DIRECT PRINTING OF LEAD ZIRCONATE TITANATE THIN FILMS FOR MICROELECTROMECHANICAL SYSTEMS

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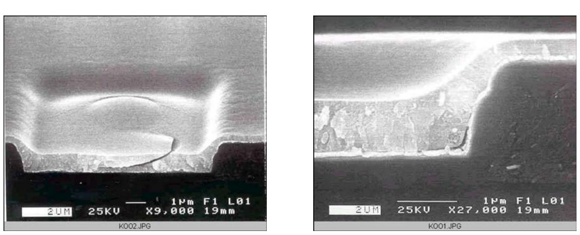
ABSTRACT

This paper reports a new method for depositing lead zirconate titanate (PZT) piezoelectric thin films via thermal ink jet (TIJ) printing of a modified sol. Direct printing of PZT eliminates the need for photolithographic patterning and etching, as well as allows for controlled deposition over non-planar topographies which cannot be accomplished with conventional spin coating process. It has been demonstrated that jetting drops between 10 pl - 200 pl can produce PZT films with acceptable uniformity for microelectromechanical systems (MEMS) in thicknesses between 100 nm and 400 nm. With a 10pl droplet, the spot size of the deposited solution on top of a platinum surface is approximately 43 µm and the edge variation is +/- 10µm. It has also been shown that edge variation can be improved to less than +/- 1µm by constraining fluid flow with a patterned barrier. These results suggest direct printing of PZT can provide a path to greater flexibility in both piezoelectric MEMS device design and process integration.

1. INTRODUCTION

It is well known that the strong piezoelectric and ferroelectric coupling present in perovskite phase PZT make it an attractive material for MEMS based sensors, actuators, and energy harvesters [1-3]. However, the use of PZT in MEMS has thus far been limited due to a lack of process compatibility with existing MEMS processing techniques. Significant work has been done towards developing reliable PZT deposition methods and integrating those methods with established semiconductor manufacturing processes [4].

Sol-gel processing has been the most favorable technique for PZT MEMS. However, the spatial distribution of the thickness of a spin coated PZT layer is affected by the undulation of the underlying layer. As the flow of the sol film crosses a step in the underlying substrate during spinning, it suffers unwanted thinning or cracking. Figure 1 shows scanning electron microscope (SEM) pictures of the typical poor step coverage cases of sol-gel processed PZT [5]. The cracked or thinned film may cause current leakage or electrical shorting which deteriorates the functioning of the PZT film. This coupled nature of sol-gel processing of PZT imposes constraints on the design of PZT MEMS devices.



(a) cracking (b) thinning & high stress

Figure 1: SEM images of spin coated sol-gel PZT films.

In recent years ink jet printing has been shown to be a promising deposition method, which has the potential to increase manufacturing flexibility and ease process integration. Ink jet printing of electronic circuitry, MEMS devices, and solutions of PZT powders, has been demonstrated [6]. This research demonstrates the printability of sol based PZT inks as well as the integration of a printed PZT layer into a ferroelectric capacitor.

Direct printing of PZT has several advantages over current spin coating methods. First, by placing the sol based ink only where needed, direct printing enables PZT deposition without requiring patterning. This eliminates the need for photolithography, etching or any type of masking processes, which shortens the manufacturing lead time and enables the possibility of rapid prototyping of PZT based devices. Direct printing also leads to a substantial reduction in the amount of sol consumed during deposition which, in combination with the removal of photolithography and etching, significantly reduces manufacturing costs. Finally, this deposition method offers increased flexibility over current methods by allowing for controlled deposition over non-planar topographies. This provides an improvement in step coverage over spin coated films, enables uniform deposition on to and around large out of plane features, and assures good performance of PZT.

2. INK JETTING APPARATUS

All of the devices for this work were deposited using a Printing of Electronic Materials (POEM) thermal ink jet printing system developed by Hewlett Packard (HP). The POEM relies on the Thermal Ink Jet Pico-Liter System (TIPS) for liquid droplet deposition. The TIPS is fixed to two linear motion stages (Primatics Inc.) designed for semiconductor wafer testing and fabrication, which have a repeatable accuracy of +/- 1 µm. Substrate temperature can be controlled between room temperature and 100°C using a heated vacuum platen.

The TIPS has the flexibility to control the droplet size, jetting energy and frequency, as well as the temperature of the jetted fluid. Power for the TIPS system is provided by a Sorenson digitally controlled power supply. Droplet size is controlled by the geometry of the nozzle and design of the ink jet head and ranges between 10pl and 200pl in this work.

