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DESIGN AGAINST THE COUPLED NATURE OF PZT SPIN COATING

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ABSTRACT

Many groups have worked to incorporate thin film lead zirconate titanate (PZT) into a wide range of devices including: actuators, energy harvesters, resonators, pressure sensors, pumps, nano-positioning stages, and MEMS switches. However, the use of PZT has been limited in many MEMS designs due to the constraints and coupled nature of the currently popular spin coating process. Not only is spin coating inherently wasteful of the expensive PZT solution, but it prevents the deposition of PZT films on non-planar substrates and requires difficult, low yield, patterning steps. Direct printing of PZT thin films eliminates the need for photolithographic patterning and etching, allows for controlled deposition over non-planar topographies, and enables the fabrication of devices with varying thickness which cannot be accomplished with conventional spin coating processes. This paper presents the design interaction analysis that lead to the development of a dot on demand deposition process as the adequate manufacturing solution for small volume MEMS products. Furthermore, it describes the various ways in which Axiomatic Design principles guides the development of this new deposition process. Included is a method of resolving coupling between solution chemistry desirable for thermal processing and fluid properties acceptable for printing. It also presents analysis of the inherent coupling that occurs in digital deposition processes between the discrete material deposition and the desire for uniform film geometry and microstructure. Finally this paper discusses the coupling that has yet to be resolved in the manufacture of robust high quality PZT films and future work that may help further facilitate the integration of this powerful material.

Keywords: Thermal ink jet (TIJ), lead zirconate titanate (PZT), micro-electromechanical systems (MEMS).

1 INTRODUCTION

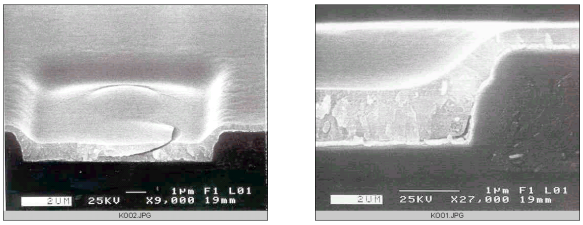
The high degree of piezoelectric and ferroelectric coupling in perovskite phase lead zirconate titanate (PZT) makes it an attractive material for use in micro-electromechanical systems (MEMS). PZT provides highly efficient energy conversion, and has been used to form devices with some of the largest mechanical-electrical coupling coefficients reported. Table 1 gives a comparison of reported coupling coefficients between common piezoelectric materials.

Table 1. Comparison of piezoelectric materials.

Material	d33, $\left[\frac{m}{V}\right]\cdot 10^{-12}$	d31, $\left[\frac{m}{V}\right]\cdot 10^{-12}$
Aluminum Nitride (AlN)	3.9	-0.86
Lithium Niobate (LiNbO3)	25	-4.6
Barium Titanate (BaTiO3)	289	-111.2
Lead Zirconate Titanate (Pb(Zr,Ti))O3	689	-150

Due to the promise of efficient large strains at relatively low voltages, many groups have worked to incorporate thin film PZT into a wide range of devices including: actuators, energy harvesters, resonators, pressure sensors, micro-pumps, nano-positioning stages, and RF MEMS switches, to name a few [1]. Similarly, much work has been done on PZT manufacturing processes. Sputtering, laser ablation, and chemical vapor deposition have all been successfully demonstrated as methods for depositing high quality PZT. However, chemical solution deposition by spin coating remains the dominant manufacturing method due to its relative simplicity and reliability. It can be performed at atmospheric temperatures and pressures, requires no complex equipment, and coating solutions are readily commercially available. Our research group in particular has experience with linear actuators, energy harvesters, and RF switches, all produced by spin coating [2-3].

