Proceedings of ICAD2014
The Eighth International Conference on Axiomatic Design
Campus de Caparica – September 24-26, 2014
ICAD-2014-27

AXIOMATIC DESIGN OF A DROP ON DEMAND DEPOSITION PROCESS FOR SOL-GEL PZT

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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 and allows electro-mechanical devices have the highest performance. However, processing of thin film PZT is not readily compatible with existing micro-electromechanical systems (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. 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. Consequently a flexible new approach is needed to easily and effectively deposit high quality PZT thin films for MEMS applications. Presented here are the functional requirements and design parameters that characterize a sol-gel ink jet printing process as well as the design matrices that guide successful development.

Keywords: PZT, Drop on Demand, Ink Jet, Sol-Gel

1 INTRODUCTION

In recent years drop-on-demand (DOD) printing has been studied as a robust, flexible, and inexpensive method of material deposition for MEMS [Fuller, *et. al.*, 2002]. Digital deposition eliminates the need for photolithography and subsequent etching steps in the manufacturing process flow. 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 [Kim and Koo, 2000].

Recently we presented a new PZT ink jet deposition method that included ink development and printing process based on axiomatic design. Film coalescence and drying processes were modelled and the conditions for uniform deposition were established. These efforts culminated in the fabrication of a printed PZT based ultrasonic transducer that demonstrated the effectiveness of the PZT printing process and also enabled 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. To our knowledge, this is the first report on the full characterization of a printed PZT thin film.

2 DESIGN OF A PZT SOL-GEL INK

A sol-gel based drop-on-demand ink must have the correct balance of surface tension and viscosity so as to ensure reliable and repeatable drop formation. Furthermore, the ink solvents must not interfere with the sensitive hydrolysis reaction that forms the gel film. An ink was formulated for this work by adding chemically compatible solvents to a PZT sol-gel spin coating solution to achieve the correct physical properties.

2.1 A JETTABLE PZT SOL-GEL INK

The starting point of the ink formulation 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. Also, the concentrations of spin coating solutions are too high to be printed reliably. Printing for this research was carried out with an HP thermal ink jet printer that is normally limited to a weight concentration of <5%. The A6 and E1 sol-gel are both 15% (wt) metal-organics and required significant dilution to jet from small nozzles.

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 (2-ME) was used as the primary solvent with 4% wt of 2-ethyhexanioc acid (EHA) 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. Different printer nozzle diameters are used to deposited different drop volumes that therefore have different decap times. Five solutions of PZT sol-gel were primed and printed through a range of seven nozzle sizes design to produce drops volumes 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. 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 would 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 solvents were added to dilute the ink the balance of viscosity and surface tension was controlled to ensure reliable drop formation for the specified nozzle size. 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 [Fromm, 1984]-[Reis and Derby, 2000].

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

where η, ρ, γ, 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 should be between 1 and 10 for successful printing. 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 surface tension of a liquid blend tends to be dominated by the low surface tension elements. All of the inks in this work were based on a primary diluting solvent (either 2-ME or 2-propanol) that was at least 50% (wt) of the solution and as such the surface tension of these solvents was used to calculate the inverse Ohnesorge number. The viscosity of the ink was used as the primary design parameter for controlling jettability. The measured viscosities of the stock A6 and E1 sol-gels were 1.7 and 8.8 mPa.s respectively. The viscosities of the inks developed for this work were adjusted between 1.8 and 2.2mPa.s. 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. Stable drop formation began around Z=11, but a value of around 6 was found to have the best drop control.

2.2 CHEMICAL COMPATIBILITY OF THE INK

The final step in creating a jettable PZT solution 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-propanidiol, 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-ethlyhexanoic 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 [Vasiljev, *et. al.*, 1998]. 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 [Nakao, *et. al.*, 1991].

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 [Zhang, *et. al.*, 1998]. 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 that 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. 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 did not significantly alter the sol-gel chemistry. Combining the chemical and physical functional requirements for a sol-jet ink, and analysing the design interactions, yields a solvable lower triangular design matrix (2).

$$\begin{bmatrix} \text{Decap} \\ \text{Jetablility} \\ \text{Drop Dynamics} \\ \text{Hydrolysis} \end{bmatrix} = \begin{bmatrix} \text{XOOO} \\ \text{XXOO} \\ \text{XXXO} \\ \text{XOOX} \end{bmatrix} \begin{bmatrix} \text{Concentration} \\ \text{Viscosity} \\ \text{Ohnesorge Number} \\ \text{Solvent Compatibility} \end{bmatrix} \tag{2}$$

3 PROCESSES PARAMETERS FOR UNIFORM THIN FILMS

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 material. Printing of uniform PZT films was achieved by using substrate temperature to balance the outward and inward capillary flows to form uniform single drops, and then joining those drops into lines and films. Evaporation driven flow drives solute material outwards towards the drop edge while surface Marangoni flows draw solute material inwards towards the drop center. The thermocapillary surface flow increases with temperature and therefore substrate temperature was used as the primary design parameter to balance these flows and ensure uniform deposition. Once internal flows are balanced drop deposition rate and spacing may be used to control drop coalescence and ensure that the uniform drops are joined into uniform lines and films.

