Ink Jet Printing of PZT Thin Films For MEMS Applications

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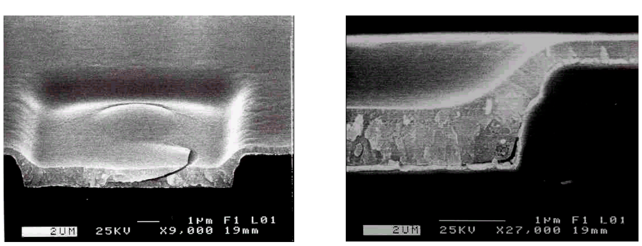
Abstract

Thermal ink jet (TIJ) deposition of lead zirconate titanate (PZT) thin films via a modified sol-gel was recently reported by our group [1-2]. Despite the strong piezoelectric performance, the use of PZT in microelectromechanical systems (MEMS) has thus far been limited due to the lack of process compatibility with existing MEMS manufacturing processes. Digital fabrication of PZT thin films eliminates the need for photolithographic patterning and etching, a major source of process incompatibility. Furthermore, direct printing of PZT films enables new device designs by allowing controlled deposition over non-planar topographies, and the fabrication of devices with varying thickness, neither of which can be accomplished with a conventional spin coating process. This paper reports conditions of deposition and crystallization for PZT thin films via thermal ink jet printing. Included are details of the solution chemistry developed, printing conditions required for MEMS quality films, and thermal processing parameters that enable a highly piezoelectric crystal structure.

Introduction

The high degree of piezoelectric and ferroelectric coupling in perovskite phase PZT make it an attractive material for use in MEMS. For that reason, many groups have worked to integrate thin film PZT into a wide range of devices including: actuators, energy harvesters, resonators, pressure sensors, pumps, nano-positioning stages, and MEMS switches [3-5]. Processing of thin film PZT is not readily compatible with existing MEMS fabrication processes, however, and significant constraints must be overcome to successfully fabricate devices based on thin film PZT.

While some recent work has demonstrated novel ways of forming sol-gel based films, spin coating remains the dominant method of forming thin film PZT for MEMS. Spin coating is not the most flexible fabrication method for PZT-based MEMS, but it is the easiest to integrate with a standard MEMS process flow and is therefore the most common deposition method at the present time. Not only is spin coating inherently wasteful of the expensive and difficult to manufacture sol material, but it prevents the deposition of PZT films on or around out of plane features.



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

Figure 1. SEM images of poor step coverage of spin coated PZT films [6].

Figure 1 shows the cracking and thinning that occurs when PZT is spin coated over a step about 2μm in height [6]. The sol is also very sensitive to other deposition parameters, including humidity, particle contamination, and substrate condition and as a result device yields are often very low. Reliable deposition requires great care and often a good deal of experience processing PZT thin films. Furthermore, patterning of PZT films is a challenging process, as wet etches tend to have significant undercut problems, and dry etches require multiple masking steps due to incompatibility with photoresists and poor selectivity. Consequently a flexible new approach is needed to easily and effectively deposit and pattern high quality PZT thin films in MEMS applications.

In recent years dot-on-demand (DOD) printing has been studied as a robust, flexible, and inexpensive method of material deposition for MEMS [7]. Some of the benefits of DOD printing for MEMS can be summarized as follows. 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 faster, more reliable, 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 based 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 [8]. 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 disruptive impact on the way PZT based MEMS structures are designed in the future.

