93</td>
<td>0.81</td>
<td>4.7</td>
</tr>
<tr>
<td>1,2-propanediol (1,2-PD)</td>
<td>44.4</td>
<td>36.6</td>
<td>1.04</td>
<td>0.4</td>
</tr>
<tr>
<td>2-ethylexanoic acid (2-EHA)</td>
<td>7.7</td>
<td>28</td>
<td>0.89</td>
<td>1.9</td>
</tr>
<tr>
<td>2-propanol (IPA)</td>
<td>2.05</td>
<td>20.93</td>
<td>0.81</td>
<td>5.7</td>
</tr>
</tbody>
</table>

*Experimentally measured **Taken as 2-methoxyethanol †Taken as 1-butanol Refs: [55]-[67]

The viscosity of the ink mixtures was estimated using the Refutas Equation for blended liquids. The details of this calculation are straightforward and may be found in [68]. Viscosities calculated in this way are only estimates; however there is good correlation to measured data for the inks tested in this work (Table 5).

Table 5: Viscosity estimation of PZT sol-gel based inks.

<table>
<thead>
<tr>
<th></th>
<th>Estimated Viscosity [mPa-s]</th>
<th>Measured Viscosity [mPa-s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT Ink 35pl (A6 Based)</td>
<td>1.89</td>
<td>1.82</td>
</tr>
<tr>
<td>PZT Ink 10pl (E1 Based)</td>
<td>2.20</td>
<td>2.13</td>
</tr>
</tbody>
</table>

*See Appendix A for viscosity measurement conditions and procedure.

Calculating the viscosity of liquid blends in this way provides a good estimate of the impact viscous forces will have on drop dynamics. Calculating the surface tension of a liquid blend however, is a complex problem that requires a detailed understanding the intermolecular forces within the fluid. For PZT sol-gel inks the problem was simplified because all of the blended inks had a significant amount of a low surface tension solvent. The surface tension of a liquid blend tends to be dominated by the low surface tension elements. When a significant amount of a blend is a low surface tension solvent then the surface tension of the blend may be approximated as that of the solvent [69]. All of the inks in this work were based on a primary diluting solvent (either 2-ME or IPA) that was at least 50% (wt) of the solution. With this estimation of surface tension combined with the viscosity calculation from the Refutas
equation values of $Z$ for different inks were able to be predicted during ink formulation. Stable drop formation began around $Z=11$, but a value of around 6 was found to have the best drop control. The final result was repeatable drop formation for a range of nozzle sizes and reliable control of a 10pl drop of PZT sol-gel ink (Figure 21).

Table 6: Fluid properties of PZT sol-gel inks for drop-on-demand printing.

<table>
<thead>
<tr>
<th>Nozzle Size [µm]</th>
<th>Viscosity [mPa·s]</th>
<th>Surface Tension [dyn/cm]</th>
<th>Density [g/cm$^3$]</th>
<th>$Z$ []</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIJ 35pl-A-A6</td>
<td>24</td>
<td>1.89</td>
<td>20.93*</td>
<td>0.89</td>
</tr>
<tr>
<td>TIJ 35pl-C-A6</td>
<td>24</td>
<td>2.09</td>
<td>20.93*</td>
<td>0.84</td>
</tr>
<tr>
<td>TIJ 20pl-C-A6</td>
<td>12.5</td>
<td>1.88</td>
<td>20.93*</td>
<td>0.89</td>
</tr>
<tr>
<td>TIJ 10pl-C-E1</td>
<td>8.5</td>
<td>2.20</td>
<td>20.93*</td>
<td>0.87</td>
</tr>
<tr>
<td>TIJ 10pl-P-E1</td>
<td>8.5</td>
<td>2.04</td>
<td>20.93*</td>
<td>0.87</td>
</tr>
</tbody>
</table>

*Taken as 2-propanol

Figure 21: A stable drop of PZT ink forming from a 10pl (r=8.5µm) nozzle.

The final step in creating a jettable PZT ink was to confirm that hydrolysis was limited within the ink. All of the solvents in this work are used in sol-gel synthesis and their effects on the metal organic precursors have been studied. 2-methoxyethanol, 1,2-propanidioi, and 1-butanol are used in the synthesis of the A6 and E1 sol-gels and are likely to have little effect on the degree of hydrolysis and condensation in the solution. 2-propanol and 2-ethylhexanoic on the other hand are not often used in PZT sol-gel solutions and may result in unwanted increase in the molecular complexity or precipitation of the precursors. In has been shown that 2-
ethlyhexanoic acid for example, will react with sol-gel metal-organic precursors dissolved in 2-methoxyethanol and increase molecular complexity [70]. This reaction however, occurs during distillation and should not readily occur under printing conditions. 2-propanol is usually neutral towards sol-gel metal-organics and has been used to dilute solutions previously [71], [72].

Direct measurement of the state of hydrolysis was also used for confirmation. Previous work has related the viscosity of PZT sol-gel solutions to the increase in particle size caused by hydrolysis and condensation polymerization [73]. To confirm that the polymer chains in the PZT inks were not growing after dilution viscosity measurements were taken for the stock PZT sol-gel and the highest dilution ink (mixed for a 10pl nozzle) over a period of 8 months. Both solutions showed a viscosity change within the margin of error (<2%) after 30 days and a small reduction in viscosity after 8 months (approximately 5%). This unexpected reduction in viscosity was attributed to a precipitation of a small amount of metal organic material over time which was visible around the edges of all of the ink vials. While precipitation did raise concerns that some material had polymerized enough to leave solution, the small amount of precipitated material and the overall reduction in viscosity indicate that the reaction is limited. Also, the matching precipitation in the stock solution confirms that any polymerization reactions are a function of the stability of the original sol-gel not the added solvents. One possible cause is the absorption of a small amount of water from the atmosphere during handling and testing which is to be expected. One sample each of the stock solution and the diluted ink were kept refrigerated and another sample of each was stored at room temperature. However there was no measureable effect on the viscosity of the aged solutions. Regardless of source of the precipitation, the effect on the sol-gel chemistry was minimal and occurred over a long time. This confirms that the added solvents do not significantly alter the sol-gel chemistry. As a further precaution, however, sol-gel inks for this work were mixed as needed and discarded after a few days. The combination of the minimal measured condensation and the short shelf life for mixed inks enables the deposition of material with confidence that the level hydrolysis of the precursors is unchanged from the stock solution.

The section presented a basic method of sol-gel drop-on-demand ink design with solvents to control the physical properties of the solution while maintaining chemical
compatibility with precursor materials. Inks were formulated that reliably produced single controllable drops for several nozzles sizes and stability over time was confirmed. One property of the ink however has yet to be addressed. Volatility is a critical design parameter for achieving a uniform thin film and additives to control volatility are a major part of the ink solvent system. This section has therefore presented a way to achieve reliable drop formation independent of the solution volatility so long as printing is within decapping limits. The next section will address film formation and drying with guidelines for tuning volatility to achieve good uniformity. During this work, as the solvent system design was completed, rheological properties and control over the condensation reaction remained primary design requirements. The tools and data from the experiments and models in this section remained invaluable as additives were considered for volatility control.

**Formation of a Uniform Thin Film**

Printing of uniform PZT films was achieved by balancing the outward and inward capillary flows for single drops, and then joining those drops into lines and films. As discussed in Chapter 3, balancing these flows requires the ink and substrate meet the conditions for strong inward Marangoni flow at room temperature. Once those conditions are met, heating may be used to tune the internal flows. After establishing a net inward flow at low temperature the correct temperature for uniform deposition was determined experimentally. Coalescence was then considered and an increase in solution volatility was used to decrease the drying time and prevent the formation of a liquid film with a high Bond number. Finally drop spacing and deposition patterns were established that enabled deposition of highly uniform gel films in the configuration needed for MEMS test devices.

**Uniform Individual Drops**

Internal flows of individual printed drops were characterized by examining the solute patterns of dried drops. The distribution of the solute after drying was examined visually and with profilometry in order to infer the balance of capillary flows. Initial drop tests were carried out on a platinum coated substrate commonly used to promote the growth of perovskite phase PZT crystals. However, these test had very little Marangoni flow making overcoming the coffee stain effect and achieving uniform drops on platinum challenging. The analysis in Chapter 3
indicates that the nonuniform surface temperature required for Marangoni flows requires high substrate thermal conductivity and a minimum contact angle. In this case the substrate is sufficiently thermally conductive therefore it is likely that the weak Marangoni forces were due to strong wetting to the platinum surface and the resulting low contact angle. Under these conditions it is probable that surface modification to increase the contact angle or substrate cooling to reduced evaporative driven flow would improve uniformity. However both would add time and complexity to the process which is undesirable. Ultimately this problem was addressed through the printing of thin multi-layer patterns for which only the first layer is affected by the strong wetting of the platinum surface. For flat geometries the contact angle for the drops in each subsequent layer is determined by the wetting between the ink solution and the pyrolyzed PZT film. The capillary flows for PZT inks deposited onto PZT films were measured by printing single drops of 0.1nL onto a flat substrate coated with PZT by spin coating. These drops show an increased contact angle and a strong inward flow at room temperature. This allowed for temperature based tuning of drop uniformity and ultimately an optimum deposition temperature of between 50°C and 60°C for an E1 sol-gel based ink printed on PZT (Figure 24).