Relative to the other common PZT manufacturing methods, spin coating is a robust and flexible deposition technique, and is has enabled the demonstration of many novel device structures. However, through our work with PZT, we became aware of significant, irresolvable couplings between the spin coating manufacturing process and the final devices structures. Specifically the centrifugal forces used to form the material layer limit the device structure to uniform, thin, flat, and continuous layers. This imposes several constraints on device design. One set of constraints arises from the process requirement of having a continuous surface coating. This means that complex patterning techniques must be used to form device shapes after deposition. Both wet and dry etching techniques have been developed for the patterning of PZT. However, each has limitations and imposes devices constraints. Typically a buffered oxide etchant solution is used as the wet etchant. It tends to have significant undercut (as much as 5:1), often it leaves behind PbClF residue, and it is not selective against other oxide layers that are commonly used as PZT seed layers. Dry etches have been demonstrated recently, but are not only poorly selective against other oxides, but are poorly selective against photoresists as well. This necessitates the deposition and pattering of a hard mask, significantly increasing process complexity. A second set of spin coating process constraints arises from the substrate flatness requirement. The thermal processing of solution deposited PZT involves a large volumetric contraction and results in a large uniform tensile stress in the final film. This means that it is not possible to spin coat PZT over even small out of plane features with significant cracking occurring at stress concentrations. Figure 1 demonstrates a failure resulting from the coating of a small (~1.5μm) step.



(a) cracking **(b) thinning & high stress**

Figure 1. SEM images of spin coated PZT films [4].

The final constraint that couples the spin coating process to the device structure is the uniformity requirement. There are many intriguing resonant device designs that require a varied strain throughout the device structure to achieve specifically tuned mode shapes. It is difficult to image how this could be accomplished without the ability to vary the thickness of the PZT layer throughout the device. Uniformly deposited layers are limited to uniformly applied strain. Together, these process limitations prompted investigation into ways to decouple the manufacturing process from the device structure, and ultimately digital fabrication techniques seemed a promising solution.

Digital fabrication of solution based PZT via dot-on-demand (DOD) printing has the potential to remove many of the major process constraints, while maintaining all the advantages of a chemical solution deposition method. It provides for as deposited patterning, coating on or around arbitrarily large out of plane features, and deterministic thickness control. However, solution based deposition of PZT involves several complex chemical and mechanical processes. Successfully addressing the challenges associated with DOD deposition of PZT without time consuming design iterations required a detailed understanding of the many process requirements and there interactions. The Axiomatic Design framework guided our understanding of this process during development, enabled the remove of key couplings, and ultimately resulted in the successful development of a new digital fabrication method for PZT.

Given the primary functional requirement is the DOD deposition of high quality PZT, four high level process requirements were identified. First, compatibility with the DOD deposition process is required. Summarized as 'Jetability', this requirement implies stable and robust droplet formation without clogging. Second is the requirement of geometric control of the film. This includes requirements governing in plane resolution, out of plane film uniformity, and thickness control. The third requirement, perovskite phase crystallization, is of primary importance for all solution based PZT deposition methods. This requirement necessitates careful morphological and chemical transformation of the PZT ink into a well crystallized ceramic thin film. The final process requirement, device integration, encompasses all of the requirements and interactions imposed by external processes in the device manufacturing flow. This includes, alignment to other device layers, preventing contamination of other manufacturing equipment, and ensuring the deposited film is compatible with further process steps. The final decoupled design matrix is shown in Figure 2. Preventing coupling between these four requirements was a constant challenge throughout the process development. The design interactions between the lower level functional requirements, with their associated chemical, environmental, and process control parameters, are numerous. The removal of a few key couplings was instrumental in the success of this manufacturing method. Those couplings, and the methods for removing them, will be briefly addressed in this paper.

	Jetability Control Properties	Geometric Control Parameters	Thermal Processing Parameters	Integration Parameters
Jetability	x			
Geometric Control	x	x		
Crystallization	x	x	x	
Device Integration		x	x	x

Figure 2. Highest level design matrix.