In order to achieve the potential benefits of direct printing of PZT, three process requirements must be addressed. First, the ink must print reliably and repeatably, forming discrete drops without clogging. Second, the geometry of the printed film must be highly uniform and controllable. Finally the properties of the printed PZT film, both mechanical and electrical, must be comparable to those of the spin coated PZT film

Solution Chemistry

The solutions developed for this work were based on two sol-gel formulations, both of which were Mitsubshi 50/49 PZT. The first (A6) is a 2-methoxyethanol based sol and the second (E1) is based on butyl alcohol and propylene glycol. As purchased, this sol is 85%(wt) solvent and 15%(wt) a mixture of lead, zirconium, and titanium oxides. Dilution is required to control the evaporation rate of the ink and prevent clogging of the printer nozzle. Combinations of 2-methoxyethanol, isopropanol, and 2-ethylhexanoic acid were added to the sol to created the diluted PZT inks. 2-methoxyethanol is the same solvent used in the manufacture of the PZT sol and helps to control hydrolysis. 2-propanol is a common mild solvent with a low boiling point that is known to be reliable in thermal inkjet printing. Finally 2-ethylhexanoic acid was used to control overall ink volatility as it has a high boiling point and is also known to be compatible with thermal ink jet.

To prevent clogging of the printer nozzle and defects in the film, three sources of particle contamination were addressed and controlled. First, to eliminate external particle contamination each ink was filtered with a 0.45µm PTFE syringe filter and deposition was carried out in a sealed glove box filtered with 99.99% efficient removal of 0.2µm and larger airborne particles. Particle formation during the printing process was also a concern due to the decomposition of the metal-organic molecules during the thermal event. Throughout this work, over thirty ink chemistries, with dilution levels ranging from the as purchased 15%wt of metal oxides down to 2%wt, were tried and empirically the appropriate levels of dilution were observed. Table 1 shows observations of the concentration required for reliable printing for different nozzle sizes. Finally, preventing clogging also requires controlling the evaporation rate of the ink such that a stable meniscus is formed at the nozzle. If the solvent evaporates too quickly, metal oxide particles are built up inside the nozzle and firing chamber and concentrations that exceed stable printing requirements result. This was prevented by maintaining a low rate ink flow through the nozzle at all times.

Table 1: Maximum allowable metal oxide concentrations for reliable printing with different droplet sizes.

Nozzle size, droplet volume (pl)	Maximum Acceptable Concentration (%wt)
180	15
80	4.7
35	2.3

To ensure predictable substrate wetting and stable droplet formation, certain dimensionless numbers known to govern drop on demand printing dynamics were calculated and observations were made to ensure the accuracy of the predicted results. The forming of a film on a substrate is characterized by the Bond number, which for these droplet sizes will be no larger than approximately $4 \cdot 10^{-3}$. As for most ink jet printing, the Bond number for this work is sufficiently low to ensure the film shape on the surface will be dominated by surface tension, forming spherical caps for single drops and cylindrical slices for a printed line. Figure 2 shows an image of a spherical cap of 2-methoxyethanol forming on a platinum substrate during contact angle measurements. The contact angle was measured between 10°-12°, although accuracy can not be guaranteed for measurements at such low angles. Previous work has shown that the ratio of the Reynolds number to the square root of the Weber number (referred to as Z) dictates the dynamics associated with droplet formation [9]. Most dot-on-demand inks have $1 < Z < 10$. Viscous dissipation can prevent droplet ejection for $Z < 1$ and for $Z > 10$ multiple drops, or even a constant stream, can result. Z is estimated to be 1-3 for the smaller nozzles sizes used in this work.

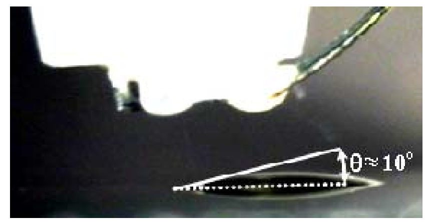


Figure 2. Advancing contact angle of 2-methoxyethanol on platinum.

Controlling Film Geometry

This work characterized the resolution limits of two methods of printed PZT patterning. The first involved printing into a predefined mold and the second, free printing method, was based only on droplet size and wetting angle with the substrate. Printing into a mold to pattern the PZT removes the coupling between pattern resolution and film uniformity that occurs due to the dependence both parameters have on film evaporation rate. When using a mold, droplet spreading and solute diffusion can be independently controlled. Therefore the evaporation rate can be very low, allowing for highly uniform films without a loss of resolution. Figure 3 demonstrates the resolution achieved for cast PZT films. In general, the in plane geometry PZT films printed into lithographically pattern molds was controlled to the accuracy of the mold itself. Thickness uniformity was also good: for printed films with a bulk mean thickness of 147 nm, the RMS roughness was 9 nm.