![Figure 22: Profilometry of PZT sol-gel drops printed at different temperatures on a PZT substrate. The coffee stain effect increases with temperature. This result indicates an optimum deposition temperature of approximately 55°C.](image-url)
Uniform Two Dimensional Films

Once the conditions for uniform drop deposition were established coalescence was studied to ensure the formation of smooth lines and films. The effects of drop spacing, substrate temperature, and solvent volatility were investigated for several solvent systems. The results from one such test are present in Figure 23.

Figure 23: Experimental testing of design parameters for uniform films. Solvent blend (% vol): 50% Isopropyl Alcohol, 27-31% 2-Methoxyethanol, 15% Mitsubishi A6 PZT Sol Gel, 4-8% 2-Ethylhexanoic acid (EHA). 10pl drop volume (approx. 43µm diameter on platinum).

The morphologies that resulted were similar to those reported by Soltman and Subramanian discussed in Chapter 3 but extended to a close packed 2-dimensional pattern. A new dimensionless ratio is introduced that is useful for determining the onset of 2-dimensional printed morphologies:
\[ \gamma_{2D} = \frac{A_s}{A_i} \left( \frac{m^2}{\text{drop}} \right) \]

Where \( A_s \) is the area per drop set by the printing pattern (determined by dividing the total pattern area by the total number of drops) and \( A_i \) is the final spread area for a single drop (determined by the impact dynamics and wetting conditions). The onset of bulging varied significantly with temperature but tended to occur at \( \gamma_{2D} \) less than approximately 0.5. A ‘stacked coin’ morphology was present at high temperatures due to the overlaying of individual drying events and patterns with \( \gamma_{2D} \) greater than approximately 1.5 did not fully coalesce. Uniform single layer films in this work were deposited with a \( \gamma_{2D} \) between 0.6-0.9 depending on the temperature.

The effect of drying time on drop coalescence was more precisely characterized by varying substrate temperature and measuring the profile of the dried solute. At long drying times (i.e. low temperature or volatility) complete coalesces occurs and the films dries together in a single drying event. If the resulting combined liquid film is large (minimum feature size of approximately 1mm or greater) the high Bond number and resulting shape of the liquid film eliminates nearly all surface tension driven flows. This leads to a significant net outward flow of solute and distinct coffee ring morphology at the edges of the coalesced film (Figure 24; 40°C). If the drying time is rapid relative to the drop deposition period then drops dry in individual drying events. The resulting morphology is the sum of the individual drying events as if they were stacked on top of each other which leads to drop scale non-uniformities in the final film (Figure 24; 80°C). As expected the best uniformity occurs when drop deposition and drying times are similar (Figure 24; 60°C).

![Figure 24: Profilometry of thermal ink jetted PZT, deposited at different substrate temperatures. Ink composition: 6% EHA, 15%PZT, 50%IPA, 29%ME.](image-url)
The strong influence that substrate temperature has on the uniformity of both single drops and lines/films indicates the potential for a coupled design in which satisfying the requirements for both may be impossible. If substrate temperature is to be used as a design parameter to control the internal capillary flows within the drying liquid then another design parameter is needed to control drop coalescence. As Figure 23 shows, the overall volatility of the solvent blend can also be used to control drop drying and coalesce. Early printed films, based on 2-methoxyethanol (boiling point 125°C), dried slowly required a substrate temperature of 70-80°C to control coalescence. At this temperature 2-methoxethanol based inks also exhibit a strong outward flow and individual drop nonuniformity (Figure 22d). Experimentation with 2-propanol (boiling point 82°C) as a dilutant successfully reduced the temperature required for uniform coalescence and enabled an inward flow at for a range of deposition temperatures. 2-propanol concentrations up to 85% were tested and 50% was found to print reliably and provide control over coalescence. Decapping time was very short for higher concentrations and lower concentrations required significantly elevated substrate temperatures. 50% dilution with 2-propanol brought the temperature required for controlled drop coalescence into the same range as the temperature required for uniform single drops. Precise control was then achieved with a small amount (3%-6%) of a high boiling point solvent (2-ethylehexanoic acid or 1,2-propanediol). Profile scans like those in Figure 24 were used to characterize the optimum deposition temperature for each ink. The optimum deposition temperature was found to be a controllable function of the amount of high boiling point solvent added (Figure 25). The concentrations of 2-EHA and 1,2-PD were then used to more precisely align the temperature required for drop uniform coalescence with that required for uniform single drops. The result was a significant improvement in overall film uniformity as the two temperatures became closer. Ultimately a film thickness variation of less than 30nm was achieved for single layer films.
Once the effect of solvent volatility on drop coalescence was considered, work on the ink solvent system was largely complete. Small changes to the concentrations of the PZT sol-gel and the high boiling point solvent were needed for each nozzle size and device geometry, but with few exceptions the inks developed for this work were 50% IPA and 30-45% 2-ME. Table 7 gives the composition of 5 inks that were successfully used to deposit high quality PZT thin films.

<table>
<thead>
<tr>
<th></th>
<th>2-ME</th>
<th>1,2-P</th>
<th>IPA</th>
<th>2-EHA</th>
<th>PZT-A6</th>
<th>PZT-E1</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIJ 35pl-A-A6</td>
<td>31%</td>
<td>-</td>
<td>50%</td>
<td>4%</td>
<td>15%</td>
<td>-</td>
</tr>
<tr>
<td>TIJ 35pl-C-A6</td>
<td>-</td>
<td>-</td>
<td>80.5%</td>
<td>4.5%</td>
<td>15%</td>
<td>-</td>
</tr>
<tr>
<td>TIJ 20pl-C-A6</td>
<td>36%</td>
<td>-</td>
<td>50%</td>
<td>4%</td>
<td>10%</td>
<td>-</td>
</tr>
<tr>
<td>TIJ 10pl-C-E1</td>
<td>36.5%</td>
<td>3.5%</td>
<td>50%</td>
<td>-</td>
<td>-</td>
<td>10%</td>
</tr>
<tr>
<td>TIJ 10pl-P-E1</td>
<td>41.5%</td>
<td>3.5%</td>
<td>50%</td>
<td>-</td>
<td>-</td>
<td>5%</td>
</tr>
</tbody>
</table>

**Pattern Resolution**

The resolution of a printed pattern is characterized by several metrics including drop spreading, minimum feature size, line edge sharpness, and thickness control. While printing
processes often provided fine edges and precise thickness control, the minimum spot size is generally no better than 30-50\mu m. For that reason, minimum feature size and spreading control were a particular focus. Drop spreading is determined primarily by drop size, but also by impact velocity and wetting conditions. PZT inks were successfully jetted in drop volumes from 0.5-180\mu l which corresponded to a minimum feature size of approximately 30-200\mu m. As described in Chapter 3, the diameter of the drop on a substrate depends initially on the impact dynamics and then on wetting conditions. Therefore drops that dry quickly will have a resolution limit determined by impact dynamics and drops that dry more slowly will spread based on wetting. Several ways of improving the resolution beyond the spreading limit were also attempted during this research the most successful of which were micro-molding and surface tension assisted patterning. Both methods improved resolution and demonstrated the promise of high resolution techniques. This section summarizes the unconstrained spreading results as well as the resolution limit of the constrained spreading methods. For completeness, edge control and thickness resolution characterization are presented. Finally, the influence of the ink jet pattern design is discussed. Together these results provide a picture of the practical resolution limits as well as what printed geometries are feasible.

Unconstrained Spreading

The resolution limit of PZT films deposited without constrained spreading is determined by the impact dynamics if the drops dry rapidly, and by wetting conditions if the drops dry more slowly. In order to determine the physical regime that governs the spreading resolution drops were deposited at different temperatures/drying times and the spreading diameters were measured.

PZT is commonly deposited onto epitaxial platinum which catalyzes the growth of the strongly piezoelectric perovskite phase of the ceramic. PZT inks printed onto platinum exhibit nearly perfect wetting due to the high surface energy of platinum. Strong wetting makes it difficult to achieve good resolution as the drops spread quickly and have a poorly defined boundary. This can be overcome if the temperature is increased and the drops are dried while spreading. Figure 26 shows the results of single PZT ink drops deposited onto a platinum substrate at different temperatures.
Resolution Defined by Wetting

Resolution Defined by Impact Driven Spreading

Figure 26: Printed PZT drops on platinum. 40°C shows strong wetting, while 50-70°C dry while spreading.

