Optimization of PZT processing using thermal ink-jet printing

by

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Submitted to the Department of Mechanical Engineering in partial fulfillment of the requirements for the degree of Bachelor of Science in Mechanical Engineering

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Abstract

Lead zirconate titanate (PZT) has been known for its strong piezoelectric property for micro-sensors and actuators. Yet, its use in MEMS has been constrained by limitations in processing PZT with current MEMS fabrication technology. The direct printing of PZT, in place of traditional manufacturing process such as spin-coating, enables on-demand deposition, allowing flexibility in thickness and shape of PZT deposition with a lower material cost. This thesis reports the thermal process optimization of the direct printing method to ensure the quality of PZT products. The pyrolysis portion of the thermal processing condition has been analyzed to show that pyrolysis performed at 360°C for 2 hours removes a sufficient amount of organic additives. There also exists a positive correlation for the duration of pyrolysis and the amount of desired perovskite phase crystal structure formed. The multi-layer printing has been experimented to remove the PZT voids in the sample. However, P-V curve or resistivity data were unable to show much improved performance. This is believed to be caused from the degradation of PZT, which were left under humid condition before the final annealing process. Further investigation will be continued to confirm the effect of multi-layer printing.

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Chapter 1

Introduction

Lead zirconate titinate (PZT) thin film has received a wide range of attention for the piezoelectric, pyroelectric, and ferroelectric properties. PZT has a very strong piezoelectric response with piezoelectric coupling coefficient nearing 0.7, which is far greater than any other materials [1]. This property enables a great opportunity for applications in micro-electromechanical systems (MEMS) such as actuators, energy harvesters, AFM cantilevers, and micro-scanning mirror devices [2, 3]. The current most prevailing methods of fabricating PZT thin films are depositing an amorphous PZT layer through sol-gel technique [4, 5]. While spin-coating is advantageous for a large-area coating, the downside is that it requires washing away most of the sol material, which becomes wasteful and expensive. Moreover, this method impose a great limit on depositing non-planar features [6].

The dot-on-demand (DOD) printing, also referred as direct printing, has been examined as an alternate method for fabricating MEMS devices [7]. However, there has not been a study made on printing active materials such as PZT. Recently, a novel method has been developed to print PZT material at a desired location identified through a computer-generated file using a thermal ink-jet (TIJ) printing head [2]. The benefits of DOD printing include low cost and flexibility. First, the low cost can be achieved through saving time and money. Because direct printing only deposits PZT at a target location, printing does not require patterned masks nor waste removing step, and also does not waste the expensive sol material. Also the level of flexibility
offered through the DOD printing is immense. Since printing is in a non-contact mode and can reach anywhere on the substrate, direct printing can fabricate features of any geometry, even out-of-plane or step features. The thickness of the film can also be controlled to vary throughout the substrate as necessary. In sum, the success of direct printing allows a higher dexterity in fabrication of MEMS device through eliminating waste producing steps and accommodating more geometries.

The work here focuses on the further optimization on thermal processing of direct printed PZT. The optimal thermal processing is essential in obtaining a high quality PZT films with strong piezoelectric properties required for MEMS.
Chapter 2

Background

2.1 Piezoelectricity and PZT

When mechanical stress is applied, certain materials have the ability to generate electric potential and vice versa. This ability is called piezoelectricity. Found mainly in crystals and ceramics, piezoelectricity can be induced with about 0.1% change of original dimension \[8\]. This makes piezoelectricity useful for detecting a fine change in dimensions. Therefore, there has been a great use of piezoelectricity in many applications including sonar, ignition systems, microphones, and scanning probe microscopies (SPM) \[9, 10\].