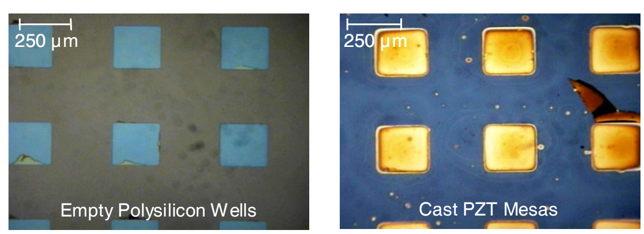


Figure 3. Thermal ink jet printed PZT into preformed polysilicon molds.

Mold-free printing for MEMS is attractive because the mold removal step after printing adds complexity to the process. However, printing without a mold makes it more difficult to achieve the geometric control required. The diffusion of solutes towards the film edges during solvent evaporation known as the coffee stain effect can lead to significant non-uniformity [10]. Figure 4 shows how early printed PZT films exhibited this effect.

In order to overcome this non-uniformity a study was conducted to determine the ink volatility and substrate temperature required to achieve the optimum level of spreading and diffusion.

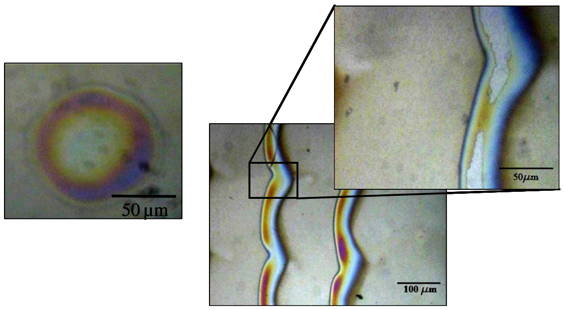


Figure 4. The coffee stain effect in dot on demand printing of PZT

Controlling the thickness uniformity of free printed PZT films requires controlling the amount of diffusion of the metal oxides towards the film edges that can occur as the volatile solvents evaporate. It was observed that ink chemistries with an excess of 2-methoxyethanol always exhibited significant metal oxide diffusion flow, and therefore substantial non-uniformity. Given the relatively high levels of dilution required, isopropanol was selected to make up the bulk of the ink given that it had a lower boiling point and would evaporate more quickly controlling diffusion of the oxides. It was found that inks that were made up of 50% isopropanol and 15% PZT sol would both print reliably as required by the clogging constraints, and evaporate quickly enough to prevent significant solute diffusion.

To achieve highly uniform films, precise control over evaporation rate is required. This was accomplished by adjusting the substrate temperature. However, the range of substrate temperatures available is limited to approximately 70°C to prevent clogging as a result evaporation of ink from the printer nozzle. Due to this limit, the volatility of the ink was controlled to bring the substrate temperature into the specified range. This was accomplished using the remaining 35% of the ink which was comprised of a mixture 2-methoxyethanol and 2-ethylhexanoic acid. The boiling point of ethylhexanoic acid is significantly higher than the other solvents (228°C), and therefore the concentration of ethylhexanoic acid was used to control the overall ink volatility, with anhydrous 2-methoxyethanol making up the remainder of the ink. Figure 5 demonstrates the control over mold free film geometry that can be achieved by adjusting the substrate temperature when the ink volatility is set at an acceptable level.