At low temperatures significant spreading is apparent and the very low contact angle localizes the Marangoni flows at the drop edges. Localized Marangoni flows create an unstable boundary which results in an undulating edge after drying (Figure 26a). As the temperature is increased, and the drop dries more rapidly, the effects of impact dynamics begin to dominate. The resolution of rapidly drying drops may be improved by increasing the temperature and drying rate (Figure 26b-c). It is clear for drops deposited onto platinum that the maximum dynamic spreading diameter is smaller than the wetting diameter and after the impact energy dissipates the drop continues to spread.

Strongly wetting inks/substrates not only limit resolution control but also make achieving uniformity difficult (Figure 26a). Drops governed entirely by impact dynamics are characterized by a ring of solute material around a relatively empty center region, likely due to the impinging ink forcing solute outwards (Figure 26c). Furthermore, strong wetting limits the effects of Marangoni flows and prevents control over internal fluid flows. In order to achieve a well-defined boundary and uniform solute deposition a higher contact angle is needed. The contact angle can be increased with surface treatment such as hexamethyldisilazane (HMDS) or by changing the substrate material. Zirconium oxide also provides a good seed layer for PZT growth and has a lower surface energy than platinum. Most of the films deposited for this work were deposited in several layers. Only the first layer was deposited onto platinum the wetting of each subsequent layer was determined by the wetting of the PZT ink to the previous PZT layer. The wetting between PZT inks and a PZT surface was characterized by printing PZT inks onto spin coated PZT films (Figure 27).
Unlike platinum, PZT surfaces showed finite wetting and a well-defined contact angle (Figure 28). Furthermore, drops deposited onto PZT have a maximum dynamic spreading diameter (Figure 27b) that is larger than the diameter determined by wetting (Figure 27a). Therefore the diameter shrinks and the drop recedes after the impact energy dissipates.

The diameter of PZT drops printed onto PZT at low temperatures was predicted using measured contact angels and the spherical cap model presented in Chapter 3. Under the spherical cap model the final diameter of the drop may be exactly determined by the fluid volume and contact angle:

\[ d_c = \left( \frac{48}{\pi} \frac{V \beta^3}{3 \beta^2 + 1} \right)^{1/3} \]  

Where \( d_c \) is the drop diameter as determined by capillary forces, \( V \) is the drop volume, and \( \beta \) is a ratio of the cap radius to height determined by the contact angle: 

\[ \beta = \frac{r}{h} = \frac{1 + \sin(90 - \theta)}{\sqrt{1 - \sin^2(90 - \theta)}} \]

The advancing contact angle was measured as ink was added and the drop grew then the receding contact angle was measured as the drop dried (Figure 28).

\[ \theta = 12^\circ \]

\[ \theta = 21^\circ \]
Using the measured contact angles the drop diameters predicted by the spherical cap model were compared to measured drop diameters for various ink volumes (Figure 29). Under conditions where wetting governs the final diameter there was significant variation in the diameter of printed drops, however, most were within the range defined by the advancing and receding contact angles.

Figure 29: Comparison between spherical cap model predictions and the measured results for PZT inks printed onto a PZT substrate.

The optimized final process parameters require a temperature of ≈55°C for uniform deposition. At this temperature the drops dry while still spreading and the final resolution is governed by impact driven spreading. Accurately modeling the impact driven resolution limit requires balancing surface tension, viscous, and inertial forces over time during impact to determine the shape as the drop dries. However a complete model is not required to infer the resolution limit from other measured data. It is possible to make first order approximation based on the maximum spreading ratio calculated by Pasandideh-Fard et al. (see Equation (14)). The spreading diameter during impact increases roughly linearly up to the maximum spreading diameter. Furthermore, experimental data shows that the spreading ratio remains roughly constant over a wide range of drops less than ≈0.5nl (Figure 30).
At 55°C, PZT drops printed onto a PZT substrate maintain a spreading ratio of approximately 2.2 which corresponds to a minimum spot size of approximately 75μm for a 20pl drop. While smaller drops were deposited, 20pl was the most commonly used drop volume during this work because 75μm was an acceptable resolution limit and smaller drops require low concentrations and high drop densities, significantly increasing deposition time.

**Constrained Printing**

Constraining the fluid flow during spreading enables printing of features smaller than the spreading diameter. Two ways of directly limiting the geometry of printed films were demonstrated and both provide a path to improved feature resolution. The first utilizes a lithographically patterned sacrificially layer as a mold for the printed material. When the sacrificial layer is removed the printed film retains the shape of the underlying pattern. The second method used a change in surface energy to guide drop flow. By patterning the substrate with materials that have different wetting conditions drops were successfully constrained and pattern resolution was improved. Both of these processes improve the resolution of printed films beyond what spreading limits would normally allow, but both also require additional process time and complexity.

Deposition and patterning of a sacrificial layer requires photolithography and etching but there result is a printing process with resolution as good as the lithographically formed mold.
The micro-molded PZT films for this work were deposited into a polysilicon mold which was deposited using electron beam evaporation and the patterned with XeF$_2$. Polysilicon was chosen because it can withstand the high annealing temperatures of PZT and is easily removed with a dry etch that does not affect the PZT layer (XeF$_2$). After the deposition and patterning of the sacrificial layer PZT was roughly printed over the exposed features, annealed, and then the polysilicon was removed (Figure 31). The resulting process is similar to a metal lift-off process where photoresist is used to pattern a subsequent coat of evaporated or sputtered material. Surface profilometry was used to characterize the step definition and the roughness of the cast PZT films. Edge effects were clearly visible on all samples due to wetting of the PZT ink to the side walls of the mold. This however, may be overcome by adjusting the height of the mold to match that of the PZT film. In general the geometry of the PZT films printed into lithographically pattern molds was controlled to the accuracy of the mold itself. Uniformity was also very good: for a printed film with a bulk mean thickness of 147 nm the RMS roughness away from the edge regions was 9 nm.

![Figure 31: Micro-molded PZT features and the sacrificial polysilicon layer used to pattern them.](image)

This molding process provided small feature sizes as well as excellent alignment, and edge definition but depositing and patterning a compatible sacrificial layer is not possible for all substrate geometries. Another way that was used to precisely control the film boundary was to release the device before printing. Often MEMS devices must be physically release from the substrate by etching before operation. If the device can be designed such that released edges define the boundary of the printed film then features smaller than a single drop can be coated after release. In this case the designer must also consider the impact of the solution that spills over the edges of the device and prevent the excess ink from impacting device operation.
In addition to physical boundaries there are ways of using the surface energy of the substrate to help control the fluid boundary. Recent work has shown the ability of monolayers of molecules assembled on a surface to radically affect the surface energy. Self-assembled monolayers (SAMs) can take a hydrophilic surface and make it highly hydrophobic, and moreover they can be applied in a controlled way using a patterned PDMS stamp. The stamp is coated in a SAM precursor solution and the pressed onto a clean hydrophilic surface. The result is a substrate with an invisible pattern of hydrophobic and hydrophilic regions. Printed drops slide towards the hydrophilic regions as they move to reduce the surface energy of the liquid interface. This improves resolution, increased edge definition, and creates a wide tolerance for errors or misprinted drops. The process of stamping SAMs using PDMS is somewhat cumbersome however and is not suited for all processes. It may be used most successfully the starting substrate is very flat, clean, and hydrophilic. Figure 32 shows an example of the resolution improvement that can be achieved by printing over a SAM template.

Using the surface energy of a self-assembled monolayer to achieve high resolution features requires a high level of precision and adds process complexity. Often times however, features with different surface energies will be part of the process already and understanding their impact can help a process engineer to use them to control the fluid meniscus or at the least, prevent unwanted surface energy influences. For example, PZT is most often deposited onto platinum electrodes which are patterned on top of a SiO$_2$ diffusion barrier. While the PZT inks wet strongly to the platinum, the contact angle is higher on SiO$_2$. It was clear throughout this work that inks wet preferentially to the electrode and that this could be used to improve edge definition of the PZT films. Printing very close to, but not over, the edge of the lithographically pattern electrodes resulted in the PZT ink flowing all the way to the electrode edge where it would stop. Whether a substrate surface energy pattern is intended to help control the printed film, or is just a result of previous processing steps, understanding the wetting conditions between the ink and the various substrate regions provides an additional tool for controlling drop spreading and device resolution.
Figure 32: Results of printing over a self-assembled monolayer template (right) as compared to the same pattern printed on an untreated substrate (left).

**Thickness Control and Edge Resolution**

Tuning drop spacing and deposition temperature as previously described enabled clear edge definition and precise thickness control for the PZT films. Thicknesses control, limited by film uniformity, was commonly better than 60nm and some constrained films were tuned within 10nm. Line edge variation for constrained films was indistinguishable from the underlying pattern while the edges of unconstrained films were typically micron scale. Even multi-layer films, when well aligned, showed edge variation of less than 10μm (Figure 33).

Figure 33: Line edge variation of printed PZT films. Unconstrained films (left) commonly varied less than 3-4μm and multi-layer films (right; 48 layers) varied by approximately 10μm.