The piezoelectricity results from the non-uniform charge distribution of a crystal’s unit cell, which can also be viewed as a change of constitutive properties of a material \[8\]. This is due to an increase polarization when the center charge is displaced while the net charge stays neutral. For instance, when a symmetric crystal is compressed for a slight perturbation, a dipole moment is induced and the polarization increases. Figure 2-1 illustrates a compression of a crystal structure resulting a polarization. Strong electromechanical coupling is found in a perovskite phase material such as barium titante, lead zirconate, and lithium niobate. Among them, the most prominent crystal exhibiting piezoelectric property is lead zirconate titante (PZT). PZT is most renown for a high piezoelectric coupling coefficient of about 0.7 and dielectric constant about 1200 that the mechano-electric conversion can be made efficiently.
Figure 2-1: Compression of crystal structure resulting dipole moment to increase polarization [11].

The piezoelectric property of a material is characterized using a hysteresis curve. The hysteresis behavior results from a lag occurring between the field applied and the polarization. The important characteristics of piezoelectric hysteresis curve are remnant polarization, saturated polarization, and coercive field. The point at which dipoles retain the polarization is remnant polarization, and the maximum polarization point on the curve is saturated polarization. The electric field at which the polarization equals zero is called the coercive field. Figure 2-2 shows a representative piezoelectric hysteresis curve.

Figure 2-2: Hysteresis curve of PZT [12].

2.1.1 Processing of PZT

The term processing of PZT implies the three main stages: maintaining the correct stoichiometry of lead, zirconium and titanium, depositing the PZT on to the wafer,
and crystallizing PZT into a desired perovskite phase [13, 14]. The sol-gel based solution of PZT is a mixture of lead acetate, zirconium-tetra-n-butoxide and titanium-tetra-iso-propoxide in 2-methoxyethanol solvent [15]. Once the ink solution is diluted and deposited on to a wafer, there are three thermal processing steps needed to be completed for PZT: drying, pyrolysis, and annealing. After drying the solution on the substrate as a thin film of gel, the metal-organic additives need to be pyrolyzed. Heating the substrate up to 360°C for a specified period of time annuls the organic material, leaving only metal molecules in a form of amorphous film. Finally, the amorphous film crystallizes into a sample of multiple microstructures when placed at 650°C chamber for annealing.

### 2.1.2 Crystal Structures

The annealing of a material indicates crystallizing the amorphous PZT deposit into a structured form. Only after crystallized, PZT exhibits the piezoelectric behavior.

Annealing process may transform the PZT into two distinctive crystal structures, perovskite and pyrochlore. Thermal process can also change the final crystal structure of the PZT samples [16]. These structures differ in their lattice orientation as shown in Figure 2-3 and 2-4. This difference in lattice orientation distinguishes the two structures since perovskite has [1 0 0] and [2 0 0] orientation while pyrochlore has [1 1 0] orientation. As mentioned earlier, perovskite phase is the only desired crystal structure which has the ideal piezoelectric properties, and the knowledge of lattice orientation of two crystals enables determining what crystal phases are present in PZT after annealing [17].

### 2.2 Thermal Inkjet Printing

#### 2.2.1 Printer

The thermal ink-jet printing system shown in Figure 2-5 deposits droplets of picoliters at selected locations using the inkjet printing technology developed by Hewlet Packard
Figure 2-3: Symmetric and asymmetric form of perovskite crystal structure [18].

Figure 2-4: Pyrochlore crystal structure. [19]

(HP). Each ejection of droplets is controlled by the tip controller, which connected with motion stage, can freely print the droplet of desired volume at the locations specified. The tip consists of multiple nozzles for dispensing the ink contained inside the tip. The tip is also replaceable for various sizes of droplets and voltages required. Both the tip and its controller are designed and manufactured by HP and sponsored for the further development of PZT printing technology.

The printing is possible through a rapid increase in temperature leading a pressure surge which forces a droplet out through the nozzle. Applying the voltage to the resistive heater increases the temperature to 330°C at the tip of the nozzle, and this rise in temperature evaporates less than 1μm layer of ink. The evaporation leads to an increase in the pressure enough for pushing the ink out of the nozzle, which then forms a droplet. Sensitive to printing parameters, the tips with slight different
configuration nozzle or heater create a specific size of droplet, ranging from 1 to 300pl when operated with 20kHz [15].