Control of the motion stages and synchronization of the droplet deposition was accomplished using a motion controller from Galil Motion Control Inc. The digital patterns were interpreted, and the control signals sent to the motion controller, by software developed in the Micro-Nano Systems Lab for this research.

The current software revision sends simple position and trigger commands that place individual drops, or burst of drops, at specific locations specified by an input file. The

POEM is equipped with a vision system that can be used to determine the absolute position of a coordinate system that is aligned to the substrate. In this way the POEM can produce patterns in either absolute coordinates or in coordinates aligned to a pre-patterned wafer. This feature allows for the integration of printed PZT layers into a fabrication process with several device layers utilizing standard lithographic alignment marks.

Environmental conditions are critically important for successful deposition and annealing of PZT. After initial printing results suffered from particle contamination and repeatability problems, the POEM system was enclosed in an acrylic glove box. The glove box is equipped with closed loop filtration and gas purge systems. Printing with the POEM is now carried out in dehumidified air in order to reduce hydrolysis of the sol gel, and particle contamination has been reduced to negligible levels.

3. DEVICE FABRICATION AND RESULTS

Ferroelectric Capacitor

The test devices are capacitor structures consisting of a printed PZT layer in between two electrodes. The bottom electrode is a common PZT seed layer, 100 nm of platinum on top of 20 nm of titanium, evaporated onto a silicon wafer covered with 200 nm of thermal oxide. The ink jetted PZT layers range from 100 nm to 400 nm thick and the top electrode is 200 nm of platinum. The capacitor area is $1.6 \cdot 10^{-3}$ cm^2. An SEM image of the cross section of a device without a top electrode is shown in Figure 2.

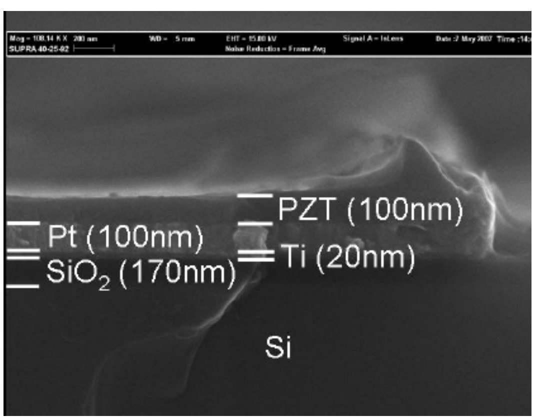


Figure 2: Cross-section of a thermal ink jetted PZT film formed by jetting into a preformed template.

PZT Sol-gel Compatibility with Thermal Ink Jet

This work used a PZT sol-gel manufactured by Mitsubishi Chemical Corp. which is based on the solvent 2-methoxyethanol and is likely manufactured in a manner similar to the sol in previous works [7]. The sol as purchased is unacceptable for printing without dilution, because the concentration and viscosity are optimized to be used as a spin coating solution. Many different solvents and concentrations of sol-gel have been tried, and work to find the most robust and printable solution is ongoing. Factors considered in choosing the solvents with which to dilute the sol-gel included viscosity, volatility, and sol compatibility.

Formation of consistent repeatable droplets was also considered in solvent selection. In dot-on-demand printing, the ratio of Reynolds number to the Webber number characterizes the dynamics associated with droplet formation. A ratio between 1 and 10 is generally considered to be ideal for droplet formation [8]. However, with the solvents under consideration, and length scales with which we were working, the ratio for our work was between 35 and 40. This indicates a high probability of stream formation. Some success with printing at higher ratios has been previously shown [9], and stream formation can be somewhat mitigated by printing at lower frequencies. It was therefore decided to carefully monitor the droplets, but to select the solvents based on the quality of film produced rather than the dynamics of droplet formation. Printing has been carried out at less than 100 Hz, and thus far stream formation has not been a problem with the modified PZT sol used.

The diluted PZT ink that has been most repeatable is a 15 % PZT sol based ink with approximately 85 % 2-methoxyethanol and isopropyl alcohol. 2-methoxyethanol was used due to its compatibility with the PZT sol and isopropyl alcohol was added because it has been well characterized as a TIJ ink solvent. Finally 2-ethylhexanoic acid was added in a small amount to improve film uniformity. The low volatility of the 2-ethylhexanoic acid allows for a small amount of flow in the film, even after the majority of the solvents have been evaporated. Furthermore, it has been shown that the amount of flow can be controlled by adjusting the substrate temperature during deposition. This control parameter provides for far greater film uniformity than can be achieved with isopropyl alcohol and 2-methoxyethanol alone. Testing was carried out with different levels of 2-ethylhexanoic acid in order to determine the appropriate amount required to achieve optimal film uniformity without excessive flow. The current modified sol-gel ink composition is shown in Table 1.