Thickness control for printed films may be easily achieved by adjusting the amount of solute material deposited per unit area. Assuming a constant film density, a given mass of solute will produce a fixed volume of PZT which, when divided by the printed area, gives an estimate of
the final film thickness after pyrolysis. The thickness may then be controlled by adjusting the drop density, the solution concentration or the number of layers deposited.

\[ t[m] = w[n] V_0 \left( \frac{m^3}{\text{drop}} \right) \rho_s \left[ \frac{\text{drops}}{m^2} \right] n[n] \]  \hspace{1cm} (20)

Where \( t \) is the thickness of the final film, \( w \) is a constant representing the volume fraction lost during pyrolysis as well as the concentration and density of the ink, \( V_0 \) is the drop volume, \( \rho_s \) is the drop surface density and \( n \) is the number of layers. The value of \( w \) was determined by experimentation and scales linearly with ink concentration; for a 1.25\%(wt) solution \( w_{1.25} \approx 2.9 \cdot 10^{-3} \). Due to the large volumetric contraction during pyrolysis, and the resulting residual stress, the thickness of an individual layer must be less than \( \approx 300\text{nm} \) or significant cracking will occur. The effects of residual stress are reduced for thin layers and if pyrolysis is carried out between layers then the final film may thickness may be increased. Figure 34 shows cross sections of the thickness of multi-layer and single layer films deposited by ink jet printing. Equation (21) demonstrates how the thickness of a multi-layer film may be estimated.

\[ 0.7 \ [\mu m] = 2.9 \cdot 10^{-3} \left( 2 \cdot 10^4 \left[ \frac{\mu m^3}{\text{drop}} \right] 5.0391 \cdot 10^{-4} \left[ \frac{\text{drops}}{\mu m^2} \right] 24[n] \right) \]  \hspace{1cm} (21)

**Pattern Design**

The final step in developing a thin film PZT printing process was the formulation of device specific printing patterns. As discussed in Chapter 3 the position of each drop and the order of deposition strongly influence coalescence and the morphology of the final film. Many of the
early patterns designed for this work exhibited significant non-uniformity even after the conditions were established to balance the internal capillary flows. As the patterns were modified to improve film quality design guidelines were establish for the creation of future patterns. Two main approaches to pattern design and film deposition were successfully able to achieve large scale uniform films. The first was based on deposition of only a few layers (1-3) and requires precise control of both internal fluid flows as well as drop and line coalescence. The second approach, which requires the deposition of many layers (>10), is to distribute nonuniformities randomly so that the aggregate film achieves a roughness less than any individual layer. The advantage of the multi-layer approach is a significant robustness to solution chemistry and processing conditions. However, the larger operating window comes at the expense of processing time and generally results in a slightly rougher film that a fully optimized single layer film.

To achieve a uniform film with only a few layers requires precise control over operating parameters and experimentation to determine their exact values. While the modeling presented in Chapter 3 provides a basis for estimating fluid properties, substrate temperature etc. experimentation over a range of conditions is the only way to guarantee uniform results from a single pass. The conditions for uniform drops and lines were estimated and then refined using a set of experimental test samples and patterns were developed to join those features into films. To ensure that uniform conditions were achievable and repeatable, patterns were developed that made the deposition time between neighboring lines long enough for each line to dry individually. This required avoiding serpentine and spiral patterns that due to their shape have a variable drying time between lines. Instead the most uniform patterns had rectangular features made up of individual, straight lines. While such patterns do have the potential for periodic non-uniformities associated with the line interfaces the extent of the nonuniformity was controlled using line spacing. Another source of nonuniformity was the line end effects. Commonly the end of each printed line was slightly thicker and the beginning slightly thinner. In order to minimize these end effects, after a pattern was generated each layer was divided into four passes and each pass was printed in a different direction (Figure 35).
Printing a pass in each direction overlaps the nonuniformities of the line ends and improves the uniformity of the aggregate films. Figure 36 shows a cross section of a PZT film printed in a single pass. The edge of the film is 190nm thicker than the bulk.

While some nonuniformity is unavoidable the best single layer films printed for this work were printed in multiple passes and had a RMS uniformity variation of approximately 32nm (Figure 37).

To avoid process tuning and upfront experimentation uniform films may be deposited under a wide range of conditions if they are made up of enough layers. Under this deposition strategy the nonuniformities of each layer are aggregated in the final film and the averaging results in a more uniform final film. This process has drawbacks as well, requiring more processing time as well as potentially introducing even larger nonuniformities depending on the
pattern design. If subsequent layers have similar periodic nonuniformities then the final film will increase the amplitude of the nonuniformity. After dividing a layer into four passes some patterns have a clear macro scale nonuniformity that results in an amplified roughness in the final film. Random patterns however, successfully average the nonuniformities produce by each layers and are almost as uniform as well tuned single layer films. Figure 38 summarizes the roughness that results after printing multilayer ink jet patterns with varying scales of periodicity.

Uniform Single Layer Films: RMS Nonuniformity 32nm

Before Heat Treatment

After Heat Treatment and Top Electrode

Figure 37: Results of single layer printed PZT films before and after annealing.

Figure 38: The effect of periodicity in the deposition pattern on the surface roughness of printed PZT films. Reducing macro-scale periodicity improves film uniformity; randomly distributed patterns are the most uniform.
Several techniques for controlling resolution were characterized for this research ranging from robust simple multi-layer process to precise highly uniform constrained printing methods. Which approach is best depends on the requirements of the device design. Often pattern or mask designs can be made to accommodate edge effects or reduce the resolution requirement of a printed layer. This makes it important to consider the printing process in to context of the other processing steps during device design. Whatever the final printing process, determining the resolution requirement both guides and streamlines process development.

Conclusion

A new manufacturing method for the deposition of PZT thin films based on ink jet printing has been developed. A solvent system was designed that is compatible with the sol-gel material and also prints reliably and repeatably. Processes parameters were established that enable the deposition of well-defined uniform thin films. To achieve uniform solute distribution, substrate temperature and ink drying were optimized to balance outward, evaporating driven, and inward, surface tension driven, capillary flows. Drop spacing was determined and deposition patterns were developed that produce uniform lines and films. Multilayer films aligned within 10µm were printed and the resolution limits for printed PZT were characterized down to a spot size of 30µm. Ultimately the morphology of the deposited films was controlled well enough to meet the requirements of most PZT based MEMS devices. The analysis presented in Chapter 3 and the results here together provide a reference point for the development of MEMS printing processes. Printing reduces manufacturing costs for current thin film PZT based devices and has the potential to enable new device geometries in the future. Most importantly however, this process makes it easy to deposit an excellent piezoelectric material which, up until this point, has not been widely used due to manufacturing difficulty.
Chapter 5: A Printed PZT Based Ultrasonic Transducer

Introduction

A piezoelectric micromachined ultrasonic transducer (pMUT) was designed, fabricated and tested to confirm the quality of the printed PZT thin films and to demonstrate their functionality. The pMUT design was based on a bulk micromachined circular diaphragm which was coated with electrode and PZT thin films. The active layers were located such that the diaphragm deformed out of plane when an electric field was applied transmitting acoustic pressure waves into the surrounding environment. Transducers of this basic design have been well characterized and provide a robust platform from which clear data about the quality of the PZT may be determined.

Throughout the course of this research a range of devices were fabricated to test the mechanical and electrical properties of the printed PZT films including fixed ferroelectric capacitors and released silicon nitride cantilever structures. While these devices provided an indication of remnant polarization and some dielectric properties they did not provide good measurements of the piezoelectric coupling coefficient or represent a real world functional application of a printed film. Unreleased devices are not good for measuring piezoelectric response as the deflection is constrained and thin silicon nitride structures are highly sensitive to residual stresses in the film. The pMUT however was formed from clamped diaphragm based on a thick (10μm) stress free structural layer which is much thicker that the stressed PZT film. As a result the final devices were relatively insensitive to film stresses and the mechanical models were significantly more accurate.