The integrated system includes the tips, TIPS controller, Primatics PLG160 motion stage, and a camera all in a clean room environment, accomplished by situating the whole system inside a glass box. The stage can travel 400mm in both x and y direction with ± 7.0 μm accuracy and is controlled using a software developed by HP or MNSL (Micro Nano Systems Laboratory at MIT) [15]. The camera is attached to the moving arm and is used for aligning a substrate with the tip once the offset between the camera to the tip found. The software for the printer loads the sets of coordinates to eject in text file format and controls the motion stage accordingly. The pattern text file can be generated using a math tool such as Matlab.

### 2.2.2 PZT as Ink

For the use of TIJ printing, sol-gel based PZT has to be diluted with other solvents. The solvents added were 2-methoxyethanol, 2-ethylhexanoic acid, and isopropanol [2]. The ratios are determined such that the ink is soluble and has characteristics necessary to be printable [15]. Numerous ink mixtures were tested for the characteristic test and the percentages of each solvent addition was determined accordingly [2].
Chapter 3

Experiment

The printer using thermal ink-jetting technology is already set-up at the Micro-Nano Systems Laboratory (MNSL) at MIT with all equipments necessary [20]. HP provided the thermal inkjet picofluidic system (TIPS), which is the hardware for the actual printing, and Printing of Electronic Materials (POEM), which is the software that controls TIPS. The MEMS printer has a printing head with nozzles of various droplet sizes. The entire system consists of the TIPS printer, X-Y motion stage where TIPS is mounted on, a camera used for aligning the substrate, and a pressure controller to maintain a certain back pressure inside the nozzle. The software that controls printing was developed by MNSL. Matlab generated input pattern files of droplet spacing and an edge offset are taken by the software.

For the experiment, HP printer tip of number 12 was used. Tip 12 has nozzles that can print 35 pl per droplet. The ink is a diluted solution as specified in the previous work [21]. This is determined to be the optimal solvent ratio with maximum PZT that is printable, so same ink chemistry was kept [15]. The printing condition variable parameters, such as droplet spacing and substrate temperature while printing, are determined experimentally after testing a number of samples as shown in Figure 3-1.

Each strip on the sample substrate is printed with a different droplet spacing, ranging from 20μm to 75μm. Also a number of substrates are printed at a temperature between 55°C and 70°C. The optimal condition is found to be printing with 65μm pitch length at 65°C to ensure a PZT film with maximum thickness without any
cracks.

3.1 Effect of Thermal Process

Once the thermal ink-jetting technology was proved that it could print PZT on to the substrate [2], the optimization of parameters became necessary to achieve the high quality of piezoelectric properties. The current printing process results in a relatively low remnant polarization value compared to the spin coated PZT. The higher remnant polarization is desired in piezoelectric hysteresis curve for the higher mechanical to electrical conversion as PZT usage is intended.

The void and cracks are the reminiscence of organic solvent added in diluting sol gel of PZT to make ink-jetting possible. In general, there are three phases of thermal process for PZT: drying, pyrolysis, annealing. The pyrolysis is the second step, and is performed to remove the organic material in PZT. When there is still organic material present in PZT pattern after the pyrolysis step, the remaining organic material leads to a formation of voids during the crystallization of PZT.

The experiment has been designed to test the effect of pyrolysis time on the level of organic material present in the sample after pyrolysis.
Using the printing parameters, the equipments and the technique described earlier, the 17 square samples with size of 10mm by 10mm are printed on a Pt coated silicon wafer substrate as shown in Figure 3-2. The entire wafer is dried for 1 hour at 235°C on a hot plate. Then the wafer are broken into the square samples using a sharp blade. Enough pressure applied with a sharp blade on a silicon wafer can break the wafer with relatively straight edges. Of the 17 samples printed, six square samples are acquired after this process. For the six samples, each was treated with a different duration of pyrolysis. Sample 1 through 6 was pyrolized for 2, 10, 20, 30, 60, and 120 minutes respectively at 365°C on a hot plate. Once the sample was on the plate, 200°C/hr ramping of temperature was used to bring the temperature up to 365°C. On the hot plate, the samples were placed inside of a glass petri dish with a cover. After all samples have been pyrolized, they are annealed at 600°C in a vacuum environment.