Table 1: Typical PZT TIJ ink composition.

isopropyl alcohol	% 50
2-methoxyethanol	% 30
PZT sol-gel	% 15
2-ethylhexanoic acid	% 5

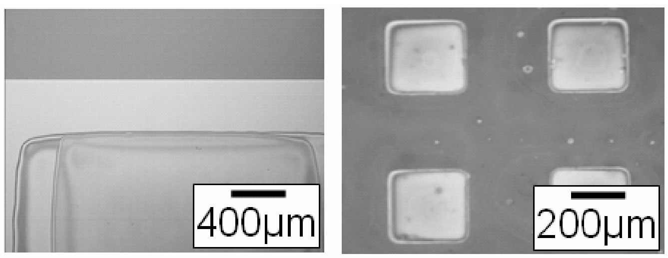
Dimensional Control of Printed Film

Controlling the dimensions of the deposited films such that they are acceptable for integration into MEMS devices requires both control of dimensions in plane, and control of the thickness and its uniformity out of plane.

Control of the line width and line edge roughness has been achieved in two ways. First, by selecting appropriately small nozzle sizes, and controlling the ink evaporation rate, unconstrained printing onto a platinum substrate has been characterized. A parametric study was conducted to choose optimal parameters which can produce resolution that is acceptable for many PZT based MEMS devices. The variation of a deposited line is determined by the spacing between deposited droplets, and the minimum line width is determined by the spot size of the ink on the substrate.

Figure 3a shows a PZT film deposited with 10 pl droplets at a spacing of 35 µm. At room temperature, the spot size of a 10 pl droplet on platinum surface is approximately 43 µm. The edge variation is estimated to be +/- 10 µm.

For a better pattern resolution, it has been shown that edge variation can be improved to less than +/- 1µm by constraining fluid flow with a barrier. Figure 3b shows printed PZT squares shaped by depositing the ink into a preformed polysilicon trench. After PZT deposition, the polysilicon was removed with a XeF_2 etch and an order of magnitude improvement in resolution of the printed PZT films was achieved.



(a) Unconstrained printing (b) Printing into a trench

Figure 3: Resolution comparison of printed PZT films.

Controlling the film uniformity and thickness after annealing of PZT is a primary concern for attaining dense, crack free films. The pyrolization of the PZT solution results in a large volumetric contraction which can lead to destructive crack formation, especially in films over 0.5 µm thick. In order to achieve high quality films, a process was developed for optimizing printing conditions to achieve crack free, highly uniform films, with a controllable thickness between 100 nm and 400 nm.

Substrate temperature during deposition is the control parameter used to adjust overall film uniformity. Studies performed on the effect of substrate temperature on film uniformity showed that at low substrate temperatures the fluid flow after deposition was excessive and led to a build up of material at the edge of the film. It is suspected that this is due to evaporation driven flow towards the edge of the film known as the coffee stain effect [10]. This is apparent in the films pictured in figures 2 and 3. It was also found that if the substrate temperature were two high, the shape of discrete droplets was retained and a film roughness was induced characteristic of the printing process. Therefore an optimal temperature exists where flow of the ink after deposition is just enough to produce a uniform film, but not so much as to produce the coffee stain effect. The details of this study can be seen in Figure 4.

All PZT films in this work were deposited in a single layer of droplets in a close packed pattern, the pitch of the pattern was the parameter used to control the overall film thickness. After the appropriate substrate temperature for a particular substrate and ink composition had been determined, samples were printed with many different pitches. After heat treatment, film thicknesses were measured to determine the relationship between droplet spacing and final film thickness. In this way the optimal substrate temperature and pattern pitch were determined to produce uniform films up to 400nm thick.

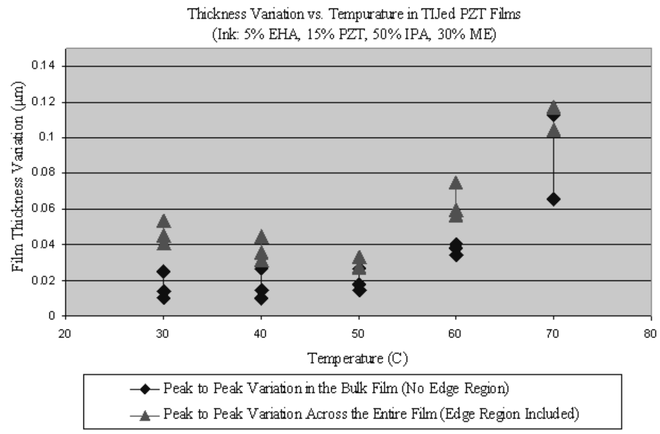


Figure 4: Study of film uniformity vs. temperature for printed PZT films

Microstructure and Piezoelectric Properties

The PZT films were pyrolyzed at 350°C and annealed at 650°C as indicated by previous works to achieve perovskite phase PZT crystal structure [11]. Figure 5 shows a comparison between the x-ray diffraction patterns of a spin coated PZT sample and a printed sample. Except for a slight reduction of the peak in [110] orientation, the printed sample appears to have the same perovskite phase as the film that was spin coated.