The goal of the pMUT fabrication was to determine the piezoelectric coupling coefficient, dielectric permittivity and dissipative losses of the PZT film. Clamped plate theory was used to develop a mechanical model for the diaphragm stiffness which predicted the deformation under static pressure loading as well as an applied DC bias. Both models were confirmed by measuring the deflection of the device under various loading conditions. The complex impedance of the transducers was measured as a function of frequency and the results were fit to a lumped element model. Based on a parametric fit to the equivalent circuit the quality factor and resonant frequencies of the devices were calculated and compared to the theoretical
frequency response. Analysis of the impedance data also provided a measurement of the
dielectric permittivity and loss tangent of the printed PZT material. Ultimately, the printed PZT
based ultrasonic transducers were devices that not only accurately demonstrated the quality of
the PZT but also represented a real world application in which printed PZT has the potential to
improve device performance and lower manufacturing costs.

pMUT Design and Modeling

Device Structure Overview

The piezoelectric micromachined ultrasonic transducer design utilizes a thin film of PZT to
couple the vibration of a clamped silicon diaphragm to the electric field between two device
electrodes (Figure 39). If an AC driving signal is applied between the electrodes the resulting
periodic strain in the PZT layer vibrates the structure sending ultrasonic pressure waves into the
surrounding fluid. This device structure, or one similar, has been used in the past by several
groups to successfully fabricate piezoelectric ultrasonic transducers with resonant frequencies
from approximately 200KHz to 10MHz [75],[76]. Previous work has also optimized the size and
shape of a single $d_{31}$ electrode pair to provide maximum displacement. If the electrodes and
PZT cover the entire top surface of the diaphragm the actuation voltage applies a uniform
tension and very little displacement occurs. If the strain is only applied in the center of the
diaphragm a net bending moment results and out-of-plane displacement of the diaphragm is
large. A complete analysis of electrode optimization for this design may be found in [76]. The
optimized design specifies a centrally located circular electrode with a radius that is
approximately 63% of the radius of the diaphragm.
Both the top and bottom electrode patterns were designed to cover the entire silicon diaphragm with metal. A small (5μm) gap was used to electrically isolate the center region and provide an active electrode radius of approximately 63% of the diaphragm radius. While the outer ring of metal is not used to drive the device it ensures a uniform residual stress across the top surface of the diaphragm. If the residual stress across the diaphragm is not uniform an undesirable bending moment results and the diaphragm deflects out of plane. The fabricated array of pMUTs consisted of four columns of eight devices. Each column of devices had a different membrane radius and corresponding electrode size (Table 8).

Table 8: Device geometry for the fabricated array of ultrasonic transducers

<table>
<thead>
<tr>
<th>Column ID</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diaphragm Radius [μm]</td>
<td>200</td>
<td>300</td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>Electrode Radius [μm]</td>
<td>126</td>
<td>189</td>
<td>252</td>
<td>315</td>
</tr>
</tbody>
</table>

Each different size device had different resonant properties and while different size devices do not perform well as an imaging system they do provide different data points for which the PZT performance may be confirmed. The frequency response of a circular diaphragm depends on the source of the restoring force and whether the structure behaves as a membrane or a plate. The restoring force from a membrane comes from tension in the diaphragm (usually caused by residual stress) while the restoring force for plates comes from the stiffness of the structure. The stiffness of a plate is measured using the flexural rigidity which has units of force per curvature (i.e., Pascals per meter or Newton meters). The flexural rigidity of a clamped thin circular membrane made up of \( n \) layers can be calculated as:
\[ D = \frac{1}{3} \sum \frac{Y_n}{(1 - v_n^2)} \left( (h_n - z_s)^3 - (h_{n-1} - z_s)^3 \right) \]  

where \( Y_n, v_n, \) and \( h_n \) are the elastic modulus, the Poisson ratio, and the height of the top surface of the layer respectively and \( z_s \) is the height of the neutral plane. Using the flexural rigidity of the diaphragm a dimensionless measure of the relative importance of the two restoring forces can be calculated:

\[ \beta = \frac{T \alpha^2}{D} \]  

where \( T \) is the tension in the diaphragm and \( \alpha \) is the diaphragm radius. If \( \beta \) is significantly greater than 1 then the diaphragm will behave like a membrane. If \( \beta \) is significantly less than one then the diaphragm will behave like a plate. Classical mechanics gives exact solutions for both the membrane and plate mode vibration frequencies based on the device geometry and stresses. However, \( \beta \) for the pMUTs fabricated for this work ranged from approximately 0.5-3 meaning that both tension and stiffness restoring forces must be taking into account. Muralt et. al. developed a method for combining the solutions for plate and membrane vibration into an integrated, mixed mode estimation of the natural frequencies of vibration [77]:

\[ f_{m+p} = \sqrt{\frac{1}{(2\pi\alpha)^2 \rho h}} \left( \frac{\alpha_p^2}{\alpha^2 D + \alpha_m^2 T} \right) \]  

where \( f_{m+p} \) is the mixed mode natural frequency, \( \alpha_p \) and \( \alpha_m \) are the vibration constants for the plate and membrane vibrations respectively, \( \rho \) is the diaphragm density and \( h \) is the diaphragm thickness. The vibration constants depend both on the source of the restoring force and on the mode of vibration. They are readily available for lower order modes including axisymmetric and non-axisymmetric vibrations [78]. The first axisymmetric mode provides the strongest response and was the main focus of this work for determining the PZT performance. The values of \( \alpha_p \) and \( \alpha_m \) for the first axisymmetric mode are 10.22 and 2.405 respectively.

**Energy Method Deflection Analysis**

In 1998 Muralt et. al. adapted a method for determining diaphragm deflection based on the balance between the stored elastic energy and the piezoelectric coupling energy [79]. Under
this method the deflection response of the diaphragm for a particular vibration mode is represented as an amplitude term multiplied by a shape function:

\[
w(x, t) = A[J_0(\lambda_0 x) - \alpha J_0(i\lambda_0 x)]e^{i\omega t}
\]  

(25)

where \(w\) is the vertical deflection of the diaphragm, \(A\) is the deflection amplitude, \(J_0\) is a Bessel function of the first kind of order 0, \(\lambda_0\) and \(\alpha\) are constants depending on the vibration mode and \(x = \frac{r}{a}\) is the dimensionless radial position equal to the radial position \((r)\) divided by the diagram radius \((a)\). The displacement function (25) can then be calculated for the first several modes and the solutions added to give the actual displacement. The final displacement converges quickly as the modes are superimposed. Static and low frequency displacement results are accurate if the first 5 modes are summed.

The value of the amplitude term in (25) is determined by the elastic and piezoelectric energy balance. Calculation of \(A\) requires integrating the elastic and piezoelectric energies over the device:

\[
A = -a^2 \frac{M_p I_p}{D I_D}
\]  

(26)

Where \(M_p\) is the moment applied by the PZT, \(I_p\) is an integral that represents the piezoelectric coupling energy, and \(I_D\) is an integral that represents the stored elastic energy. These terms are calculated:

\[
I_p = \int_0^{r_e} \left( x \frac{d^2 w}{dx^2} + \frac{dw}{dx} \right) dx
\]  

(27)

Figure 40: Energy method displacement model results for the superposition of 1, 5, and 15 modes.

The value of the amplitude term in (25) is determined by the elastic and piezoelectric energy balance. Calculation of \(A\) requires integrating the elastic and piezoelectric energies over the device:

\[
A = -a^2 \frac{M_p I_p}{D I_D}
\]  

(26)

Where \(M_p\) is the moment applied by the PZT, \(I_p\) is an integral that represents the piezoelectric coupling energy, and \(I_D\) is an integral that represents the stored elastic energy. These terms are calculated:

\[
I_p = \int_0^{r_e} \left( x \frac{d^2 w}{dx^2} + \frac{dw}{dx} \right) dx
\]  

(27)
\[
I_D = \int_0^1 \left[ \left( \frac{d^2w}{dx^2} + \frac{1}{x} \frac{dw}{dx} \right)^2 - 2(1-\nu) \frac{1}{x} \frac{dw}{dx} \frac{d^2w}{dx^2} \right] \, dx
\]  
(28)

Where \( e_{31,f} \) is the piezoelectric coefficient (adapted for thin films), \( E_3 \) is the applied electric field, \( t_p \) is the thickness of the PZT layer, and \( z_p \) is the distance from the neutral axis to the center of the PZT layer. These integrals were calculated numerically for the first five modes and the resulting displacement function was used to predict pMUT behavior. See Appendix D for the full MATLAB solution. The displacement results from the energy method model were confirmed with both finite element analysis and a Green’s function differential equation solution thanks to generous help from Prof. Firas Sammoura and Katherine Smyth.

**Resonator Lumped Element Equivalent Circuit**

The impedance properties of a piezoelectric resonator may be represented by a lumped element circuit shown in Figure 41. This circuit model is accurate so long as the parameters are independent of frequency which is true over a narrow frequency range [80].

![Figure 41: Equivalent circuit for a piezoelectric resonator.](image)

\( R_1 \) represents the mechanical dissipation of the resonator, \( C_1 \) is the motional capacitance, \( L_1 \) is the resonator inductance and \( C_0 \) is the parallel electrical capacitance. The complex impedance of a resonator may be easily measured with an impedance analyzer and the response may be fit to the above circuit model. With values of \( C_1, R_1, L_1, \) and \( C_0 \) determined the quality factor, a dimensionless measure of mechanical dissipative losses, may be easily calculated.

\[
Q = \frac{\sqrt{L_1/C_1}}{R_1}
\]  
(30)
Furthermore the frequency of maximum conductance, $f_s$, can also be calculated and may be used to estimate the natural frequency high Q devices.

$$f_s = \frac{1}{2\pi\sqrt{C_1L_1}}$$

With this basic lumped element model easily measurable impedance data can provide detailed information about the performance of the pMUT as well as the quality of the piezoelectric.