Figure 3-2: Diagram of a wafer with 17 square samples to be printed generated by Matlab.
3.2 Effect of multi-layer printing

The effect of multi-layer is tested by printing the normal single layer as a control group, and printing second and third layer to a number of samples on top of the bottom layer already printed. This can be done by printing one wafer since a whole wafer contains 42 large samples that can be evenly distributed between one, two, and three layers. The experiment is designed such that the number of layers placed for samples are determined accordingly with the types of electrodes placed later on the top of PZT layer. The experiment has 4-6 samples to be printed for each layer groups per one type of piezoelectric device. The schematic of layers printed on the wafer is shown in Figure 3-3 and the overall picture is shown in Figure 3-4.

![Figure 3-3](image)

Figure 3-3: Diagrams showing the spots to be printed for first, second, and third layer.

The total amount of ink that can be deposited is limited for a certain fixed area from the result of temperature-pitch test. This is because an additional amount of ink will make the film too dense and eventually crack. To maintain the same amount of PZT placed on the sample throughout the total number layer of prints, the number of droplet per area is calculated. Then the number is divided by 2 or 3 regarding 2 or 3 layer prints intended for the sample. Finally, the droplet spacing required to achieve the calculated droplet per area is determined. The calculated droplet spacing is $91 \mu m$ for the 2 layer print, and $113 \mu m$ for the 3 layer print.

After each layer of the print job, 2 hours of pyrolysis at 365°C was performed using the same 200°C/hr ramping rate. After the pyrolysis, the next layer pattern has been
Figure 3-4: Schematic of wafer with samples showing 1, 2, or 3 layers to be printed.

printed on top of the same wafer. Aligning the wafer, printing and pyrolyzing was repeated for three times for each wafer tested. Once all three layers have been printed and pyrolized, the substrate was put in a vacuum environment for final thermal process of annealing. After the thermal processing, top electrodes are deposited on top of the processed PZT as a final step in fabricating the piezoelectric device.
Chapter 4

Results and Discussions

The goal of this study is to improve the polarization performance of thermally ink-jetted PZT film. The pyrolysis time of the thermal process has been varied to find the optimal duration.

4.1 Duration of Pyrolysis

As the pyrolysis step is removing the organic materials before the crystallization, Fourier transform infrared spectroscopy (FTIR) is performed to see the level of organic material left in the films after the pyrolysis. Figure 4-1 shows the data from the analysis of FTIR for samples as deposited, after drying phase is completed, and after drying and pyrolysis phase are completed. Although not completely removed, the level of organic material in the film treated for 2 hours of pyrolysis at 360°C is minimal compared to the film with no or only drying phase of thermal process performed. The duration of pyrolysis for more than 2 hours may eventually remove the organics completely, but such procedure would lengthen the entire fabrication process significantly.

For six thermally annealed samples, x-ray diffraction (XRD) is performed to determine the crystal structure. By determining the angle at which x-ray beam diffracts, XRD shows the crystal structures existing in the sample. Figure 4-2 below shows the result of XRD on all 6 samples with PZT pyrolized at 365°C for durations of 2, 10,
As Deposited

After 2hrs at 260°C Under Vacuum

After 2hrs at 360°C

Figure 4-1: FTIR of heat treated printed PZT thin film samples to see the level of organic present in the samples of no thermal process, drying phase complete, and drying and pyrolysis phase complete.

20, 30, 60, 120 minutes. The rest of the thermal process, drying and annealing, has been performed equally throughout the samples.