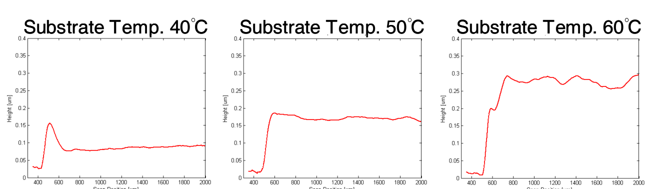


Figure 5. Profilometry of PZT TIJed at different substrate temperatures. Ink composition: 6% EHA, 15%PZT sol-gel, 50%IPA, 29%ME.

In order to determine the optimal substrate temperature for this ink (6% EHA, 15%PZT, 50%IPA, 29%ME), 15 samples were prepared at different temperatures. The results of the study clearly showed an optimum deposition temperature at 60°C. However, to ensure that clogging of the nozzle due to excessive solvent evaporation would not be a problem, it is desirable to reduce the substrate temperature during deposition. A new ink was prepared made up of 5% EHA, 15%PZT, 50%IPA, 30%ME, and the study was conducted again. The results of the second uniformity vs. substrate temperature study show a reduction in optimum deposition temperature from 60°C to 50°C (Figure 6). These two studies demonstrate the effectiveness of using substrate temperature to control deposition uniformity, and using ink volatility to ensure that the substrate temperature doesn't cause clogging.

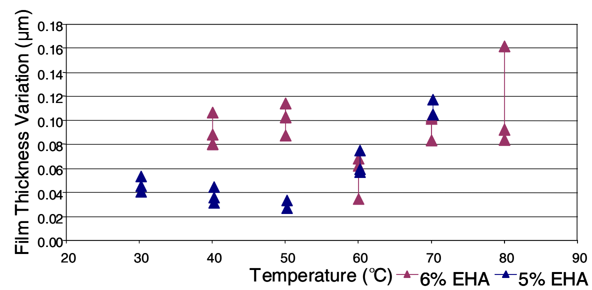


Figure 6. Study of thickness variation vs. substrate temperature for thermal ink jetted PZT on Pt.

After optimization of solution chemistry and substrate temperature, PZT films of between 100 - 500 nm thickness with less than 40nm variation could be printed with a droplet size of 80pl. Spot sizes as small as 43µm were achieved with a 10pl droplet of PZT ink deposited on Pt substrate. The edge variation of printed lines was controlled within +/- 10µm. An example of a free printed PZT device is shown in Figure 7.

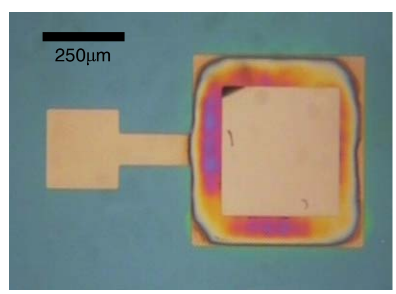


Figure 7. A ferroelectric test capacitor with an thermal ink jetted PZT layer integrated.

Thermal Processing Of Printed PZT Films

There are three steps to properly crystallize a sol gel based PZT thin film into a piezoelectric, perovskite phase. The first is the drying of the solvent in which the metal organics are dispersed. The second is the decomposition of the metal organics into an amorphous film. Finally the film must be annealed into a perovskite structure. The thermal processing of the early printed PZT films was determined based on manufacturer's recommendation and authors' experience in processing spin coated films of the Mitsubshi A-6 50/49 PZT sol gel (Table 2). With the same thermal treatment, the printed PZT showed very poor piezoelectric performance and low film resistivity. At 5V the film resistivity measured was 4.5•10^{10} Ω•cm, however at 15V the resistivity dropped to 8.3•10^{2} Ω•cm. In order to improve piezoelectric performance, the drying and pyrolysis steps were lengthened to ensure complete evaporation of the solvent and removal of added organics prior to annealing. FTIR analysis after 2 hours of pyrolysis showed the removal of a significant fraction of the organic material.

Table 2: Thermal processing conditions for spin coated PZT.

Processing Step	Temp. [°C]	Time [min]
Dry	260	3
Pyrolysis	360	8
Anneal	650	20

Under this new thermal treatment the dielectric properties of printed films were significantly increased. At 5V the film resistivity measured was 6.4•10^{10} Ω•cm, and at 15V the resistivity was still 6.2•10^{10} Ω•cm.