3.1 UNIFORM SOLUTE DISTRIBUTION IN SINGLE PRINTED DROP

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. 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. In 1997 Deegan et. al. identified evaporation driven capillary flow as the main cause of this outward solute movement [Deegan, *et. al.*, 1997]. They showed that if the contact line of a drying film is held fixed then the resulting surface evaporation and droplet geometry evolution requires an outward fluid flow. To maintain a fixed contact line position fluid from the interior of the drop must be constantly flowing outwards to replenish the evaporating solvent. However, 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 [Hu and Larson, 2006]. 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 [Hegseth, *et. al.*, 1996]. For most liquids surface tension decreases with increasing temperature, therefore if the edge of the drop is heated by a warm substrate then a surface tension gradient will be formed and inward surface flow will occur.

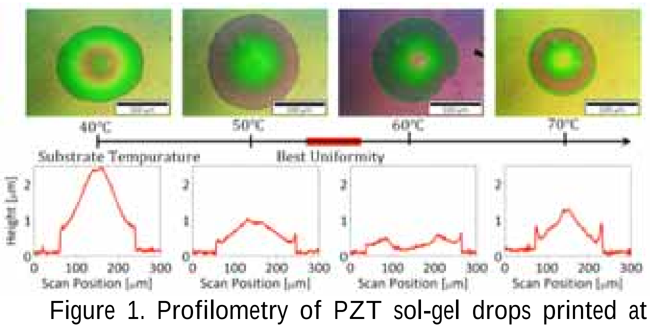

Figure 1. Profilometry of PZT sol-gel drops printed at different temperatures on a PZT substrate. This result indicates an optimum deposition temperature of approximately 55°C.

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. The nonuniform surface temperature required for Marangoni flows depends on high substrate thermal conductivity and a minimum contact angle. The contact angle for the drops in each printed layer is determined by the wetting between the ink solution and the pyrolyzed PZT of the previous printed layer. 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. The temperature was then increased to tune 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 1).

3.2 DROP COALESCENCE AND THE FORMATION OF UNIFORM THIN FILMS

Once the conditions for uniform drop deposition were established coalescence was studied to ensure the formation of smooth lines and films. The effect of drying time on drop coalescence was characterized by varying substrate temperature and measuring the profile of the dried solute. The morphologies that resulted were similar to 1-D line morphologies that have been previously reported but extended to a close packed 2-D film [Soltman and Subramanian, 2008]. When ink drying is slow the drops coalesce completely and the aggregate film 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. 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 that leads to drop scale non-uniformities in the final film. As expected the best uniformity occurs when drop deposition and drying times are similar.

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. However, the parameter that controls drop coalescence is the ratio of drying time to drop deposition period. If drops are deposited more slowly more time is allowed for drying. Therefore substrate temperature was used to balance capillary flows and deposition frequency and spacing was used to control line and film uniformity (3).

$$\begin{bmatrix}\text{Marangoni Flows}\\ \text{Coalescence}\end{bmatrix} = \begin{bmatrix}X & O\\ X & X\end{bmatrix}\begin{bmatrix}\text{Substrate Temp}\\ \text{Dry Time/Dep. Period}\end{bmatrix} \tag{3}$$

4 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. Ultimately the morphology of the deposited films was controlled well enough to meet the requirements of most PZT based MEMS devices.

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.

This process would not have been realized without the decoupling of the complex functional relationships between the controlling design parameters. Axiomatic design analysis uncovered the lower triangular sequential nature of this design problem and provided the correct order in which to address each FR/DP pair. Observing that each of the ink properties will impact the printing process design we can combine (2) and (3) into one equation which governs the design of a sol-gel drop on demand printing process (4).

$$\begin{bmatrix}\text{Decap}\\ \text{Jetablility}\\ \text{Drop Dynamics}\\ \text{Hydrolysis}\\ \text{Marangoni Flows}\\ \text{Coalescence}\end{bmatrix} = \begin{bmatrix}XOOOOO\\ XXOOOO\\ XXXOOO\\ XOOXOO\\ XXXXXO\\ XXXXXX\end{bmatrix}\begin{bmatrix}\text{Concentration}\\ \text{Viscosity}\\ \text{Ohnesorge Number}\\ \text{Solvent Compatibility}\\ \text{Substrate Temp}\\ \text{Dry Time/Dep. Period}\end{bmatrix} \tag{4}$$

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