Figure 4-2: X-ray diffraction of PZT pyrolized for durations of 2, 10, 20, 30, 60, 120 minutes. Data shown from sample 1 at the front to sample 6 at the back.

The comparison of the samples in Figure 4-2 makes it apparent that the regardless of the duration of pyrolysis, all film do not contain any pyrochlore phase, and all films have pure perovskite structure. The difference, however, occurs in the intensity of the [1 0 0] and [2 0 0] phase at 22° and 45° two-theta angle. From the figure, there is a clear increase in the intensity of the crystal structures [1 0 0] and [2 0 0] with the increase in the duration of pyrolysis. This result implies that there exist a
correlation in the amount of perovskite crystals present in the sample with the longer pyrolysis time. It is also noticeable that the level of perovskite remains the same for sample 5 and 6 while there is steep increase in the intensity of perovskite phase for samples 1 through 5. This result indicates that the pyrolysis duration does not affect crystallization beyond 60 minutes of pyrolysis.

The comparison for XRD of ink-jet printed film pyrolized for 60 minutes and spin-coated sample is shown in Figure 4-3. The close match of the peaks between the two samples suggests that the printing can indeed achieve the same level of material microstructures as in spin-coating method.

![X-ray diffraction data of sample pyrolized for 60 minutes compared with XRD data of spin-coated sample.](image)

Figure 4-3: X-ray diffraction data of sample pyrolized for 60 minutes compared with XRD data of spin-coated sample.

The resulting polarization voltage hysteresis (P-V) curve of sample with pyrolysis duration of 2 hours is shown in Figure 4-4 (b). There is a significant improvement in extending the hysteresis curve with high saturated polarization with longer duration of pyrolysis when compared to Figure 4-4 (a), which was obtained under the standard pyrolysis of 8 minutes. Yet, the remnant polarization value is still relatively low compared to the spin-coated film of Figure 4-4 (c). The following section discuss the results obtained in attempts to redress this issue.
4.2 Multi-layer Printing

As PZT is deposited in ink droplets in a heavily diluted solution, PZT sol-gel material may not be free from many voids. With speculation that this void is a possible cause of the low resistivity for the piezoelectric film, an experiment is designed to redeem a possible void and ensure uniform and dense PZT dispersion.

![Figure 4-5: Comparison of (a) single layer and (b) multi-layer printing to ensure filling possible PZT voids.](image)

The printed film with one layer of PZT has a thickness of about 0.3μm when profilometry was performed after the pyrolysis [?]. The XRD data in the previous section indicate that the crystal structure of PZT are well formed on the substrate. However, these results only confirm that the ink containing PZT is deposited uniformly, and does not conclude that PZT is deposited densely on the substrate. Incomplete
removal of organics may have left some voids among PZT particles when the ink solution is dried, which would lead to creating defects in the grain boundaries. Evidently, in scanning electron microscopy (SEM) image of one layer printed sample in Figure 4-6 (a) shows many inter-boundary defects. In contrast, SEM image of a sample with two layers of prints in Figure 4-6 (b) shows relatively immaculate PZT layer throughout the intergranular sites.

Figure 4-6: SEM images of (a) single layer printed sample with vacancy defects at grain boundaries, and (b) double layer printed sample with uniform PZT layer throughout the intergranular sites.

Next, the piezoelectric properties of one layer and multi-layer samples are compared. The P-V curves in Figure 4-7 exhibit characteristics of low remnant polarization and saturation point regardless of number of layers printed. This result is startling as the minimum performance of the piezoelectric device was expected to be similar to one layer printed sample with P-V curve as shown in Figure 4-4 since the same condition of one layer printing was applied.

Relatively poor piezoelectric performance throughout all samples may be due to aging of PZT solution, as at least one study has shown that aging of sol-gel films reduce the piezoelectric coefficient within minutes of aging time [22]. The thermal processing of the samples was delayed for several days before anneal was done once pyrolysis performed, and it is possible that such delay caused significant decrease in piezoelectric response. There has been a number of samples with similar values to
Figure 4-7 (a) for single layer print, while few multi-layer print samples reached higher saturation point values such as Figure 4-7 (b). However, in those case, the leakage current was substantial that not much can be concluded whether the multi-layer prints achieved improvement in piezoelectric property of the devices.