To date, all of the printed PZT films have had undesirably low resistivity. This leads to current leakage and poor piezoelectric performance. We believe this poor resistivity to be a result of thermal processing and not a limit of the deposition process. When the sol-gel is diluted through the adding of other solvents, those solvents must be completely removed in order to achieve a dense film with high resistivity. Furthermore, complete pyrolysis of the film must be ensured, as well as appropriate annealing, to achieve the perovskite phase. To demonstrate the importance of thermal processing the resistivities of two printed films pyrolyzed for different times were measured at 15V. A printed film pyrolyzed for 2 min had a resistivity of approximately $8.3\cdot10^2$ Ω·cm, A film pyrolyzed for 120min had a resistivity of approximately $6.2\cdot10^{10}$ Ω·cm. Dense high quality PZT has a resistivity of $>1\cdot10^{11}$ Ω·cm [12]. Work to properly characterize the thermal processing and improve the resistivity of the printed films is currently on going.

Figure 6 shows the polarization vs. voltage characteristic data of the printed PZT as measured on the test device. The test device has a remnant polarization of approximately +/- 4.36 µC/cm^2

4. CONCLUSION

This work reports the first measurement of piezoelectric properties of printed PZT thin films. Thermal ink jet deposition not only offers a promising new way to integrate PZT into existing MEMS fabrication processes, but it enables new device geometries to be produced.

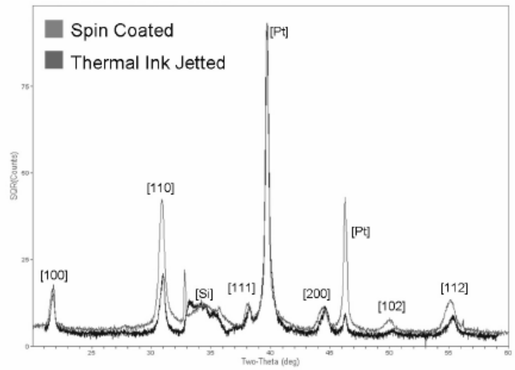


Figure 5: Comparison of X-ray diffraction of spin-coated PZT film with thermal ink-jetted film.

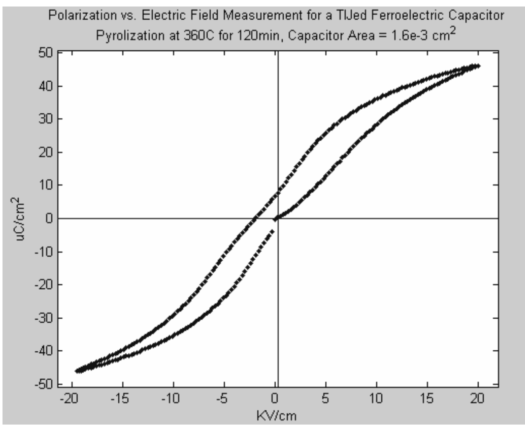


Figure 6: Polarization vs. voltage measurement for printed PZT test device.

Contrary to what has been suggested in previous printed MEMS work [6], this research has found thermal ink jet printing to be a robust deposition tool for a range of ink solvents and viscosities. Furthermore, due to the relatively low cost of producing TIJ print heads, frequent replacement of the print head has been possible. This has prevented contamination of the various inks and provided for particle free deposition, essential in preventing cracking during the thermal processing of the PZT films.

Processes have been developed that enable the optimization of printing conditions and the integration of printed films into a standard fabrication process flow. Furthermore, methods for control of film geometry have been characterized such that the printed films can be deposited with resolution and thickness control acceptable for PZT MEMS fabrication.

Current films have low resistivities that limit the excellent piezoelectric properties that are expected of PZT thin films, but work to improve thermally process and density the films is on going. If printed PZT becomes a reality it will facilitate the integration of PZT into MEMS devices, reduce manufacturing cost, and enable a new set of devices to be fabricated with PZT coating on non-planer surfaces and over large out of plane features.

5. AKNOWLEDGEMENTS

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