2 MAJOR COUPLINGS

Perhaps the most complex and critical of the functional relationships that exists for all DOD deposition for MEMS relates the final geometry of the film, and the many parameters that influence that geometry, to the jetability of the ink and the health of the nozzle-printer system. These two important aspects of printing are inextricably linked through the ink chemistry and printing environment, and in order to achieve a decoupled design matrix the relationships that govern these functional requirements must be in some way modeled. Once each of these requirements is decomposed to a low enough functional level, previously studied relationships can be used to provide a clearer understanding of the functional relationship. Figure 3 is a simplified decomposition of the jetability requirement, and it conveys some of the complex requirements of DOD printing. The selection of appropriate design parameters was informed by early work on sol-gel chemistry, advice from ink development chemists at Hewlet-Packard, and published dynamic models of ink jet printing. Many of these fluid parameters ultimately affect the final film geometry as well; therefore much of this research was focused on reducing or removing the influence that the geometric control parameters have on the jetability of the ink. Figure 4 is a simplified decomposition of the factors affecting film final geometry.

	Jetability Control Properties	Nozzle Health Control Parameters	Evaporation Rate Of Ink At The Nozzle	% 2-Methoxyethanol	Solid loading (% Sol Gel)	Ink Fluid Properties	Inverse Ohnesorge Number	Droplet Kinetic Energy Operating Point
Jetability	x							
Maintain stable ink flow		x						
Prevent nozzle drying			x					
Control Ink hydrolysis				x				
Prevent nozzle clogging			x	x	x			
Droplet dynamic stability		x				x		
Stable droplet formation				x	x		x	
Prevent splashing								x

Figure 3. Simplified functional decomposition of ink jetability requirements.

	Geometry Control Parameters	% EHA	Multiple layer deposition	Nozzle Size	Droplet spacing
Control Film Geometry	x				
Control Uniformity (control coffee stain solute diffusion)		x			
Ensure continuous film coverage (prevent pin holes)			x		
Control printed resolution		x		x	
Control Mean Thickness			x		x

Figure 4. Simplified functional decomposition of film geometry requirements.

In order to achieve the decoupled matrix in Figure 2, two couplings with film geometry needed to be removed. The first arises from the uniformity control requirement, which is critical in crack sensitive PZT deposition. The second comes from the influence the added solvents have on pin holes in the film.

Film non-uniformities arise from evaporation driven flow of the solutes, referred to as the coffee stain effect [5]. Previous work to overcome this effect and produce uniform films had relied on droplet spacing and temperature, as well as deposition rate. Due to nozzle health concerns, the substrate deposition temperature must be maintained low enough to prevent decaping, or disruption of a stable ink meniscus on the printer nozzle. Furthermore, because the solid content was also determined by nozzle health requirements, the droplet spacing was needed as a control parameter for the final mean thickness of the film. As a result a new method of controlling film uniformity must be found for a decoupled matrix to be achieved. This was accomplished by adding a small amount, 3-6%, of a low vapor pressure solvent, 2-ethylheaxanoic acid (EHA). This allows a controllable amount of reflow on the substrate after deposition which can be used to determine the final film uniformity. Figure 5 shows the results of a temperature uniformity study that demonstrates how the optimum deposition temperature can be independent from uniformity if the concentration of EHA is varied.

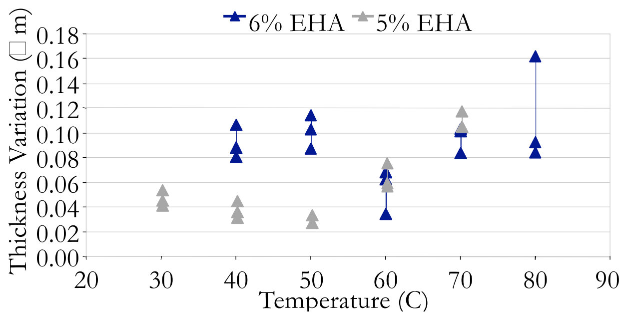
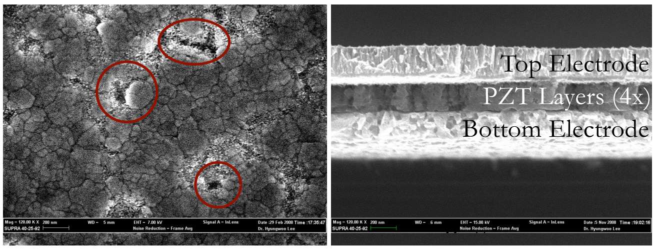


Figure 5. Thickness variation vs. substrate temperature for TIJed PZT on Pt.