Figure 4-7: P-V curve comparison of (a) single layer print that has low saturation point and (b) double layer print with relatively high negative saturation point while most of the current is leaked.

In addition to P-V curves, the resistivity values of working devices were measured for each layers of samples tested in Figure 4-8. Despite the low percentage of working devices and poor P-V curve data, the resistivity values are compared for each layers of prints to see if there seem to exist any correlation. From the plot, the mean resistivity values are $9.178 \cdot 10^6 \Omega cm$ for monolayer and $9.73 \cdot 10^6 \Omega cm$ for double layer prints when 5V were applied to each samples. This value is far smaller than previously reported resistivity of $4.5 \cdot 10^{10} \Omega cm$ of the same fabrication condition for regular one layer printing, that there seem to be great loss of PZT response due to aging [?]. Even yet, unfortunately, all triple layer printed samples either failed to work or proved to have only 2 layer printed. This was confirmed using the profilometer to check the thickness of PZT layer, knowing that all devices should have equal thickness of PZT layer since overall, constant volume of ink was deposited per sample. The single and double layer prints have similar resistivity values, meaning that no change has occurred whether single or double layer print was adopted. Samples that were supposedly triple layer
print, but only had 2 layers printed exhibit resistivity of $5.75 \times 10^7 \Omega \text{cm}$, which is slightly greater than the other two groups, but there is little evidence that there is any correlation. As whole, resistivity data seem to provide little information since the standard deviations are about the same if not greater than the mean resistivity values, and also statistically insignificant since the the number of devices working for data collection was few.

![Figure 4-8: The resistivity values of one, two, and three layer prints plotted, which mean resistivity values denoted with *.

The multi-layer print experiment performed thus far may have had little impact on improving piezoelectric property. The biggest issue in the experiment was that aging of PZT may have resulted in weak piezoelectric response. To remedy this issue, one suggestion for the future experiment is to execute all thermal processing in rapid sequence.

One variation of the experiment may provide more useful data with improved the performance. This is by finding the maximum volume of ink solution that can be deposited for each number of layers, and using that droplet spacing rather than maintaining the constant volume of ink solution. The constant volume of ink was maintained with assumption that more ink on the fixed area will make PZT too dense that it would crack. However, because each layer is pyrolized after its deposition, the
maximum volume of ink that can be dropped may be per layer of pyrolysis, and not per area of substrate. Trying to maintain the constant total volume of ink used, the amount of ink solution deposited at each time for the multi-layer sample reduced significantly. The reduced amount may be too sparse when deposited, and result in drops of PZT formation rather than an uniform film.
Chapter 5

Conclusions

The recently developed thermal ink-jet PZT deposition method shows several advantages over the traditional spin-coating method including low cost, flexibility and film formation on non-planar surfaces. MIT has demonstrated successfully that PZT sol can be ink-jetted to a thin PZT film [?]. However, the piezoelectric performance measured using polarization voltage hysteresis curve lacked in the level of remnant polarization and saturated polarization.

In order to investigate and remedy the issue, the pyrolysis portion of the thermal processing conditions has been studied extensively. From the pyrolysis duration experiments, Fourier transform infrared spectroscopy shows that most organics in the sample were removed which may lead to forming undesirable voids otherwise. A positive correlation of an amount of perovskite and the duration of pyrolysis is also observed from x-ray diffraction test. There are occasions that a single-layer printing seem to result voids in the PZT samples when examined using a scanning electron microscope. Multi-layer printing has been tried to conceal the voids by overlapping two or three layers of prints. Nevertheless, P-V curve or resistivity data are less successful in showing much improved performance. This is believed to be caused from aging of PZT. Further investigation should be continued to confirm the effect of multi-layer printing.
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