**pMUT Fabrication**

The transducer was formed by depositing PZT and electrode layers onto a silicon diaphragm that was released with a bulk micromachining process. A silicon-on-insulator (SOI) wafer was chosen because the silicon device layer provides a robust, stress free membrane structure and the buried oxide layer is a good etch stop for the deep reactive ion etch process. Figure 42 shows a simplified process flow for the pMUT fabrication process which is summarized below (see Appendix B for a detailed process flow and Appendix C for photomask images):

1) Blank SOI wafers (10μm device layer and a 0.5μm buried oxide layer) were first cleaned with an RCA process to remove any trace organic material and native oxide layer.

2) Wet thermal oxidation was then carried out at 1000°C for 70min to grow 200nm of silicon dioxide. The dense thermal oxide provides a necessary diffusion barrier under the PZT that prevents lead loss due to diffusion during annealing.

3) Next, the front side of the wafer was coated with 1μm of OCG 925 photoresist and immersed in a buffered hydrogen fluoride solution for 5min. The photoresist was then striped with 10min in Nano-Strip™ organic solvent, rinsed and dried. This step exposes the silicon on the back side of the wafer to facilitate diaphragm release.

4) To form the transducer diaphragms the back side of the wafer was coated in ≈20μm of OCG thick resist, exposed using mask one and developed. Deep reactive ion etching was then carried out from the back side up to the buried oxide layer (≈500μm). Etching depth across the wafer was slightly nonuniform and selective masking with Kapton tape was used to improve uniformity. Mask one included both the circular features to form the diaphragms and trenches that separate the wafer.
into 15mm dies. After this step the wafer is easily separated into individual dies by hand.

5) The bottom electrode was pattern using a liftoff process. A released 15mm die was coated with AZ5214 negative photo resist, exposed using mask two and developed. Then eBeam evaporation was used to deposit a 20nm titanium adhesion layer and a 200nm platinum seed layer.

6) PZT printing was used to coat the bottom electrode in 22 layers of PZT sol-gel. Each layer was approximately 32nm resulting in a final film thickness of 700nm. Pyrolysis at 385°C was carried out between each layer, and after the final layer the film was annealed at 650°C for 10min.

7) Finally, another liftoff process was used to pattern the top electrode. The top electrode process was identical to that of the bottom electrode with the exception of the photomask used (the top electrode is patterned with mask 3).
After fabrication was completed device geometry was measured and confirmed. Microscope images and white light interferometry scans of the top surface were used to confirm in plane device dimensions. In addition a focused ion beam was used to cross section and image one device so that thicknesses of each layer could be confirmed. Figure 43 is an image of the complete 15mm square pMUT array. Devices in the left most column (A) have a diaphragm radius of 200μm, (B): 300μm, (C) 400μm, and the right most column (D) 500μm.
Figure 43: Top view of a completed array of pMUTs based on printed PZT.

Figure 44: Focused ion beam cross section of a completed pMUT diaphragm.
The cross section of the device (Figure 44) confirms the thickness of the buried oxide, device and electrode layers were as expected. Process variation during oxidation resulted in a slightly thinner than expected diffusion barrier which was confirmed by reflectance measurements. Finally, the PZT thickness measurement was used to confirm the relationship between solution concentration and amount of material deposited to the final thickness. The precision of the measurement of the material thickness and device geometry resulted in a high level of accuracy in the mechanical models. This ensured that the material and devices parameters measured accurately represent the printed PZT film.

pMUT Testing and Results
The goal of the mechanical and electrical testing of the pMUTs was to determine the quality of the printed PZT film including: piezoelectric coupling, permittivity, and dissipative losses. Additionally, device frequency response and mechanical energy dissipation were also characterized. The PZT film properties are measured by the piezoelectric coupling coefficient ($d_{31}$), the dielectric constant ($\varepsilon_{33}$), and the loss tangent ($\tan \delta$). Pressure loading and DC bias measurements were used to measure the coupling coefficient while the dielectric constant and loss tangent were calculated from impedance data. Finally, the impedance data was fit to an equivalent circuit (Figure 41) and the resonant frequency and quality factor were calculated. Together this data provides a complete picture of both the device and the piezoelectric material.

Static Testing
Before characterization of the printed PZT film the flexural rigidity of the pMUT was measured and checked against the predicted value. A weak vacuum was applied to the back side of the released pMUTs and the displacements of the diaphragms were measured with a WYKO NT3300 optical profiling system (Figure 45). The displacement of a clamped circular plate under a uniform pressure load $P_0$ relates to the flexural rigidity by:

$$w(r) = \frac{P_0 a^4}{64D \left[1 - \left(\frac{r}{a}\right)^2\right]^2}$$

(32)
Therefore, at \( r = 0 \):

\[
\omega_0 = \frac{P_0 \alpha^4}{64D}
\]  

(33)

\[
\begin{align*}
P_1 &= P_{atm} \\
\Delta P &= P_2 - P_{atm} \\
\Delta Z &= Z_0 - Z
\end{align*}
\]

\[
\Delta P = -24 \text{kPa} \quad \Delta Z = -482 \text{nm}
\]

Figure 45: Pressure testing of the pMUT to confirm the mechanical stiffness of the diaphragm.

Using equation (33) the center displacement as a function of pressure was compared with a linear fit to the measured data. Figure 46 shows the results for a 400\( \mu \)m radius diaphragm. Based on the device structure previously discussed, the predicted flexural rigidity of this plate was 21.8\( \mu \)Nm which corresponds to a center displacement of 18.3nm/kPa. The linear fit to the measured displacement had a slope of 18.1nm/kPa which gives a flexural rigidity of 22.0\( \mu \)Nm. The error between the measured and predicted flexural rigidity was approximately 1%.

Figure 46: Comparison of the pressure deflection modeling result with a linear fit to measured data for a pMUT with a diaphragm radius of 400\( \mu \)m. The error between the model and the data is approximately 1%.
Once the rigidity model was removed as a significant source of error the piezoelectric
coupling coefficient could be measured with confidence. Using a ZYGO white light
interferometer the displacement of the pMUT was measured over a range of DC bias voltages
from 0-27V (Figure 47). Deflection of the diaphragm was approximately 700nm at the center
under a 27V bias.

Figure 47: White light interferometry of a pMUT under 0V (left) and 27V (right) DC bias. a=400µm, r=252µm.

The data was next fit to the energy method model previously described using only the $d_{31}$
coefficient of the printed PZT film as a free variable. Figure 48 shows the measured deflection
at the center of a diaphragm as a function of voltage and also the predicted center deflection
based on equation (25) and a $d_{31}$ of -75pC/N.

Figure 48: Measured center displacement

There are nonlinearities at both small and large deflections which make the fit imperfect. At
small bias voltages it is likely that the PZT film is not sufficiently polarized and therefore
displacement is reduced. At large deflections, tension in the diaphragm contributes to the restoring force which reduces the deflection at higher bias voltages. It is possible that a more accurate measure of the $d_{31}$ coupling coefficient may be made by eliminating the low and high bias measurements. Fitting just the data between 5V and 20V provides a better linear fit and results in a stronger coupling ($d_{31} = -95\text{pC/N}$). Conservatively it can be concluded that the $d_{31}$ for printed PZT is between -75pC/N and -95pC/N. This compares well with other reported values for thin film PZT which are commonly around -100pC/N and for films with optimized chemistry and heat treatment values up to -150pC/N have been reported [81],[82].

**Impedance Spectroscopy**

The dielectric properties of the PZT film as well as the natural frequency, and quality factor of the pMUT may be readily determined from impedance analysis. A solartron model 1260A impedance/gain-phase analyzer was used to measure the real and imaginary parts of the impedance over a range of frequencies. The permittivity and electrical dissipative losses can change significantly with frequency and as a result a standard measurement frequency of 1kHz has been established to allow the comparison of dielectric thin films. While the dielectric properties were measured at 1kHz, the device impedance was measured over small frequency range centered around the natural frequency. The lumped element model was then fit to the data to provide the circuit parameters and device performance.

First the properties of the PZT film were characterized by measuring the impedance at 1kHz and fitting the resulting data to the parallel ideal capacitor and equivalent series resistor (ESR) model shown in Figure 49.

\[
\begin{align*}
C_{\text{real}} & \rightarrow C_{\text{ideal}} \quad \text{ESR} \\
\end{align*}
\]

*Figure 49: A model of the PZT electrical capacitance including dielectric losses as an equivalent series resistor.*

From the capacitance and the ESR values the loss tangent and dielectric constant were calculated as follows:

\[\tan \delta = \omega \cdot C_{\text{ideal}} \cdot \text{ESR} \quad (34)\]
\[ \varepsilon_{33} = \frac{t_p C_{\text{ideal}}}{A \varepsilon_0} \]  

where \( \omega \) is the measurement frequency, \( A \) is the electrode area, and \( \varepsilon_0 \) is the permittivity of free space \( \varepsilon_0 = 8.85 \times 10^{-12} \). The loss tangent and relative permittivity were calculated for several devices and an expected range for each value was established. The relative permittivity of the devices calculated for this work ranged between 750 and 890 which are slightly lower than reported values of 960-1035 for other sol-gel based pMUTs [83]. The loss tangent ranged between 2.4% and 2.8% which is within the range previously reported for PZT thin films but slightly higher than Muralt’s sol-gel based PMUTs (Table 9).