The second coupling removal that was critical to the printing of PZT was between this new EHA solvent design parameter, and the requirement of a pin hole free continuous film. Experiments showed that printed films were especially susceptible to voids forming at the grain boundaries (Figure 6a). Previous sol gel work indicated that large organic molecules like EHA can impede the formation of a dense gel matrix, and hence a defect free amorphous film. As a result, a new functional requirement was needed to accommodate or overcome these defects. We hypothesized that multi-layer deposition would allow for the sealing of the pin hole defects in one layer by the material in subsequent layers. This theory was supported by consultations with experienced industry sol gel chemists. While investigation into new solvents that are less likely to produce these defects is ongoing, results of multiple layer devices have proven it to be a reliable method for sealing defects and improving dielectric properties (Figure 6b).



(a) (b)

Figure 6. SEM images of (a) voids at PZT grain boundaries of a singe PZT layer and (b) a multilayer film with no defects through the complete structure.

3 RESULTS

Using this decoupled process, and setting the process parameters in the correct order as prescribed by the lower triangular design matrix, ferroelectric capacitors were fabricated to test the piezoelectric performance of the printed PZT films. Polarization vs. electric field hysteresis measurements, along with the remanent polarization and coercive field data that they provide, are a standard way to determine the properties of a piezoelectric material. Throughout this work polarization-field and resistivity data (measured with a Radiant Technologies RT66A), were recorded to determine film quality. To test the electrical properties of the printed films, capacitor structures were fabricated with approximately 400nm thick printed PZT between two platinum electrodes. The bottom electrode on which the PZT was printed was a known effective PZT seed layer (200nm Pt / 20nm Ti / 200nm SiO2 / Si). The capacitor area was 6.25x10-4cm^2.The complete devices exhibited similar hysteresis response to the spin coated PZT based devices (Figure 7). The measure remnant polarizations were also similar, approx. 7.69 uC/cm^2 as compared to 10-20 uC/cm^2 for spin coating. Both indicate similar piezoelectric performance of the printed PZT films. Work to produce MEMS devices for d33, d31 testing is ongoing.

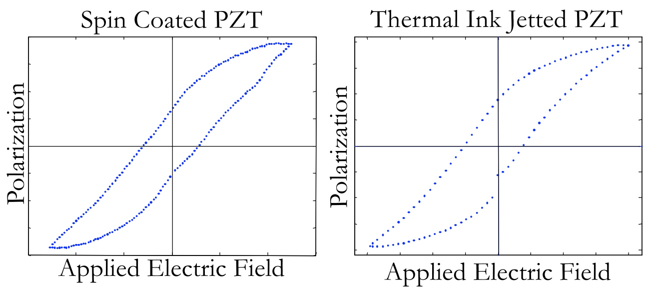


Figure 7. Polarization vs field tests for spin coated and printed PZT devices, units removed for comparison.

4 CONCLUSION

A new solution based dot-on-demand PZT deposition method has been developed using Axiomatic Design theory. This process provides increased design flexibility over the current spin coating deposition method. Ink chemistry that can be reliably jetted has been developed, and that chemistry has been decoupled from both the final film geometry and electrical performance. A method for ensuring that the optimum deposition temperature is independent of the final film uniformity for dot on demand thin films on a nonporous surface was presented. A multi-layer printing process has been presented as a means of film defect repair. Finally, ferroelectric capacitors were design, fabricated, and tested to demonstrate the viability of this new manufacturing method. This work demonstrates a robust and efficient method of depositing PZT thin films for MEMS applications that may enable a novel class MEMS device designs that were not previously possible.

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