An X-ray diffraction study was performed after annealing to investigate the influence of pyrolysis annealing times on crystallization. All films had a pure perovskite, pyroclore free, crystal phase. The pyrolysis study further showed that the amount of crystalline PZT increases significantly with pyrolysis time, a result which we attribute to a more complete removal of organic material from the films. The anneal study showed that the crystallographic orientation of the film can be controlled between a (111) preferred orientation at short anneal times (1-4min) to (110) at longer anneal times (30min and greater). This is consistent with previous sol-gel work.

Simple capacitor test devices were fabricated with approximately 400nm thick printed PZT between two platinum electrodes. The bottom electrode on which the PZT was printed was platinum (200nm Pt / 20nm Ti / 200nm SiO2 / Si). Despite optimization of thermal processing conditions, many test devices still exhibited poor resistivity and low remanent polarization. It is believed that the relatively low polarization was due to defects/voids forming at the grain boundaries (Figure 8). These defects are likely due to incomplete removal of the organics which were added when the sol was diluted for jettability. The resulting voids after annealing reduce both resistivity and remanent polarization.

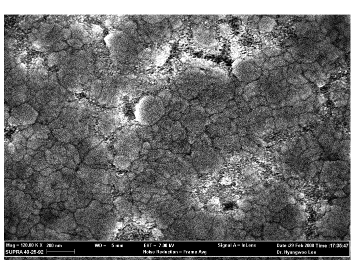


Figure 8. SEM image of printed PZT film showing intergranular defects.

In order to reduce the effects of the voids and improve the film properties, test devices were manufactured with extended annealing time (180min) in order to increase the grain size and reduce the effect of intergranular defects. The resulting performance was significantly improved. The remanent polarization was increased from approximately +/- 5µC/cm^2 to approximately +/- 20µC/cm^2 (Figure 9). This level of remnant polarization is comparable to spin coated PZT films produced under similar processing conditions.

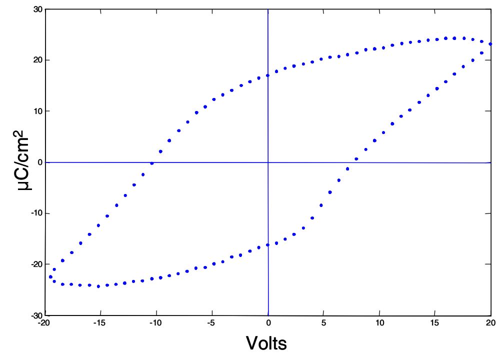


Figure 9. Piezoelectric response of a thermal ink jetted PZT test device. Anneal time 180min.

Conclusion

A new solution based DOD PZT deposition method has been developed that provides increased flexibility and lower manufacturing costs over standard deposition methods. Ink chemistry that can be reliably ink jetted has been developed and optimized; printing conditions are optimally determined; the appropriate thermal processing parameters are identified and characterized to ensure a high resistivity and good perovskite phase of crystallized PZT films after annealing. This required implementing particle control measures, determining the right amount of dilution required to control droplet formation, and ensuring minimal evaporation at the printer nozzle.

Analysis was performed on droplet formation dynamics and on substrate wetting conditions. A method for determining the optimum deposition temperature for dot on demand printing of highly uniform thin films on a nonporous surface was presented. Furthermore, a method for creating and using cast features as mold for thin film deposition was developed. Printing of cast films was demonstrated to have significantly improved resolution and uniformity over standard drop on demand deposited films.

Finally the thermal processing conditions were determined for the annealing of printed PZT films into pure perovskite phase poly crystalline films. Pyrolysis time was investigated as a means for controlling film crystallization.

The results from this work provide a robust and efficient method of depositing PZT thin films for MEMS applications and enables novel MEMS device designs that were not previously possible.

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