Table 9: Loss tangent comparision between the printed PZT PMUT and other published values [83],[84].

<table>
<thead>
<tr>
<th></th>
<th>ZnO</th>
<th>AlN</th>
<th>PZT (thin film)</th>
<th>Muralt’s pMUT</th>
<th>Printed pMUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>tan ( \delta ) @1kHz</td>
<td>1-10%</td>
<td>0.3%</td>
<td>1-3%</td>
<td>2.1-2.5%</td>
<td>2.4-2.8%</td>
</tr>
</tbody>
</table>

After the characterization of the printed PZT film, the frequency response of the devices were determined by measuring impedance data near resonance and fitting to the piezoelectric resonator equivalent circuit shown in Figure 41. Models of the fitted response were nearly identical to the measured response. Figure 50 shows the strong correlation between the measured impedance data for one device (\( a=400\mu m \)) and a fit to lumped element model over a frequency range of 10kHz.

Figure 50: Measured impedance data overlaid with the result of an equivalent circuit fit.
Fitting to the equivalent circuit provided the circuit parameters $C_1$, $R_1$, $L_1$, and $C_0$ which then enable the calculation of the device quality factor and resonant frequency.

Table 10: Parameters that extracted from the lumped element resonator model fitting.

<table>
<thead>
<tr>
<th>Device</th>
<th>Diaphragm Radius [µm]</th>
<th>Electrode Radius [µm]</th>
<th>$C_0$ [F]</th>
<th>$R_1$ [Ohm]</th>
<th>$C_1$ [F]</th>
<th>$L_1$ [H]</th>
<th>$Q$</th>
<th>$f_s$ [kHz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6</td>
<td>400</td>
<td>252</td>
<td>1.90E-09</td>
<td>4256</td>
<td>3.25E-13</td>
<td>1.904</td>
<td>569</td>
<td>202</td>
</tr>
<tr>
<td>B5</td>
<td>300</td>
<td>189</td>
<td>1.21E-09</td>
<td>4527</td>
<td>2.63E-13</td>
<td>0.818</td>
<td>390</td>
<td>343</td>
</tr>
<tr>
<td>A6</td>
<td>200</td>
<td>126</td>
<td>2.65E-09</td>
<td>1271</td>
<td>3.34E-13</td>
<td>0.148</td>
<td>523</td>
<td>716</td>
</tr>
</tbody>
</table>

The impedance measurements for the data in Table 10 were taken at an ambient pressure of 100Torr. These quality factors cannot easily be related to those of other PZT based pMUTs, however 400-600 is similar to reported quality factor data for other pMUTs taken at this pressure [75]. The resonant frequencies calculated from the data fitting are consistently lower than what is predicted by equation (24). This difference was most likely a result of etching nonuniformity and air damping which can both reduce the measured resonate frequency. In particular, it has been recently shown that the boundary conditions of the pMUT diaphragm, and hence resonant frequency, are significantly affected by etching conditions [85]. Despite the slightly reduced frequencies, the measured values are proportional to $1/a^2$ as would be expected for plate mode dominated vibration (Figure 51).

![Figure 51: Comparison between the measured and modeled resonance frequency of three different size devices.](image)

Finally, impedance measurements were taken at a range of pressures to measure the effects of air damping. The quality factors for one device with a diaphragm radius of 400µm ranged from
116 at 760Torr to 1743 at 3Torr which is consistent with the damping and mass loading effects reported for other pMUTs [75].

![Graph](image)

Figure 52: Air damping effects on pMUT resonance (diaphragm radius 400μm).

With the exception of the resonant frequency values the impedance measurements correlate well with the expected results for both the PZT film and the devices response. The match between predicted results form a variety of models ensures the accuracy of the performance data and the resulting PZT film properties.

**Conclusion**

To confirm the quality of the printed PZT film a piezoelectric micromachined ultrasonic transducer was designed fabricated and tested. The resulting data was fit to established performance models to determine piezoelectric coupling and dielectric properties. Mechanical loading was used to confirm the device stiffness model and DC bias loading was then fit to and energy method based model. The piezoelectric coupling coefficient, $d_{31}$, for printed PZT was determined to be between -75pC/N and -95pC/N. Impedance data at 1kHz provided the relative permittivity (750-890) and the dielectric loss tangent (2.4%-2.8%). Further impedance measurements near resonance were used to determine device performance and to confirm air mass loading and damping effects. Ultimately the strong correlation between measured and predicted results made it clear that printed PZT is suitable for pMUT fabrication and has the potential to be used in other piezoelectric MEMS devices.
Chapter 6: Summary and Conclusions

Results and Impact

A new manufacturing method for the deposition of PZT thin films based on ink jet printing has been developed and used to fabricate a piezoelectric micromachined ultrasonic transducer. A solvent system and processes parameters were established that enable the deposition of high quality PZT thin films. Substrate temperature and drop spacing for uniform deposition were determined and both multilayer and single layer PZT films were successfully deposited. Alignment within 10μm and a resolution limit of 30μm were demonstrated. The performance of a printed PZT based ultrasonic transducer was fit to established models to determine piezoelectric coupling and dielectric properties. The piezoelectric coupling coefficient, \(d_{31}\), for printed PZT was between -75pC/N and -95pC/N. Impedance data at 1kHz provided the relative permittivity (750-890) and the dielectric loss tangent (2.4%-2.8%). The final printing process enabled the first digital deposition of thin film PZT and the printed PZT based pMUT confirmed the properties of the film are within the range required for a high performance piezoelectric MEMS devices.

The results of this research have implications for both PZT based devices and printed MEMS in general. Printing PZT can reduce manufacturing costs for current thin film PZT based devices and enable new device designs that were not previously possible. Digital fabrication reduces cycle time and material consumption, eliminates the need for lithographic patterning and enables deposition over steps and other out-of-plane features. In addition, the printing process analysis and results provide a procedure and reference for the development of other MEMS printing processes. Following the method outlined in Chapter 3 will ensure that new materials can be reliably printed without requiring significant iteration and experimentation. Furthermore, the ink chemistries developed for this work were also successfully used to print zirconium oxide, zinc oxide, and tin oxide sol gels. While more testing is required, it is likely that this process or one similar is more broadly applicable to the drop-on-demand deposition of a range of sol-gel materials. Drop-on-demand deposition of sol-gels may increase the flexibility and lower the manufacturing cost for several important MEMS materials. Ultimately the process developed here removes many of the process constraints on
PZT based MEMS and also provides a basis for the development of other enabling printing process.

**Future Work**

In the future, ink jet printing of sol-gel based PZT may be improved by addressing some of the issues that have thus far limited the yield of printed PZT devices. Two main challenges remain that have caused poor device performance: particle contamination and cracking due to residual stresses. Particle contamination was never fully eliminated in this research. Printing in a cleanroom environment and filtering of sol-gel inks both significantly improved device yield over some early processes that were carried out without particle control. Single layer devices ultimately achieved a yield of 65-70%, however, the yield for multilayer devices was lower (20-30%). The reduced yield was attributed to particle contamination due to the fact that larger devices tended to fail more often than smaller devices. This is consistent with particle contamination defects as larger devices would be more likely to have a particle in the active area of the deposited film. It is likely that the increased particle contamination in multilayer films is due to one of two sources. It could be that the increased time it takes to print multilayer films gives more time for particles to land on the film. This may be address by speeding up the process or improving the cleanliness of the printing environment. It is also possible that contamination is due to particle generation in the print head from decomposition of the metal-organic material during the drop firing event. If this is the case switching to a piezoelectric printer would reduce particle generation and improve yield. Residual stress has been a problem with solution based PZT processes since they were developed and has limited the maximum device thickness for PZT sol-gel films. It is particularly problematic for printing processes as small nonuniformities in the film can concentrate residual stresses and lead to cracking and shorted devices. This problem has been recognized by PZT researchers for some time and work to identify stress relaxing additives has been ongoing. While this thesis was unable to incorporate the latest PZT sol-gel chemistries any future sol-gel inks should be based on the current state of the art solutions to minimize the effects of stress cracking. Nevertheless, problems with device yield are common in new manufacturing processes and they will most likely be improved naturally as process development progresses.
Appendix A – Viscometry

Viscometry for this work was carried out using a glass capillary or Ostwald viscometer (Figure 53). The viscosity of a liquid sample is calculated by measuring the time it takes for a fixed volume of sample fluid to flow through a narrow capillary tube. The sample fluid is pulled up through the capillary tube until the measurement reservoir bulb is filled (Figure 53: right side), then the time for the fluid meniscus to move between the two measurement lines is measured. For a given viscometer the dynamic fluid viscosity is proportional to the time measured. Therefore, after calibration with a known liquid, the viscosity of any other liquid may be measured.

Table 11: Viscosity measurements taken with an Ostwald glass capillary viscometer.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Temp. [°C]</th>
<th>Time* [s]</th>
<th>Viscosity [mPa s]</th>
<th>K=V/(pt) [m²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI Water</td>
<td>21</td>
<td>85</td>
<td>1.002</td>
<td>1.181E-08</td>
</tr>
<tr>
<td>Ethanol</td>
<td>21</td>
<td>130</td>
<td>1.200</td>
<td>1.170E-08</td>
</tr>
<tr>
<td>PZT-E1</td>
<td>21</td>
<td>849</td>
<td>8.81</td>
<td>1.175E-08</td>
</tr>
<tr>
<td>35pL-A Ink</td>
<td>21</td>
<td>168</td>
<td>1.82</td>
<td>1.175E-08</td>
</tr>
<tr>
<td>10pL-C Ink</td>
<td>21</td>
<td>198</td>
<td>2.13</td>
<td>1.175E-08</td>
</tr>
</tbody>
</table>

*Times were averaged over three measurements.

Figure 53: Capillary flow viscometer used to measure the viscosity of solvents and inks for this research.
Appendix B - PZT Micro-Ultrasonic Transducer Process Recipe

Beginning substrate:

SOI Wafer: device layer thickness: 10µm, buried oxide layer: 0.5µm.

Step 1: Cleaning of the wafer
- RCA clean
- Location: ICL RCA Station

Step 2: Thermal Oxide Layer
- Target deposition 2000Å SiO₂
- 70 min at 1000°C
- Location: TRL Tube A2

Step 3: Back-side Thermal Oxide Removal
- Front-side photoresist mask
- Location: TRL coater
- BOE (5min) / Nanostrip (10min) / rinse
- Location: TRL acid-hood2

Step 4: Back-side Etch
- Back-side OCG thick photoresist coat
- Expose and develop
- STS1 JB-etch
- Strip OCG with acetone / methanol / 2-propanol / rinse dump.
- Location: TRL Coater/EV1/STS1/photo-wet

Step 5: Bottom Electrode Deposition and Lift-off
Image reversal photo and develop
- After HMDS, spin coat resist AZ 5214E
- Prebake (30min, 90°C)
- Expose (EV1 with mask)
- Flat bake on hot plate in post-bake oven: (65 to 90sec, 120°C)
- Flood exposure without mask: (60sec on EV1)
- Develop – no post-bake required
- Note: Developing time ~2-3min
- Location: TRL coater / oven / EV1

eBeam Metal Deposition
- Target deposition: 200Å Ti (Deposition rate: 1Å/s)
- Target deposition: 2000Å Platinum (Deposition rate: 1Å/s)
- Location: TRL e-beam (eBeam FP)

Lift off
• Acetone lift-off on bottom electrode; followed by methanol and 2-propanol for cleaning.
• Location: TRL photo-wet

Step 6: PZT Deposition, and anneal

Printing
• PZT deposition will be done using ink jet in a filtered glove box and then transferred back to the TRL for further processing.

Annealing
• Place in PZT furnace and ramp to 650°C, hold for 15min and cool.
• Location: TRL PZT Furnace

Step 7: Top Electrode Deposition and Lift-off

Image reversal photo and develop
• After HMDS, spin coat resist AZ 5214E
• Prebake (30min, 90°C)
• Expose (EV1 with mask)
• Flat bake on hot plate in post-bake oven: (65 to 90sec, 120°C)
• Flood exposure without mask: (60sec on EV1)
• Develop – no post-bake required
• Note: Developing time ~2-3min
• Location: TRL coater / oven / EV1

eBeam Metal Deposition
• Target deposition: 200Å Ti (Deposition rate: 1Å/s)
• Target deposition: 2000Å Platinum (Deposition rate: 1Å/s)
• Location: TRL e-beam (eBeam FP)

Liftoff
• Acetone lift-off on bottom electrode; followed by methanol and 2-propanol for cleaning.
• Location: TRL photo-wet
Appendix C - pMUT Photomasks

Mask 1: Deep Reactive Ion Etch
Mask 2: Bottom Electrode
Mask 3: Top Electrode

[Diagram of top electrode arrangement with labels and measurements]

500\mu m
Appendix D – MATLAB Code

clear all; close all; tic;
% C1 Thickness - t [m]
% C2 Poisson’s Ratio - nu []
% C3 Elastic Modulus - Y [Pa]
% C4 Residual Stress - R [Pa]

Input=[
    0.50e-6 0.170  69e9  -300e6 % R1 BOX
  10.0e-6 0.278  180e9 0e6 % R2 Si
   0.20e-6 0.170  69e9  -300e6 % R3 TOX
   0.02e-6 0.320  110e9 0e6 % R4 Ti
   0.20e-6 0.380  170e9  275e6 % R5 Pt
   0.70e-6 0.295  63e9  695e6 % R6 PZT
   0.02e-6 0.320  110e9 0e6 % R7 Ti
   0.20e-6 0.380  170e9  275e6 % R8 Pt
];
PZT=6;
Si=2;

a=400e-6; % [m] Membrane Radius
re=252e-6; % [m] Electrode Radius (d31)

%% Derived Inputs
Input(:,5:8)=0;
layers=length(Input(:,1)); % []
% C5 Distance from top of layer to beam bottom surface - h [m]
Input(:,5)=tril(ones(layers,layers))*Input(:,1); % [m]
% C6 Compliance - se [Pa]^-1
Input(:,6)=(1-Input(:,2).^2)/Input(:,3); % [Pa]^-1

%% Neutral Axis
h1=Input(:,5); % [m]
h2=[0;Input(1:(layers-1),5)]; % [m]
se=Input(:,6); % [Pa]^-1
zs=(1/2)*
    (sum((h1.^2-h2.^2)./se))/...
    (sum((h1-h2)./se)); % [m]

%% Flexural Rigidity
h1_=Input(:,5)-zs; % [m]
h2_=h2-[0;Input(1:(layers-1),5)]-zs; % [m]
D=(1/3)*sum((h1_).^3-h2_).^3./se); % [N*m]

%% More Derived Inputs
% C7 Tension due to residual stress - T [N/m]
Input(:,7)=Input(:,4).*Input(:,1); % [N/m]
% C8 Distance from center of layer to neutral axis - z [m]
Input(:,8)=Input(:,5)-Input(:,1)/2-zs; % [m]
% C9 Moment due to residual stress per circumferential length - [N]
Input(:,9)=Input(:,7).*Input(:,8); % [m]

%% Shape Function
x=0:0.025:1; % []
nu_avg = sum(Input(:,2).*Input(:,1))/sum(Input(:,1)); % []
  28.2790 31.4210 34.5620 37.7030 40.8440 43.9860 47.1270]';
  28.2790 31.4210 34.5620 37.7030 40.8440 43.9860 47.1270]'; % []
g = -(besselj(0, L)./besseli(0, L)); % []

% 

ip = @(x)(x*(
  (1/2)*g.*L.^2.*(besseli(0, L*x) + besseli(2, L*x)) - ...
  (1/2)*L.^2.*(besseli(0, L*x) - besseli(2, L*x))) ... 
  + g.*L*besseli(1, L*x) - L*besseli(1, L*x)); % []

id = @(x)(x*(
  -((2*(1 - nu_avg)*
      ((-li)*g.*L.*besselj(1, li*L*x) - L*besselj(1, L*x)).* ... 
      ((1/2)*g.*L.^2.*(besseli(0, li*L*x) - besseli(2, li*L*x)) - ... 
      (1/2)*L.^2.*(besseli(0, L*x) - besseli(2, L*x)))/x) + ... 
      (((-li)*g.*L.*besselj(1, li*L*x) - L*besselj(1, L*x))/x + ... 
      (1/2)*g.*L.^2.*(besseli(0, li*L*x) - besseli(2, li*L*x)) - ... 
      (1/2)*L.^2.*(besseli(0, L*x) - besseli(2, L*x))).^2)); % []

% Piezoelectric Moment
Ip=real(quadv(ip,0,re/a)); % []
Id=real(quadv(id,0,1)); % []
zp=Input(PZT,8); % [m]
d_31 = -96*10^(-12); % (C/N)
e31_f = d_31*Input(PZT,3)/(1-Input(PZT,2)); % [C/m^2]
V=20; % [V]
E=V/Input(PZT,1); % [V/m]
Mp=-e31_f*E*Input(PZT,1)*Input(PZT,8); % [N] Moment per circumferential length
% Amplitude
Ap=-a^2*Mp./((D*Id); % [m]

% 

figure
plot([wrev(-x*a) x*a],[wrev(w_pzt) w_pzt],'C-','Linewidth',2);
toc
References


